# 13th International Conference on Heterogeneous Catalysis

1-5 September 2024, Burgas, Bulgaria

# Book of Abstracts



Bulgarian Catalysis Society

Institute of Catalysis
Bulgarian Academy of Sciences

Thirteenth International Symposium on Heterogeneous Catalysis
1–5 September 2024, Bulgaria Hotel, Burgas, Bulgaria

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## Sunday, 1st September 2024

| | | |
|---|---|---|
| 15.00–20.00 | **Registration and information** | |

## Monday, 2nd September 2024

| | | |
|---|---|---|
| 08:00–18:00 | **Registration and information** | |

**Symposium Hall**

| | | |
|---|---|---|
| 09:00–09:15 | **Opening ceremony** | S. Todorova, D. Nikolova, D. Kubička |
| 09:15–10:00 | **sL1-Invited lecture**: The peculiar role of supports in hydrogenation of biomass-derived oxygenates | D. Kubička*, S. Dutta, B. Amin, J. Aubrecht, O. Kikhtyanin, K. Pacultová, A. Ruppert |
| 10:00–10:45 | **sL2-Invited lecture**: Bimetallic Ir-Sn catalysts with non-carbon catalytic support as oxide electrocatalysts for PEMEC | I. Boshnakova, D. Paskalev, G. Borisov, E. Lefterova, E. Slavcheva* |
| 10:45–11:15 | **Coffee break** | |
| 11:15–11:45 | **sK1-Keynote lecture**: The remarkable synergistic effect between perovskites and BiOBr for visible-light enhanced activation of peroxy compounds for organic pollutant degradation | M. Tsvetkov |

**Oral presentations**

| | | |
|---|---|---|
| 11:45–12:10 | **sO1**: Structure related functional properties of complex oxides prepared via mechanochemical route | M. Fabián |
| 12:10–12:35 | **sO2**: Enhanced catalytic activation of peroxy-monosulphate over $SmFeO_3$/CuO composite for antibiotics removal from water | E. Encheva*, M. Tsvetkov |
| 12:35–13:00 | **sO3**: Unveiling the synergistic effects of pH and Sn content for tuning the catalytic performance of $Ni^0/Ni_xSn_y$ intermetallic compounds dispersed on Ce-Zr mixed oxides in aqueous-phase ethylene glycol reforming | C. Rosmini*, M. Pazos Urrea, E. Tusini, S Indris, D. Kovacheva, D. Karashanova, H. Kolev, A. Zimina, J.-D. Grunwaldt, M. Rønning, M. Dimitrov, M. Popova |
| 13:00–14:00 | **Lunch break** | |
| 14:00–14:45 | **sL3-Invited lecture**: Method for the synthesis of ammonia by electrochemically reducing reactive nitrogen-oxygen species formed from air | G. Finkelshtain |

**Oral presentations**

| | | |
|---|---|---|
| 14:45–15:10 | **sO4**: Alkaline fuel cell HOR catalyst evolution from noble to non-noble, from idea to a scale-up product | D. Nikolova*, Y. H. Wijsboom, M. Gabrovska, N. Borchtchoukova, G. Finkelshtain |
| 15:10–15:35 | **sO5**: Selectivity optimization of cobalt-based catalysts for $CO_2$ utilization by alkali promotion: atomic scale insights from molecular modelling | A. Can Kizilkaya |
| 15:35–15:45 | **Company presentation**: ZEISS research innovative solutions in catalysis science | A. Tonchev |
| 15:45–16:15 | **Coffee break** | |

16:15–18:15 **Symposium poster session**

| | |
|---|---|
| **sP1**: Effect of mechanical activation on processing of alumina-supported CoPd catalyst precursors for CO hydrogenation | M. Shopska, M. Fabián*, H. Kolev, K. Tenchev, G. Kadinov, K. Aleksieva |
| **sP2**: Heterogeneity of adsorption and reaction sites of oxide-supported (10%Co+0.5%Pd) catalyst surfaces in the course of the CO hydrogenation reaction | M. Shopska*, K. Tenchev, G. Kadinov |
| **sP3**: Enhancing alkaline oxygen evolution reaction performance through comparative N-doping of a waste fossil-derived Ni-Fe/activated carbon | C. Rosmini*, M. Dimitrov, D. Karashanova, H. Kolev, N. Velinov, M. Popova |
| **sP4**: Initial exploring of Ni- and Co-based coatings in hydrogen evolution reaction electrodeposited on different supports | V. Chakarova, Ts. Parvanova-Mancheva*, M. Gabrovska, D. Nikolova |
| **sP5**: Hydrogenation of renewable levulinic acid to γ-valerolactone on Ni-Cu sodalite zeolite catalysts prepared from fly ash | I. Dimitrov*, M. Dimitrov, Y. Mitrev, D. Kovacheva, D. Karashanova, S. Boycheva, N. Velinov, M. Popova |
| **sP6**: Catalytic properties of selenium and phosphorus ionic liquids heterogenised on algae-based biochar | I. Tankov*, L. Gonsalvesh, G. Kolchakova, Z. Mustafa, A. Ilieva, Y. Hristov |
| **sP7**: Conversion variation in a commercial vacuum residue hydrocracker investigated by intercriteria analysis and pilot plant tests | D. Stratiev*, I. Shishkova, I. Kolev, G. Palichev |
| **sP8**: Methane conversion to add-value compounds over transition metal cations in zeolites | J. Sobalska, K. A. Tarach, A. Kordek*, K. Mlekodaj, E. Tabor, K. Góra-Marek |
| **sP9**: MCR-ALS analysis for active species identification in alcohol to hydrocarbon process | A. Kordek*, K. A. Tarach, A. Walczyk, K. Góra-Marek |
| **sP10**: Coke assessment in spectroscopic and chromatographic studies of spent zeolite catalysts for ethylene oligomerization | O. Rogala*, K. Tarach, M. Smoliło-Utrata, J. Martínez-Triguero, F. Rey, K. Góra-Marek |
| **sP11**: Polystyrene cracking over commercial zeolites Y | O. Rogala*, K. A. Tarach, K. Góra-Marek |

19.00 **Welcome reception at Bulgaria restaurant**

## Tuesday, 3rd September 2024

08:00–14:00 **Registration and information**

**Symposium Hall**

| | | |
|---|---|---|
| 09:00–09:45 | **sL4-Invited lecture**: Enhancement of catalytic performance of zeolites with newer frameworks by controlling defect sites | Y. Kubota |
| 09:45–10:30 | **sL5-Invited lecture**: Heterogeneous catalysis in nanopores: the benefit of hierarchical pore systems | R. Gläser |
| 10:30–11:00 | **Coffee break** | |
| 11:00–11:45 | **sL6-Invited lecture**: Atomistic investigations of hydrogen diffusion in wurtzite-type zinc oxide nanowires | V. Chihaia*, D. A. Neacsu, V. Alexiev, A. Marcu |

**Oral presentations**

| | | |
|---|---|---|
| 11:45–12:15 | **sO6**: Dual system for $CO_2$ capture and hydrogenation to methane based on the modified mesoporous silica prepared from rice husks | M. Popova*, I. Slavchev, S. Simeonov, M. Dimitrov, P. Shestakova, D. Kovacheva, G. Atanasova |
| 12:15–12:45 | **sO7**: Cobalt-based catalysts supported on porous materials for the complete oxidation of volatile organic compounds | S. Todorova*, B. Grahovski, R. Velinova, J.-L. Blin[3], L. Richaudeau, H. Kolev, I. Yordanova, K, Tenchev, A. Naydenov |

13:00–14:00 **Lunch break**

14:15–19:00 **Nesebar sightseeing tour**

## Wednesday, 4th September 2024

08:30–18:30 **Registration and information**

**Symposium Hall**

| | | |
|---|---|---|
| 09:00–09:45 | **sL7-Invited lecture**: Operando IR spectroscopy for a greener catalysis and process enhancement | M. Daturi |
| 09:45–10:30 | **sL8-Invited lecture**: PROMETHEUS catalyst: the first ever copper-based automotive catalyst homologated for Euro6 application. Current and future challenges | I. Yakoumis |

10:30–11:00 **Coffee break**

**Oral presentations**

| | | |
|---|---|---|
| 11:00–11:30 | **sO8**: Recycling and reuse of spent automotive catalysts: challenges and solutions | Z. Cherkezova-Zheleva*, M. L. Grilli, K. Sakkas, I. Yakoumis |
| 11:30–12:00 | **sO9**: Photoelectrochemical and photocatalytic activity of photodeposition-functionalized Ag/$TiO_2$ and $MnO_x$/$TiO_2$ thin films | B. I. Stefanov |

12:30–13:30 **Lunch break**

14:00–16:00 **Flash orals of poster presentations (5 min)**

B. Grahovski, Ts. Lazarova, O. Dimitrov, K. Tumbalova, G. Theochari, P. Karakashkova, D. Ivanova, E. Petrova, G. Zarkova, Ts. Goshova, D. Nicheva, M. Sabeva, A. Vasileva, K. Ivanov, K. Mihaylova, O. Porodko, A. Neacsu, A. Lyuczkanova

16:00–16:30 **Coffee break**

16:30–18:30 **Symposium poster session**

| | |
|---|---|
| **sP12**: Highly resistible RGO-supported palladium catalyst to sulphur dioxide and water vapour for low-temperature VOCs oxidation | R. Velinova, D. Kichukova, G. Atanasova, A. Naydenov, D. Kovacheva, I. Spassova* |
| **sP13**: Catalytic oxidation of VOCs over Co and Co-Mn oxides supported on hierarchically macro-mesoporous silica | B. Grahovski*, H. Kolev, K. Tenchev, S. Todorova, R. Velinova, G. Ivanov, A. Naydenov, J.-L. Blin , L. Richaudeau, B. Lebeau |
| **sP14**: Bimetallic Pd-Au and Pd-Ag nanoparticles supported on MCM-41, MCM-22, and Beta-11 as catalysts for BTEX complete oxidation | P. Konova, P. Nikolov, P. Petrova*, M. Anchina*, V. Zdravkova, O. Dimitrov, M. Shipochka, P. Markov, I. Stambolova, G. Ivanov, A. Naydenov |

| | |
|---|---|
| **sP15**: Structural and catalytic properties of $MnO_x$-$CeO_2$ oxides supported on SBA-15 | Y. Karakirova*, B. Grahovski, R. Velinova, H. Kolev, I. Yordanova, K. Tenchev, A. Naydenov, S. Todorova |
| **sP16**: Co-modified SBA-15 catalysts for waste gases purification processes: effect of precursor | B. Grahovski, J.-L. Blin, B. Lebeau, A. Naydenov, R. Velinova*, D. Karashanova, L. Richaudeau, H. Kolev, L. Michelin, K. Tenchev, S. Todorova |
| **sP17**: Effect of preparation method on cobalt-modified SBA-15 catalysts for waste gas purification processes | G. Ivanov*, B. Grahovski, J.-L. Blin, B. Lebeau, A. Naydenov, R. Velinova, L. Richaudeau, H. Kolev, L. Michelin, K. Tenchev, S. Todorova |
| **sP18**: Catalytic combustion of VOCs and CO over noble metals supported on MCM-22 zeolite | P. Konova, P. Nikolov, R. Velinova*, O. Dimitrov, M. Shipochka, P. Markov, V. Zdravkova, D. Stoyanova, G. Ivanov, A. Naydenov |
| **sP19**: Application of graphene oxide as adsorbent for the removal of toluidine blue from aqueous solutions | P. Vassileva*, Ts. Lazarova, D. Kichukova, D. Voykova, D. Kovacheva, I. Spassova |
| **sP20**: Combined purification of methylene blue from aqueous media by adsorption and photocatalysis using 3D graphene-based material | P. Vassileva*, V. Tumbalev, D. Kichukova, D. Voykova, D. Kovacheva, I. Spassova |
| **sP21**: Photocatalytic activity of $TiO_2$ particles obtained by *Mentha Spicata*-mediated green synthesis | O. Dimitrov*, I. Stambolova, D. Stoyanova, K. Zaharieva, M. Shipochka, G. Avdeev |
| **sP22**: Photocatalytic degradation of azo dye using AB-PBI/plant-synthesized $TiO_2$ hybrid membranes | K. Zaharieva*, I. Stambolova, D. Stoyanova, I. Tsacheva, R. Mladenova, M. Shipochka, B. Barbov, S. Dimova, O. Dimitrov, H. Penchev |
| **sP23**: Ti-zeolite Y nanocomposites modified by Au and $CeO_2$ and their photocatalytic activity | G. Petcu, E. M. Anghel, F. Papa, I. Atkinson, A. Baran, S. Petrescu, S. Todorova*, V. Parvulescu |
| **sP24**: Investigation of NiO/Pd/$Al_2O_3$, CuO/Pd/$Al_2O_3$, and CoO/Pd/$Al_2O_3$ as catalysts for ozone decomposition and as photocatalysts | K. Milenova*, I. Avramova |
| **sP25**: Catalytic combustion of methane over Pd-modified La-Ce-Zr-Al catalyst | K. Tumbalova*, Z. Zlatanova, R. Velinova, M. Shipochka, P. Markov, D. Kovacheva, G. Ivanov, E. Vassileva, L. Mihaylov, S. Todorova, A. Naydenov |
| **sP26**: Composite carbon material with excellent adsorption properties toward $CO_2$ prepared by new one-step approach | Ts. Lazarova, D. Kichukova, G. Atanasova, D. Kovacheva*, I. Spassova |
| **sP27**: $Ni^0$ supported on biowaste-derived porous aluminosilicates for $CO_2$ methanation | G. Theochari*, C. Rosmini, D. Kovacheva, M. Dimitrov, P. Shestakova, V. Toteva, M. Popova |
| **sP28**: C-C coupling of 1-butanol over Mg- and Li-doped zeolite | R. Palcheva*, L. Kaluza, J. Moravcik, A. Lyutskanova, T. Petrova, V. V. Idakiev, G. Tyuliev, Y. Kalvachev |
| **sP29**: Ozone decomposition at ambient temperature over noble metals modified MCM-22 and MCM-41 catalysts | P. Konova, P. Nikolov, P. Karakashkova*, O. Dimitrov, M. Shipochka, P. Markov, V. Zdravkov, D. Stoyanova, A. Naydenov |
| **sP30**: $M_xO_y/CeO_2$ (M = Cu, Co, Fe, Ni) derived from Ce-MOFs as a highly efficient catalyst for light-assisted Fenton-like reaction for water purification | D. Gagashev*, D. Elenkova, M. Tsvetkov |
| **sP31**: Ruddlesden-Popper type perovskite $La_2CuO_4$ decorated active carbon as a Fenton-like catalyst for antibiotic degradation | P. Nikolov*, S. Stefanova, M. Tsvetkov |
| **sP32**: Enhanced heterogeneous photocatalysis for antibiotic degradation using ZnO nanostructured films co-catalytically modified with Pd/MnOx | D. Ivanova*, H. Kolev, N. Kaneva |

| | |
|---|---|
| **sP33**: Structure engineering of $Ni/SiO_2$ vegetable oil hydrogenation catalyst via $CeO_2$ | M. Gabrovska, D. Nikolova, V. Radonjić, D. Karashanova, A. Baeva, Ts. Parvanova-Mancheva, P. Tzvetkov, E. Petrova*, G. Zarkova, J. Krstić |
| **sP34**: Catalytic ability of K- and Co-promoted oxo-Re and oxo-ReMo nanosized compositions for water-gas shift reaction | D. Nikolova, I. Ivanov, J. Vakros, M. Gabrovska, J. Krstić, P. Tzvetkov, E. Petrova, G. Zarkova*, T. Petrova, T. Tabakova |
| **sP35**: Synthesis and structural analysis of heat-generating cobalt-substituted magnetite nanoparticles with organic coatings | Ts. Goshova*, M. Ognjanović, M. Bošković, B. Dojčinović, S. Vranješ-Đurić, B. Antić |
| **sP36**: Electronic structure, magnetic properties, cobalt heating efficacy, and gadolinium-substituted magnetite nanoparticles | H. Kolev*, R. Mladenova, M. Ognjanović, M. Bošković, B. Dojčinović, S. Vranješ-Đurić, B. Antić |
| **sP37**: Pt-modified iron oxide magnetic nanoparticles for catalytic applications | I. Yordanova*, H. Kolev, S. Todorova, M. Shopska, Z. Cherkezova-Zheleva, N. Velinov |
| **sP38**: Combined EPR and Mössbauer investigation of soda-lime silicate glass-crystalline materials of high iron oxide concentration | I. Mihailova*, R. Harizanova, D. Paneva, Z. Cherkezova-Zheleva, R. Kukeva, R. Stoyanova, G. Avdeev, C. Rüssel |
| **sP39**: Dielectric properties of $Ce_{1-x}Gd_xO_{2-x/2}$ ceramics | D. Nicheva*, R. Harizanova, V. Boev, V. Ilcheva, N. Bozhanova, K. Kolev, O. Dimitrov, T. Petkova |
| **sP40**: Catalytic behaviour of materials prepared by reusing recycled spent automotive catalysts | B. Grahovski, M. Sabeva*, C. Papadopoulos, S. Todorova, H. Kolev, Z. Cherkezova-Zheleva, D. Paneva, A.-M. Moschovi, I. Yakoumis |
| **sP41**: Characterization of catalytic materials prepared by reuse of recycled Pt from spent automotive catalysts | M. Sabeva*, B. Kunev*, E. Encheva, A. Vasileva, K. Ivanov, M. Shopska, I. Christova, D. Paneva, A.-M. Moschovi, Z. Cherkezova-Zheleva, I. Yakoumis |
| **sP42**: Application of mechanochemistry in recycling platinum group metals from spent automotive catalysts | A. Vasileva*, K. Ivanov, Z. Cherkezova-Zheleva, I. Yakoumis, D. Paneva |
| **sP43**: Recycling of spent automotive catalysts and their reuse in CO oxidation reaction | K. Ivanov*, B. Grahovski, A. Vasileva, D. Paneva, S. Todorova, I. Yakoumis, Z. Cherkezova-Zheleva |
| **sP44**: SEM investigation of spent automotive catalysts for further PGM reuse | I. Piroeva*, B. Rangelov, S. Atanasova-Vladimirova, D. Paneva, F. Hodzhaoglu, I. Yakoumis, Z. Cherkezova-Zheleva |
| **sP45**: Thermal analysis of spent catalysts: a TG/DTG-DSC-MS investigation of thermal behaviour in different gas atmosphere | K. Mihaylova*, D. Paneva, V. Petkova, A.-M. Moschovi, Z. Cherkezova-Zheleva |
| **sP46**: Structure and morphology of high entropy oxides with spinel structure prepared via ball milling and their electrochemical properties | O. Porodko*, M. Fabián, H. Kolev, M. Zukalová |
| **sP47**: Development of photochromic spironaphthoxazine molecular systems as photocontrollable 'smart' detectors for metal ions | S. Minkovska*, V. Chihaia, A. Neacsu, G. Hadjichristov |
| **sP48**: Spirooxazine derivative DFT simulations and spectroscopic properties of solid powder and solvent solutions | A. Neacsu*, V. Chihaia, V. Alexiev, S. Minkovska |
| **sP49**: The effect of ion exchange of clinoptilolite as a soil on radish physiological response | A. Lyuczkanova*, T. Todorova, D. Ilkov, V. Velikova, Y. Kalvachev |
| **sP50**: Hydrogen production over nickel-based catalysts | S. Damyanova*, I. Stereva, M. Gabrovska, D. Nikolova, T. Petrova, A. Stanev |

19:00 **Dinner at A-la-carte Bulgaria restaurant (optional)**

## Tuesday, 5th September 2024

09:00–14:00 **Registration and information**

**Symposium Hall**

| | | |
|---|---|---|
| 09:30–10:15 | **sL9-Invited lecture**: Ni active phase and catalyst composition effect on hydrogen production by methane reforming and decomposition | L. Francesca Liotta |
| 10:15–11:00 | **sL10-Invited lecture**: Roles of catalyst and feedstock in optimizing performance of heavy oil conversion processes of fluid catalytic cracking and ebullated bed vacuum residue hydrocracking | D. Stratiev*, I. Shishkova, G. Argirov, R. Dinkov |
| 11:00–11:30 | **Coffee break** | |
| 11:30–12:15 | **sK2-Keynote lecture**: Support effects for the water-gas shift performance of gold-based catalysts | T. Tabakova |
| 12:15–12:30 | **Closing ceremony** | S. Todorova, D. Nikolova |

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Invited lecture

# sL1. The peculiar role of supports in hydrogenation of biomass-derived oxygenates

D. Kubička[1,2]*, S. Dutta[1], B. Amin[1], J. Aubrecht[1], O. Kikhtyanin[2], K. Pacultová[3], A. Ruppert[4]

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Lignocellulosic biomass is undoubtedly a promising raw material having a great potential to provide sustainable chemicals and fuels. Consequently, valorisation of the key plant-based macromolecules, i.e. lignin and cellulose, has attracted enormous attention of the scientific community in the academia and industry alike. While lignin comprises about 25% of biomass and is a naturally occurring polymer of oxygen-containing aromatic monomers, cellulose is the most abundant biopolymer consisting of glucose units and forming up to 50% of biomass. Valorisation of these biopolymers relies on their depolymerisation and subsequent transformation of the 'monomers', i.e. methoxy-phenolic compounds and glucose, respectively, that often include their (partial) deoxygenation and hydrogenation.

Supported metal catalysts are crucial catalysts to facilitate both deoxygenation and hydrogenation upgrading of biomass-derived oxygenates. Their activity and selectivity, as well as their stability, depends not only on the nature of the active metal, but also on the support used. Although the role of the support on the catalyst's performance is frequently recognized, often only the influence of the support on the metal particle size (metal dispersion) or on the electronic state of the metal (metal-support interaction) or on the adsorption of reactants (e.g. on the Lewis acid sites in the metal-oxide supports) are considered. Unless the supports have a pronounced Brönsted acidity like zeolites, their intrinsic catalytic activity is often neglected or overlooked.

The lecture will consider two common supports, namely $Al_2O_3$ and $TiO_2$, and discuss their intrinsic activity in the transformation of anisole and 5-hydroxymethylfurfural, respectively. It will be demonstrated that alumina in $Ni/Al_2O_3$ and $Cu/Al_2O_3$ catalysts helps to maximize the carbon retention in desired liquid products, i.e. helps to prevent formation of $C_1$ products, in hydrogenation and/or deoxygenation of anisole that can be considered a representative model compound for lignin-derived phenolics. Further, it will be shown that $TiO_2$ and its properties are crucial for the selectivity in the selective hydrogenation of 5-hydroxymethylfurfural over $Ru/TiO_2$. Ultimately, the primarily desired selectivity to 2,5-bis(hydroxymethyl) furan can be switched completely to high selectivity to another compound of interest, namely 5-methylfurfural.

# sL2. Bimetallic Ir-Sn catalysts with non-carbon catalytic support as oxide electrocatalysts for PEMEC

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The electrochemical water splitting in polymer electrolyte membrane electrolysis cells (PEMEC) is the most attractive technology for producing pure hydrogen, If powered by renewable energy source (sunlight, wind, etc.) it is a zero emission environmentally friendly process. The main challenge preventing the use of PEMEC for massive industrial hydrogen production is the sluggish kinetics of the oxygen evolution reaction (OER). The OER takes place at high potentials, which in combination with the intensive gassing, high humidity, and elevated temperatures create critical operative conditions at which most catalysts are not stable and gradually degrade due to oxidation and corrosion phenomena. It has been proven that $RuO_2$ and $IrO_2$ are the most effective OER catalysts in practical applications, the former being more active, the latter – more stable under harsh operating environment. However, as a precious metal oxide, $IrO_2$ is too expensive for large-scale industrial PEMEC applications. Various efforts have been made and new strategies developed to reduce the cost of the catalysis. These include the increase of catalytic activity through synthesis of nanosized Ir oxides allowing reduction of the catalyst loading without sacrifice of efficiency deposition of the nanoparticles on catalytic supports with high surface area, which prevents their agglomeration thus, increasing the catalyst utilization. The reduction of the noble-metal loading by preparing mesoporous metal oxide films and multi-component catalysts is another research direction aimed at improving the selectivity and stability by synergetic effects. In this work, the innovative bimetallic Ir-Sn catalysts are synthesized and investigated.

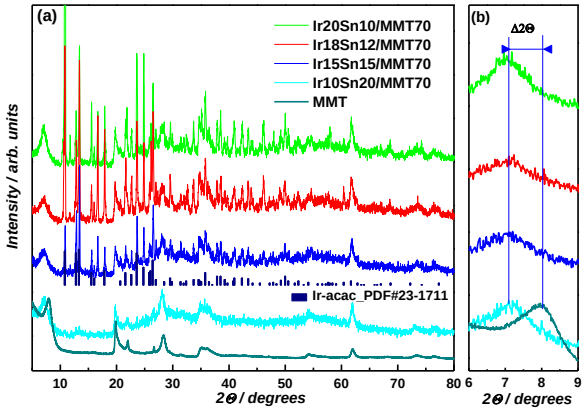



Fig. 1. XRD patterns of the synthesized catalysts.

Both metals were deposited on a cheap natural mixed oxide with double layered structure montmorillonite having a formula $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. A series of IrSn/MMT samples with 30 wt.% metal content and different Ir:Sn ratios were synthesized by a modified sol-gel method using $Ir(C_5H_7O_2)_3$ and $C_{10}H_{14}O_4Sn$ precursors. The structural and phase composition was examined by XRD (Fig. 1). In all tested samples the (001) diffraction peak of the MMT is shifted to smaller 2Θ angles (Fig. 1b) concerning the pure MMT (from 8.03° to 7.00°).

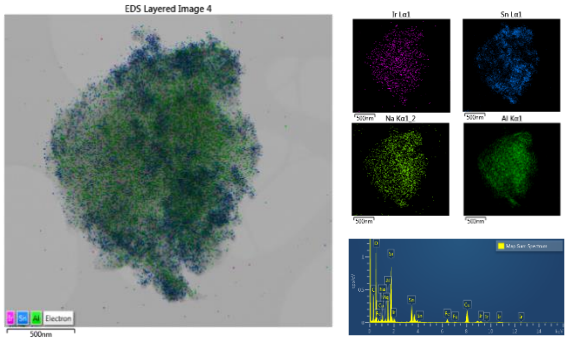



Fig. 2. Elemental mapping and EDX data.

Such a displacement corresponds to an increase in the interlayer spacing of MMT from 1.1 nm to 1.26 nm due to intercalation of foreign ions in the MMT basal spacing, in this case Ir and Sn. The by HRTEM and EDX analysis showed that both metals nanoparticles having size of around 13 nm. are homogenously distributed morphology on the substrate (Fig. 2).

The electrochemical performance of the synthesized electrocatalysts with different Ir:Sn ratio was evaluated firstly in 0.5M $H_2SO_4$ by cyclovoltammetry. The shape of the curves obtained (Fig. 3) and the potential range where the redox peaks appear show that the proceeding electrochemical reactions are associated with transformations between different Ir oxidation states ($Ir^{3+}/Ir^{4+}$ and/or $Ir^{4+}/Ir^{5+}$, rather than with changes in the oxidation state of Sn.

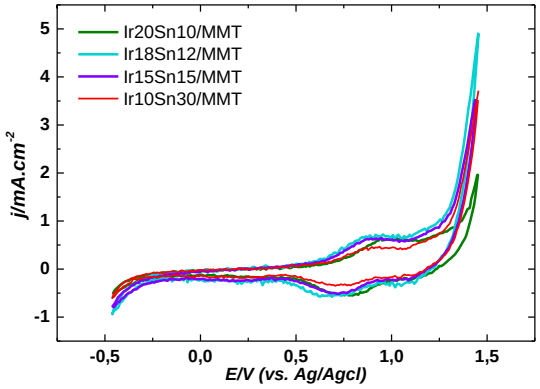



Fig. 3. CV curves of the catalysts under study in 0.5M $H_2SO_4$; scan rate 100 mV $s^{-1}$.

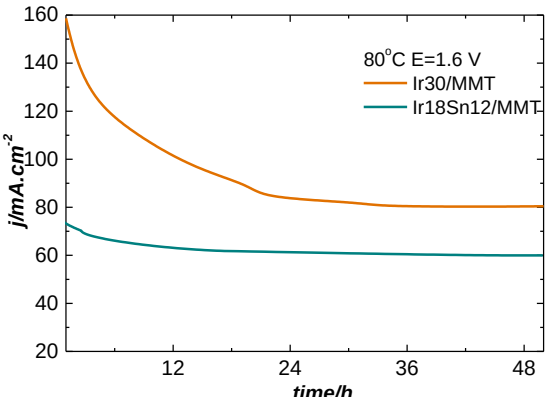



Fig.4. CV curves of Ir18Sn12/MMT in PEMEC at varying temperatures; 100 mV $s^{-1}$.

The increase of Sn content intensifies the OER. The achieved current density at anodic potential limit of 1.8 V was superior for the Ir18Sn12/MMT sample, having the most homogeneous distribution into the structure of the montmorillonite. This sample was integrated in membrane electrode assembly using Nafion 117 membrane and Pt as cathode catalyst and tested in a single PEMEC at varying operative conditions. It was found that with the increasing temperature the set-off potential of the oxygen evolution shifts to lower values implying activation phenomena prescribed to degradation of the organic precursor residues in the as-prepared catalyst. The best performance of 65 mA $cm^{-2}$ at 1.6V was obtained at 80°C. The performed stability tests showed that the current density stabilizes after first several hours and does not change until the end of examination (Fig. 4).

The research performed proved the applicability of montmorillonite as a proper catalytic support and demonstrated the superior performance of the synthesized bimetallic Ir18Sn12/MMT catalyst compared to pure Ir/MMT concerning both efficiency and noble metal utilisation.

# sL3. Method for the synthesis of ammonia by electrochemically reducing reactive nitrogen-oxygen species formed from air

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Ammonia ($NH_3$) is a widely crucial chemical, which is currently commonly produced in large-scale by the one-step Haber-Bosch (H-B) process. Ammonia production in this process is energetically demanding with low efficiency. Century-old Haber-Bosch process for ammonia synthesis requires harsh operating conditions including high temperatures (400–500°C) and high pressures (150–300 atm) using pure $N_2$ and $H_2$ gases together with heterogeneous iron-based catalysts. Thus, the Haber-Bosch process is costly and requires significant plant infrastructure. Ammonia had a worldwide production of approximately 240 million tons in 2023, which accounts for 1–2% of the world's energy supply and causes approximately to 1.5% of total global energy-related $CO_2$ emissions. An emerging alternative to the Haber-Bosch process is the electrochemical synthesis of ammonia through the nitrogen reduction reaction (NRR). The electrocatalytic reduction process is considered an environmentally friendly approach for $NH_3$ production; in fact, it can be performed under mild conditions, such as room temperature and atmospheric pressure, and it can also be powered by renewable energy. However, the direct electrochemical conversion of $N_2$ to ammonia suffers from disadvantages such as an extremely low $NH_3$ yield and a low Faradaic efficiency. These disadvantages arise due to the highly unreactive nature of $N_2$. Moreover, the electrochemical NRR is hampered by a competition with the hydrogen evolution reaction (HER), as the hydrogen generation usually occurs at a lower overpotential than the eNRR.

It has now been found that the disadvantages relating to the NRR can be overcome by the activation of $N_2$ into a more reactive intermediate form. An attractive intermediate species are charged nitrogen oxides ($NO_x^-$) as starting materials for the electrochemical ammonia synthesis, due to their relatively low N–O bond dissociation energy and superior solubility in water.

Inspired by the natural lightning fixation of nitrogen, and the rapid development of the atmospheric pressure non-thermal plasma (APNTP) technology, the activation of $N_2$, in the presence of $O_2$, into reactive nitrogen oxide species of formula $NO_x$ has been found to be achievable by energetic electrons of a plasma. An additional advantage of APNTP is that air may be used directly as a gas source and starting material for converting $N_2$ into nitrogen oxide species that can then be absorbed by the electrolyte to form reactive negatively charged species of formula $NO_x^-NO_x^-$, which in turn can be directly reduced to $NH_3$ at the cathode of an electrochemical cell. The reduction reactions of $NO_x^-$ that occur in the electrochemical cell are:

$$NO_3^- + 9\ H^+ + 8e^- \rightarrow NH_3 + 3H_2O,\ E^o = 0.88\ V\ vs.\ RHE\ ,$$

$$NO_2^- + 7\ H^+ + 6e^- \rightarrow NH_3 + 2H_2O,\ E^o = 0.86\ V\ vs.\ RHE\ .$$

The key to achieving a selective electrocatalytic $NO_x^-$-to-$NH_3$ conversion at low potentials is a rational design and electrocatalysts with the ability to favourably catalyse the reduction of $NO_x^-$ while concurrently supplying sufficient H* that can participate in intermediate hydrogenation rather than undergoing dimerization to form $H_2$. The additional tuning of components, e.g., in the electrochemical nitrate reduction reaction system, such as electrolyte, electrodes, and applied potentials can also contribute to a high ammonia yield and Faradaic efficiency.

# sL4. Enhancement of catalytic performance of zeolites with newer frameworks by controlling defect sites

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It is important to understand the atomic position in the zeolite framework for designing high performance catalyst based on microporous crystals. In the field of fine-chemicals synthesis, there is a persistent demand for zeolite catalysts that have large-pores and multi-dimensional channel systems. However, the number of such zeolites is still limited. We focused on two 3-dimensional, large-pore zeolite framework types. One is YNU-2 (**MSE** topology) with a pore system of 12−10−10-ring [1,2], and the other is YNU-5 (**YFI** topology) with a pore system of 12−12−8-ring as well as an isolated 8-ring channel [3] (Fig. 1).

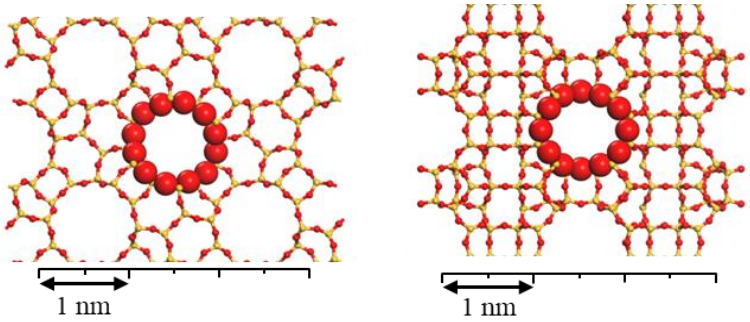
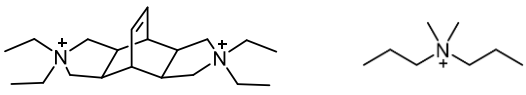



Fig. 1. **MSE** and **YFI** frameworks with a 12-ring emphasized.

The properties of zeolites depend on the method of preparation including starting gel composition and synthesis conditions. For example, the synthesis using organic structure-directing agent (OSDA) usually gives high-silica zeolites while OSDA-free synthesis gives materials with much lower silica contents. In both cases, some post-synthetic modifications are necessary for preparing catalysts that have suitable amounts of active sites, proper hydrophobicity and stability. In this work, we used relatively hydrophilic OSDAs, $TEBOP^{2+}$ and $Me_2Pr_2N^+$, as shown in figure 2.



$TEBOP^{2+}$ $Me_2Pr_2N^+$

Fig. 2**.** The structures of OSDAs used for the syntheses of **MSE** and **YFI** frameworks, respectively.

Site defects (vacancies; silanol nests) are useful in the light of heteroatom substitutions, whereas too many site defects lead to framework collapse. Thus, the control of the site defects is a main issue in the post-synthetic modification of zeolite towards catalyst preparation. In this presentation, some examples of the modification of zeolite frameworks will be given:

(i) preparation of high-performance titanosilicate Ti-YNU-2 from YNU-2P that is a highly defective, zeolitic framework-OSDA composite;

(ii) preparation of novel titanosilicate Ti-YNU-5 from YNU-5 zeolite that is originally an aluminosilicate with Si/Al = 9. The dealumination by careful acid-leaching enables framework stabilization. If there are too many framework Al sites and the Al atoms are removed without repairing the newly generated vacancies, then the framework is unstable and collapses along with the dealumination.

In both **MSE** and **YFI** cases, Si-migration played important roles to stabilize the frameworks by repairing the site defects. The Si-migration is supported by several characterization results such as $^{29}$Si MAS NMR. Computational modelling based on DFT helped understand the preference for the formation on silanol nests and the replacement of Si by Ti or Al in different crystallographic positions of the **MSE** framework [4]. TEM results have been disclosed as a powerful support [5].

These results could afford new insights into the understanding of structural stability of high-silica zeolites towards preparation of high-performance catalysts.

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References

1. Y. Koyama, T. Ikeda, T. Tatsumi, Y. Kubota, Angew. Chem. Int. Ed., 47 (2008) 1042.
2. M. Sasaki, Y. Sato, Y. Tsuboi, S. Inagaki,. Kubota, ACS Catal., 4 (2014) 2653.
3. N. Nakazawa, T. Ikeda, N. Hiyoshi, Y. Yoshida, Q. Han, S. Inagaki, Y. Kubota, J. Am. Chem. Soc., 139 (2017) 7989.
4. P. St. Petkov, K. Simeonova, I. Z. Koleva, H. A. Aleksandrov, Y. Kubota, S. Inagaki, V. Valtchev, G. N. Vayssilov, Molecules, 26 (2021) 7296.
5. J. Li, A. Mayoral, Y. Kubota, S. Inagaki, J. Yu, O. Terasaki, Angew. Chem. Int. Ed., 61 (2022) e202211196.

# sL5. Heterogeneous catalysis in nanopores: the benefit of hierarchical pore systems

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Nanoporous catalysts are applied in a broad range of chemical conversions. Often, however, low catalyst effectiveness factors may result, if mass-transfer limitations exist [1]. Additional pore systems with larger dimensions in the macro- and mesoporous range may help to increase accessibility and mass transfer to and away from the catalytically active sites. This presentation will highlight several examples in the field of catalysis over hierarchically structured materials. In particular, the role of diffusion for chemical reactions occurring on and in hierarchical nanoporous catalysts will be emphasized. First, microporous catalysts with a secondary 'auxiliary' system of larger, mainly mesopores and, thus, improved catalytic activity or stability will be treated [2-5]. The discussion will involve the transport scenarios of fast and slow molecular exchange, accessibility of active sites as well as the potential influence of surface barriers on the prevailing transport properties within the catalysts. Secondly, the potential of introducing larger (macro)pores and optimizing the geometry of hierarchical pore systems for the use in heterogeneous catalysis will be outlined. Considerable rate enhancements can be achieved, e.g., for the selective catalytic reduction of NO with $NH_3$ over meso-/macroporous $V_2O_5/TiO_2$ catalysts, based on theoretical evidence [6,7], or for the methanation of $CO_2$ over Ni on meso-/macroporous $Al_2O_3$ monoliths [8,9]. Finally, future challenges will be derived enabling a rational design of catalysts with complex hierarchical pore systems based on advanced experimental and theoretical methods to study molecular diffusion and conversion.

References

1. J. Kärger, M. Goepel, R. Gläser, in: Nanotechnology in Catalysis, B. Sels, M. Van de Voorde, eds., Ch. 13, Wiley-VCH, Weinheim (2017).
2. N. Wilde, M. Pelz, S. G. Gebhardt, R. Gläser, Green Chem., 17 (2015) 3378.
3. M. Dvoyashkin, N. Wilde, J. Haase, R. Gläser, RSC Advances, 8 (2018) 38941.
4. N. Wilde, J. Přech, M. Pelz, J. Kubů, J. Čejka, R. Gläser, Catal. Sci. Technol., 6 (2016) 7280.
5. H.-T. Vu, F. M. Harth, M. Goepel, N. Linares, J. García-Martínez, R. Gläser, Chem. Eng. J., 430 (2022) 132763.
6. G. Wang, M.-O. Coppens, Ind. Eng. Chem. Res., 47 (2008) 3847.
7. P. Trogadas, M. M. Nigra, M.-O. Coppens, New J. Chem., 40 (2016) 4016.
8. S. Weber, K. L. Abel, R. T. Zimmermann, X. Huang, J. Bremer, L. K. Rihko-Struckmann, D. Batey, S. Cipiccia, J. Titus, D. Poppitz, C. Kübel, K. Sundmacher, R. Gläser, T. L. Sheppard, Catalysts, 10 (2020) 1471.
9. K. L. Abel, T. Beger, D. Poppitz, R. T. Zimmermann, O. Kuschel, K. Sundmacher, R. Gläser, ChemCatChem, 14 (2022) e202200288.

# sL6. Atomistic investigations of hydrogen diffusion in wurtzite-type zinc oxide nanowires

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The electric, optoelectronic, and mechanic properties of zinc oxide nanowire are controlled by its diameter and length, and by the intrinsic and induced defects. The subsurface penetration of the adsorbed atoms modifies the electronic properties of the zinc oxide nano-films and wires, which affects many of their static and dynamic properties. Therefore, the application as sensing elements of the ZnO nanowires could be more attractive than the bulk and film ZnO systems. In the present work, adsorption, subsurface penetration, and interior diffusion of the hydrogen atoms in zinc oxide were characterized by DFT calculations. Activation energies, diffusion rates, and bulk diffusion coefficients were evaluated. Such data are essential for investigation of hydrogen diffusion in the zinc oxide nanowires by kinetic Monte Carlo simulations. Temperature effects on hydrogen diffusion coefficients are discussed.

# sL7. *Operando* IR spectroscopy for a greener catalysis and process enhancement

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In the last decades, concerns about air quality in environment and sustainability of industryal activities have requested a continuous development of efficient catalytic converters, being heterogeneous catalysis a pivotal step in the production of all the needs of humanity. Not only the air quality is on the way to be improved via a better abatement of the pollutants, but also the use of catalysts and processes, which economise rare elements, energy and avoid the use of hazardous compounds represents the way for sustainability.

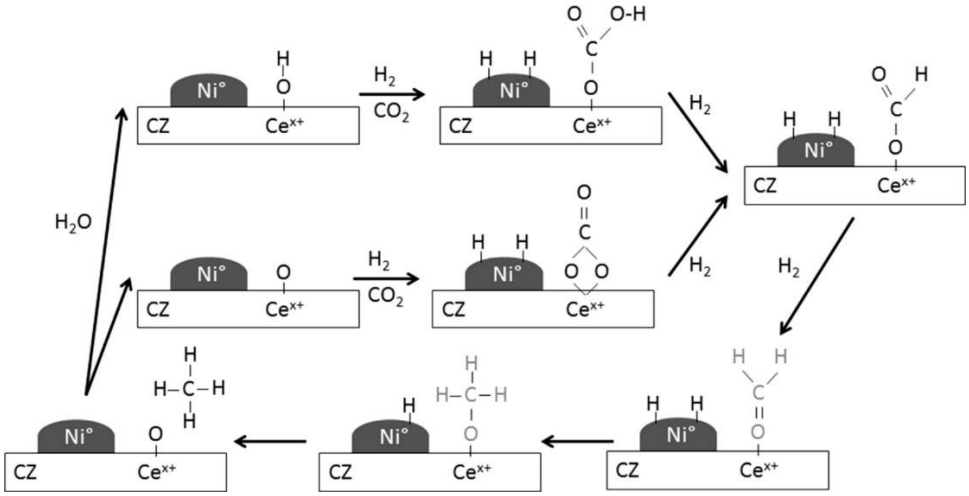
In general, high surface area metal oxides are used as major catalysts, notably in energy conversion.

Zeolites, thanks to their adaptable porosity, acidity, and molecular sieve properties, stand at the forefront of innovation. Notably, ferrierites provide a unique environment for iron sites, a biocompatible, inexpensive, and efficient chemical element able to solve several pollution threats.

Metal-organic frameworks (MOFs) start to arouse the interest of industry for specific applications at low temperature, where their giant porosity and tailorable structures represent the best solution to design and develop single sites catalysts for high selective processes [1].

In the present talk, we will present different proofs of concept in the domain of heterogeneous catalysis, based on the approach of reaction mechanism investigation to identify the main parameters for process enhancement.

We will show the assessment of the reaction mechanism of carbon dioxide methanation on nickel supported on ceria-based catalyst. It will be of high interest to represent all the reaction intermediates and their outbreak sequence, thanks to quantitative infrared analysis, as well as the explanation of product selectivity [2].




In addition, we will highlight the properties of Fe sites in ferrierites through a few examples of applications in the domains of NOx removal from exhaust gases and $N_2O$ abate-

ment from factory emissions. First, we will show how we have set the state and the distribution of iron in FER (in particular in the so-called α, β, and γ positions) by *in situ* IR, with the help of adapted probe molecules. Then, using the IR *operando* approach as main investigation tool [3] and coupling complementary techniques, we will detail how we have been able to describe the reaction mechanisms of those processes at the molecular scale, in order to propose next generation catalysts with specific properties, and promote efficient solutions for process intensification.

We will show that the key for the success is the possibility to 'visualise' dynamically the active sites (in particular $Fe^{II}$), under reaction stream, thanks to spectroscopic techniques and the use of tailored probe molecules.

References


1. S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. Olivos, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, Metal-organic and covalent organic frameworks as single-site catalysts. Chem. Soc. Rev., 46 (2017) 3134–3184.
2. P. A. Ussa Aldana, F. Ocampo, K. Kobl, B. Louis, F. Thibault-Starzyk, M. Daturi, P. Bazin, S. Thomas, A. C. Roger, Catalytic $CO_2$ valorization into $CH_4$ on Ni-based ceria-zirconia. Reaction mechanism by operando IR spectroscopy, Catal. Today, 215 (2013) 201–207.
3. M. A. Bañares, M. Daturi, Understanding catalysts by time-/space-resolved operando methodologies, Catal. Today, 423 (2023) 114255.

Invited lecture

# sL8. PROMETHEUS catalyst: the first ever copper-based automotive catalyst homologated for Euro6 application – current and future challenges

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During the last decades, the large growth of vehicle fleet and the extensive use of cars have been linked with serious environmental impacts such as climate change as well as the greenhouse effect. To address this issue, increasingly stringent emission standards that determine the highest permissible amounts of pollutants that can be emitted by vehicles equipped with internal combustion engines have been implemented globally. The main measure adopted by the car manufacturers in order to control the pollutant emissions of vehicles equipped with internal combustion engines, is the use of advanced catalytic devices in the exhaust aftertreatment systems. These devices (three-way catalysts for petrol-fuelled vehicles, diesel oxidation catalysts, catalyzed diesel particulate filters for diesel-fuelled vehicles) are characterized by the incorporation of concentrated quantities of platinum group metals (PGMs, platinum, palladium, rhodium) as the active catalytic phase to transform the toxic emissions (such as CO, HCs and $NO_x$) to non-toxic compounds. As a result, there is a constantly increasing global demand for PGMs leading to a subsequent increase in their market prices. Therefore, the development of catalytic converters that combine high efficiency with reduced cost and/or PGM loading is of great interest from an economic as well as an environmental point of view.

Among many relevant efforts that have been reported in literature aiming at the development of automotive catalytic converters with partial or complete substitution of PGMs with transient metals, MONOLITHOS Catalysts & Recycling Ltd. has succeeded in developing and patenting a disruptive technology called 'PROMETHEUS catalyst' that allows partial substitution of PGMs by Cu without compromising catalytic activity compared to the state-of-the-art PGM-based catalysts [1]. PROMETHEUS is a novel polymetallic nanosized copper-based catalyst produced in large scale, which is designed taking advantage of the synergistic effects among copper, noble metals, and the high ionic conductivity or oxygen storage capacity of the ceramic carrier, in order to achieve high catalytic activity and stability for the abatement of CO, $NO_x$, and HCs. The three-way Prometheus catalyst for automotive emission control applications, incorporates copper, palladium, and rhodium nanoparticles as the active catalytic material supported on a $CeO_2$-$ZrO_2$ mixed oxide showing high oxygen storage capacity. The novelty of Prometheus catalyst lies in the fact that by utilizing copper in the active catalytic phase, the successful reduction of PGMs loading up to 85% has been confirmed, resulting in a catalytic device with similar or improved catalytic performance compared to state-of-the-art automotive catalysts. Recently, PROMETHEUS catalyst became the first ever Cu-based autocatalyst being homologated for Euro6 application (Approval No. E24*103R00/04*0796*00). Homologation has been granted by the National Standards Authority of Ireland (NSAI). The emission tests have been conducted by TÜV SÜD Auto Service GmbH) and the results obtained are included in figure 1.

For all pollutants, the reduction in emissions using the full-scale PROMETHEUS catalyst varied within 25–55% compared to the legislative Euro6 limits, even though it incorporates 50–85% less PGMs compared to the PGM-based commercial catalysts through their partial substitution by copper [2,3]. The homologation is valid inside the whole European Union for

Euro6 applications up to 1.2 lt engines, while homologation procedure for vehicles with higher engine displacements is currently under way.

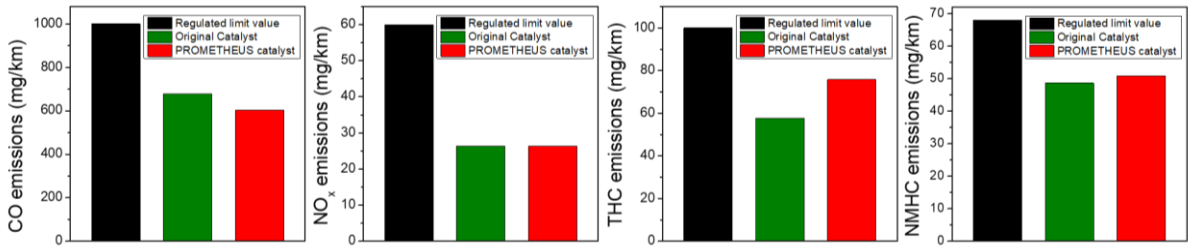
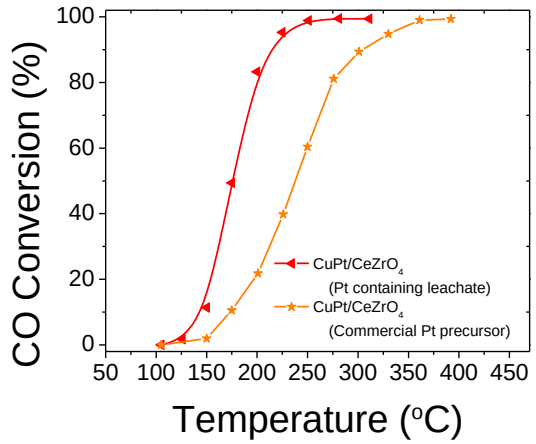



Fig. 1. Results of emission tests performed during the type approval procedure of PROMETHEUS catalyst. TÜV SÜD Auto Service GmbH performed tests.

The proven exceptional activity of Cu for oxidation reactions further allows the utilization of PROMETHEUS catalyst as a diesel oxidation catalyst (DOC) employing formulations that include combination of Cu, Pt, and Pd nanoparticles, allowing Cu substitution for PGMs, similarly to the case of TWCs.




Fig, 2. CO oxidation activity of $CuPt/CeZrO_4$ catalysts prepared using recycled and commercial PGMs as precursors. Gas feed composition: 1% CO, 12% $CO_2$, 10% $H_2O$, 2500 ppm $CH_4$, 800 ppm NO, 0.99% $O_2$ (balance $N_2$).

Considering a challenge of impure/ recycled precursors, the feasibility of using recycled PGM containing leachate solutions, without the need of any refinement steps for the production of new autocatalysts for both TWC and DOC applications has already been reported [4]. The catalysts prepared with recycled PGMs are found to outperform the corresponding benchmark catalysts prepared using commercially available PGMs, both as fresh and hydrothermally aged catalysts (Fig. 2). The combined use of recycled PGMs for the synthesis of new catalysts as well as the incorporation of Cu for the partial substitution of PGMs results in further reduction of catalytic converter's production cost.

PROMETHEUS technology has been also further expanded to other applications besides automotive catalysts, by slightly modifying the synthesis procedure as well as the formulation of the active phase. Such applications already tested include:

- the development of nanocatalysts for maritime applications,
- photocatalysts with tailored activities (nanoparticles with virucidal and/or antibacterial properties to be used in coatings),
- vulcanization catalysts for tire industry as well as
- catalytic conversion of $CO_2$ to value-added products.

References

1. I. Yakoumis, European Patent EP3569309, 20 November 2019.
2. I. Yakoumis, Materials, 14 (2021) 622, doi: 10.3390/ma14030622.
3. I. Yakoumis, E. Polyzou, A. Moschovi, Materials, (2021) 2226, doi: 10.3390/ma14092226.
4. A. M. Moschovi, M. Giuliano, M. Kourtelesis, G. Nicol, E. Polyzou, F. Parussa, I. Yakoumis, M. F. Sgroi, Catalysts, 11 (2021) 942, doi:10.3390/catal11080942

# sL9. Ni active phase and catalyst composition effect on $H_2$ production by $CH_4$ reforming and decomposition

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It is generally accepted that the greenhouse gas emissions such as $CO_2$ and $CH_4$ must be reduced because of their harmful effect on the climate. Therefore, renewable energy carriers instead of combustion of fossil fuels should satisfy the always-increasing energy demand. Dry reforming of methane (DRM) is an attractive process producing syngas and linking $CO_2$ with the synthesis chain of value-added chemicals. Despite the significant potential of such process, the DRM is accompanied by the formation of undesirable by-products and may cause catalyst deactivation due to carbon deposition. Therefore, it is urgently required to develop new catalytic systems that can withstand coke deposition and can be regenerated after poisoning.

In this context, supported nickel-based catalysts exhibit a promising potential owing to their catalytic activity and stability in reforming processes [1]. The nature of the support and the preparation methods are crucial in order to design active and stable catalysts with proper Ni particle size and support interaction, tailored redox properties, and enhanced catalytic performance. In a recent review the most important synthetic approaches, the advances, and the perspectives of lanthanoid-containing Ni-based catalysts for dry reforming have been summarized [2]. The proper combinations of different lanthanoid oxides can yield to an optimal basicity ensuring homogeneous distribution of Ni nanoparticles and lanthanoid oxides over the catalyst surface. Moreover, using promoters, optimizing synthesis conditions, and modifying the support materials [1-5], can significantly improve the performance of Ni-based catalysts in DRM. The use of suitable support oxides and promoters can enhance the dispersion of the Ni particles, control carbon deposition, and improve the redox properties of the catalyst, leading to higher catalytic activity and selectivity towards syngas production. Recently, indium effect (0.25 wt.%) was investigated on alumina and ceria-promoted alumina (8 wt.% $CeO_2$) supported Ni prepared by both deposition precipitation method and wetness impregnation [4,5]. Very strong In-impact was observed to mitigate the carbon deposition on $Ni/Al_2O_3$, while the $CeO_2$ promotion in the $Ni/CeO_2$-$Al_2O_3$ was much less effective. During 4 days of long run tests at 675 °C, stable activity was achieved by the In-promoted catalyst in contrast with the continuous deactivation of registered for the unpromoted Ni sample due to coking and sintering. Indium is partially alloyed with nickel and helps in keep nickel in metallic state. Moreover, the intimate Ni(In)-$CeO_2$ interface inside the support pores resulted in stable conversion of reactants, increased $CO_2$ activation ability, and practically no coking.

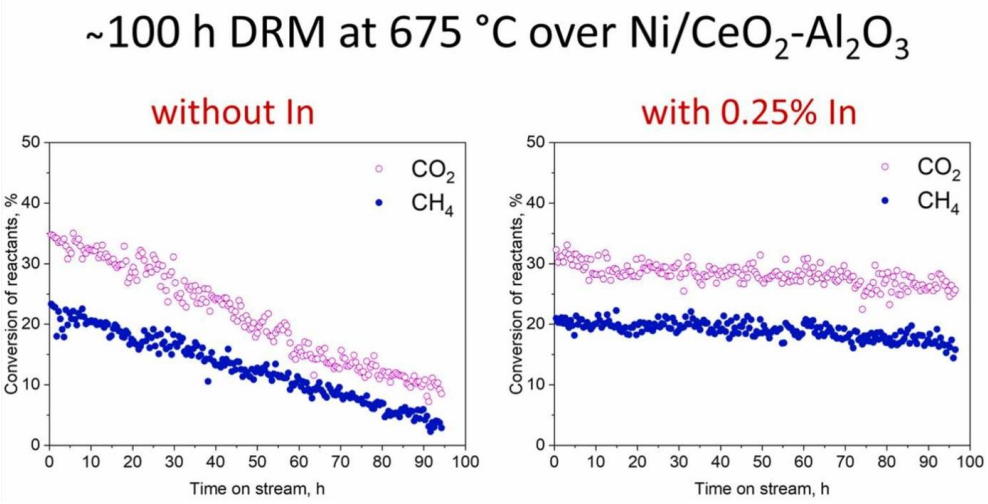



Fig. 1. Methane and $CO_2$ conversion curves during the longevity DRM tests over Ni-CeAl and NiIn-CeAl samples. Conditions: after reduction at 750°C/1 h cooling to T = 675°C in $N_2$, then DRM with $CH_4$:$CO_2$ = 1:1 mixture, 210 L/h/gcat, TOS= 96 h [5].

All these findings provide insights for the development of new efficient and stable catalysts for $CO_2$ conversion through dry reforming, which is a promising approach for addressing both energy and environmental challenges.

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References

1. H. Wu, G. Pantaleo, V. La Parola, A. M. Venezia, X. Collard, C. Aprile, L. F. Liotta, Bi- and trimetallic Ni catalysts over $Al_2O_3$ and $Al_2O_3$-$MO_x$ (M=Ce or Mg) oxides for methane dry reforming: Au and Pt additive effects, Appl. Catal. B: Environ., 156–157 (2014) 350–361.
2. M. A. Salaev, L. F. Liotta, O. V. Vodyankina, Lanthanoid-containing Ni-based catalysts for dry reforming of methane: A review, Int. J. Hydrogen Energy, 47 (7), (2022) 4489–4535.
3. M. V. Grabchenko, N. V. Dorofeeva, V. A. Svetlichnyi, Y. V. Larichev, V. La Parola, L. F. Liotta, S. A. Kulinich, O. V. Vodyankina, Ni-based SBA-15 catalysts modified with CeMnOx for $CO_2$ valorisation via dry reforming of methane: effect of composition on modulating activity and $H_2$/CO ratio, Nanomaterials, 13 (19), (2023) art. no. 2641.
4. A. Horváth, M. Németh, A. Beck, B. Maróti, G. Sáfrán, G. Pantaleo, L. F. Liotta, A. M. Venezia, V. La Parola, Strong impact of indium promoter on Ni/$Al_2O_3$ and Ni/$CeO_2$-$Al_2O_3$ catalysts used in dry reforming of methane, Appl. Catal. A: Gen., 621 (2021) art. no. 118174.
5. A. Horváth, M. Németh, A. Beck, G. Sáfrán, V. La Parola, L. F. Liotta, G. Žerjav, M. Roškarič, A. Pintar, Longevity increase of an impregnated Ni/$CeO_2$-$Al_2O_3$ dry reforming catalyst by indium, Appl. Catal. A: Gen., 669 (2024) art. no. 119495.

Invited lecture

# sL10. Roles of catalyst and feedstock in optimizing performance of heavy oil conversion processes of fluid catalytic cracking and ebullated bed vacuum residue hydrocracking

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The oil refining is a branch of industry that delivers energy to move our vehicles. The transportation of people and goods by airplanes, ships, trains, trucks, buses, and cars are unthinkable for the modern mankind without the use of petroleum refined automotive fuels. Thus, the optimal functioning of this industrial branch is vital to the contemporary human society. The petroleum refineries operating now all over the world are 825, and the most profitable refinery units are those, which convert the bottom of the barrel into high value transportation fuels and feeds for petrochemistry. Among them the fluid catalytic cracking (FCC) with more than 600 units around the world is the most applicable technology to convert heavy oils (vacuum gas oils, and atmospheric residue). The ebullated bed vacuum residue hydrocracking (EBVRHC) is the technology that hydroprocesses over 95% of vacuum residues. Although the number of EBVRHC units in the oil refineries presents only 21 the conversion level they can achieve usually surpasses that attained by the FCC. Investigations performed in laboratory, pilot, and commercial FCC units in the LUKOIL Neftohim Burgas (LNB) refinery have indicated that the conversion of vacuum gas oils (VGOs) from primary origin in the FCC can vary between 69 and 85 wt.%, while the VGO obtained from the EBVRHC can reach a conversion of as low as 53 wt.%. Although the influence of catalyst properties on FCC plant performance is not as great as that of feedstock properties, it was shown in this study that activity and selectivity must be fine-tuned to FCC plant conditions to ensure optimum performance. Reconstruction of FCC unit with selection of the most appropriate catalyst to optimize FCC action is discussed. Correlations were developed to relate feed properties, and catalyst activity to VGO conversion and catalyst delta coke observed at the commercial FCC unit. The research performed at the commercial EBVRHC unit in the LNB refinery demonstrated that the vacuum residue conversion can fluctuate between 55 and 93 wt.% depending on feed quality, operating conditions, and catalyst status. Correlations were developed to relate vacuum residue properties to conversion level and sediment formation rate in the EBVRHC unit. It was found that only depending on catalyst properties the vacuum residue conversion can oscillate by 16 wt.%. It was also established that the catalyst properties, and consequently performance can be better controlled by replacing the design cascade fresh catalyst addition to the ebullated bed reactors with parallel one. The use of the parallel fresh catalyst addition allowed to avoid formation of black powder observed in the first reactor of the LNB EBVRHC unit during two cycles of operation. An investigation of the black powder formed in the first reactor, that surprisingly was found to replace the catalyst revealed that it consisted of $FeV_2S_4$, $NiV_2S_4$, (Ni, Fe)S, NaCl, and coke. The possible mechanism of black powder formation, its properties indicating the presence of catalytic activity, and its influence on the performance of the EBVRHC unit are discussed.

References

1. P. D. Fortain, Étude de la réactivité des résidus pétroliers en hydroconversion, PhD thesis, l'Université Bordeaux 1, 2010.
2. R. H. Harding, X. Zhao, K. Qian, K. Rajagopalan, W. Ch. Cheng, The fluid catalytic cracking selectivities of gas oil boiling point and hydrocarbon fractions, Ind. Eng. Chem. Res., 35,(1996) 2561–2569, https://doi.org/10.1021/ie950449e.

# sK1. The remarkable synergistic effect between perovskites and BiOBr for visible-light enhanced activation of peroxy compounds for organic pollutants degradation

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In recent years, the synergistic degradation of organic pollutants in water through combined activation of peroxy compounds and photocatalysis gained increased attention. The combination of two advanced oxidation processes helps overcome the drawbacks of the two processes and allows excellent performance in a wide range of conditions.

Among the different materials, perovskites are found to be promising catalysts for activetion of peroxy compounds such as peroxymonosulphate, persulphate, percarbonate, and $H_2O_2$. On the other hand, BiOBr in recent years emerged as an excellent material due to its relatively narrow band gap (2.75 eV) making it capable of maximum visible sunlight energy harvesting photocatalyst. Despite numerous research showing the great potential of combining BiOBr and different mixed metal oxides for photo-assisted activation of peroxy compounds, to this date there is no available data on the successful combination of BiOBr and inorganic perovskites.

The aim of this research is to shed light on the synergistic effect of the combination of two different samarium-based perovskites: the classical $ABO_3$ perovskite $SmFeO_3$ and the layered Ruddlesden-Popper type $Sm_2CuO_4$ and BiOBr. For this reason, two series of $SmFeO_3$/BiOBr and $Sm_2CuO_4$/BiOBr catalysts were prepared by a facile solvothermal method. The materials were characterized by several physicochemical methods to evaluate their phase composition, microstructural characteristics, optical and morphological properties. The obtained materials were tested as catalysts for degradation of organic pollutants in water in different photocatalytic processes utilizing various peroxy compounds. The reaction mechanisms were evaluated by a series of radical scavenging experiments. Various factors affecting the catalytic activity were determined such as type and content of the perovskite, water matrix, and light irradiation type.

The obtained results showed the remarkable catalytic activity of the prepared catalysts of all the materials. Furthermore, the synergistic effect between the two co-catalysts was proven and the catalytic activity of the composites significantly exceeded the activity of the individual components.

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# sK2. Support effects for the water-gas shift performance of gold-based catalysts

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The use of hydrogen as an alternative source of energy able to tackle various environmental problems is a subject of increased worldwide interest. Our society has already recognized the benefits of transition from carbon age to hydrogen times. Growing hydrogen demand and advancement in fuel cell technology contributed to the renewed interest in the water-gas shift (WGS) reaction. It is a well-established industrial process for hydrogen production that leads to increase of hydrogen concentration in the synthesis gas (CO and $H_2$ mixture) obtained by processes utilizing fossil fuels or biomass-derived sources. Efficient upgrading the purity of hydrogen for fuel cell applications impose new goals and challenges for design of WGS catalysts. Among variety of compositions developed for high- and low-temperature shift reaction, supported gold catalysts attract special attention during the last three decades. Compared to commercial WGS catalysts, the main advantage is the combination of high activity at low temperature and favourable features enabling use in small-scale applications such as on-board hydrogen generators or residential fuel cells. Various strategies and approaches to design efficient gold-based catalysts were developed. Special attention was given to exploration of appropriate carriers owing to undisputed role of support nature in determining the catalytic activity [1]. The support may participate in the reaction or control catalytic behaviour by affecting gold-support interface interaction, shape and gold particle size, and stabilization of gold's structural/electronic properties. The first evidence signifying a decisive role of the support in WGS activity was provided by comparison of gold with mean particle size of about 3.5 nm supported on $Fe_2O_3$ and $Al_2O_3$ where a very low activity of $Au/Al_2O_3$ was observed [2]. Later on, a much higher WGS activity of $Au/TiO_2$ and $Au/CeO_2$ than gold nanoparticles supported on non-reducible supports, such as $Al_2O_3$ and $SiO_2$ was reported [3].

Among various oxides, ceria-based gold systems received a special attention. Ceria became an attractive support in a new generation of WGS catalysts due to its ability to undergo fast $Ce^{4+} \leftrightarrow Ce^{3+}$ transfer and to dissociate water on created oxygen vacancies, as well to keep high dispersion of supported noble metals. Numerous studies of $Au/CeO_2$ catalysts have addressed how various factors, including the method of preparation, gold loading and support surface area, gold particle size, structure and oxidation state, and reactivity of surface species, correlate with catalytic performance in the WGS reaction. The modification of ceria was considered an important approach to improvement of WGS activity of gold/ceria catalysts. Different additives (Sm, La, Zn, Fe, Mn, Sn, and Y) were incorporated in the ceria lattice to increase the amount of oxygen vacancies owing to their crucial role in water dissociation. In depth characterization by different techniques (XRD, HRTEM/HAADF, XPS, FTIR, Raman and Mössbauer spectroscopy, TPR) was performed aiming to clarify the effect of dopant nature on WGS activity. Special emphasis was put for elucidation of the role of Zn addition, because in contrast to expectation for enhanced activity, no positive effect on the WGS activity was observed. Significant effect on the WGS performance of Au/ceria catalysts was achieved by using yttrium as dopant of ceria. The influence of two different preparation methods (impregnation and co-precipitation) and dopant amount (1, 2.5, 5, and 7.5 wt.% $Y_2O_3$) was examined. High catalytic

activity, very close to equilibrium 99.3% CO conversion, was measured at 260°C over gold catalyst supported on ceria doped by impregnation with 1 wt.% $Y_2O_3$ [4]. The role of iron as dopant of $Au/CeO_2$ catalysts was also investigated in depth. The influence of mixed Ce-Fe oxides preparation approach and composition were studied. Significantly, higher activity of gold catalysts on mechanochemically prepared supports in comparison with those on impregnated Fe-Ce oxides was explained with the availability of higher amount highly dispersed Au particles and the presence of separate defective magnetite phase.

Preparation of appropriate and economically viable carriers with complex composition by various synthesis procedures emerged as a successful strategy for improved WGS performance. Commercial γ-alumina was modified with well dispersed surface fraction of Ce–Fe mixed oxides and used as a support of gold-based catalysts. This synthesis concept allows maximizing the activity per mass of gold due to its high dispersion on the support surface, thus achieving greater interfacial area between gold nanoparticles and supported on alumina mixed oxides, as well as enhanced oxygen mobility. Further advantage from economical point of view was the lower amount of ceria in the catalysts formulation as compared to $Au/CeO_2$ [5]. The favourable properties of transition metal oxides and gold nanoparticles were combined in preparing gold-based catalysts on alumina-supported Cu-Mn mixed oxides. Addition of gold contributed to spinel $Cu_{1.5}Mn_{1.5}O_4$ decomposition and formation of highly dispersed copper particles during the reaction without the need of reduction pretreatment. It was found that the high activity originated not only from the gold-assisted reduction of CuO, but also from the presence of Au and Cu metallic particles, which dispersion was strongly affected by the composition of alumina-supported Cu-Mn mixed oxides[6].

Novel catalytic systems with enhanced efficiency for the WGS reaction were thoroughly investigated, harnessing the advantageous properties of hydrotalcite materials and supported gold nanoparticles. In the case of $CuO/ZnO/Al_2O_3$, it was established that gold addition facilitated CuO reduction at the early stages of reaction and ensured the presence of Cu and Au active phases avoiding the requirement for catalyst conditioning [7]. Deposition of gold on layered double hydroxide with $Ni^{2+}/Al^{3+}$ molar ratio of 2.5 produced an efficient catalytic material, which reached equilibrium CO conversion of 97.6 % at 240°C. Further improvement of Au/NiAl catalyst was achieved via modification by ceria [8].

Upon analysing the correlation between WGS activity and carrier characteristics, it becomes evident that employing the right chemical composition and synthesis method enables the development of gold catalysts with highly promising practical applications.

References


1. T. Tabakova, Frontiers in Chemistry, 7 (2019) 517.
2. D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, J. Catal. 158 (1996) 354.
3. A. Sandoval, A. Gomez-Cortes, R. Zanella, G. Diaz, J. M. Saniger, J. Mol. Catal. A, 278 (2007) 200.
4. T. Tabakova, L. Ilieva, I. Ivanov, M. Manzoli, R. Zanella, P. Petrova, Z. Kaszkur, J. Rare Earths, 37 (2019) 383.
5. T. R. Reina, S. Ivanova, V. Idakiev, J. J. Delgado, I. Ivanov, T. Tabakova, M. A. Centeno, J. A. Odriozola, Catal. Sci. Technol., 3 (2013) 779.
6. T. Tabakova, I. Ivanov, Y. Karakirova, D. Karashanova, A. M. Venezia, P. Petrova, G. Avdeev, E. Kolentsova, K. Ivanov, Catalysts, 8 (2018) 563.
7. J. L. Santos, T. R. Reina, I. Ivanov, A. Penkova, S. Ivanova, T. Tabakova, M. A. Centeno, V. Idakiev, J. A. Odriozola, Appl. Catal A, 558 (2018) 91.
8. M. Gabrovska, I. Ivanov, D. Nikolova, J. Krstic, A. M. Venezia, D. Crişan, M. Crişan, K. Tenchev, V. Idakiev, T. Tabakova, Nanomaterials, 11 (2021) 366.

# sO1. Structure related functional properties of complex oxides prepared via mechanochemical route

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The properties of nanomaterials are sensitive to structural/microstructural parameters, which in turn strongly depend on the preparation method. There is a challenge to improve physical performance as magnetization, conductivity, photoluminescence, catalytic activity, etc., by varying microstructural parameters (e.g. particle size and shape, strain, defects) using new or modified synthesis procedures. Among the many types of preparation techniques, nonconventional mechanochemical synthesis has been recognized as a powerful route to novel, high-performance, and low-cost nanomaterials. In this work, structure response of the various mechanosynthesized complex and/or doped oxides like spinels and perovskites to mechanical action due to high-energy ball milling is reported. Substances functional properties including optical, catalytic, electrical, or magnetic behaviour are influenced by milling conditions. Understanding the interconnection between functional and structural features of mechanosynthesized materials plays very often a key role in optimization of their synthesis and properties. The work is focused on combination of diffraction, spectroscopic and microscopic methods to evaluate local structure of synthesized materials. It is shown that as-prepared nanoparticles exhibit wide range of modified physical behaviour.

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# sO2. Enhanced catalytic activation of peroxymonosulphate over $SmFeO_3$/CuO composite for antibiotics removal from water

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Over the last few decades, rapid industrial development and growth of the human population has led to significant pollution of water ecosystems. One of the most serious problems is water contamination with organic pollutants, such as dyes, antibiotics, cosmetic products, etc. that is stable and this enables contaminants to persist in the ecosystems for a long time. Traditional biological, chemical, and physical methods are unable to remove completely these organic compounds or bring about significant accumulation of secondary pollutants. Thus, search for new ways to purify water continues.

Recently advanced oxidation processes (AOP) emerged as one of the most promising technologies by which sulphate radical-based AOP (SR-AOP) showed excellent capabilities to mineralize organic matter in water. Full characterization of the materials was realised by powder XRD and other methods in order to determine their properties. The catalysts were then tested for activation of peroxymonosulphate and Fenton-like reaction for organic pollutants degradation. Various factors affecting the catalytic process were examined and series of reactive oxygen species scavenging experiments were conducted in order to propose a reaction mechanism based on the results.

Due to their excellent performance, perovskites of the type $ABO_3$ have gained increased attention as catalysts in various AOP processes such as photocatalysis, Fenton-like reactions, and sonochemical and electrochemical oxidation processes.

In this work for the first time, we present results about catalytic activation of peroxymonosulphate over novel composite $SmFeO_3$/CuO prepared by a simple chemical route. The obtained catalysts showed excellent catalytic activity surpassing that of the individual components proving a synergistic effect. The effect of various parameters was evaluated such as $SmFeO_3$ to CuO ratio, water matrix, and light irradiation. The reaction mechanism was evaluated by series of radical scavenging experiments.

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# sO3. Unveiling the synergistic effects of pH and Sn content for tuning the catalytic performance of $Ni^0/Ni_xSn_y$ intermetallic compounds dispersed on Ce-Zr mixed oxides in aqueous-phase ethylene glycol reforming

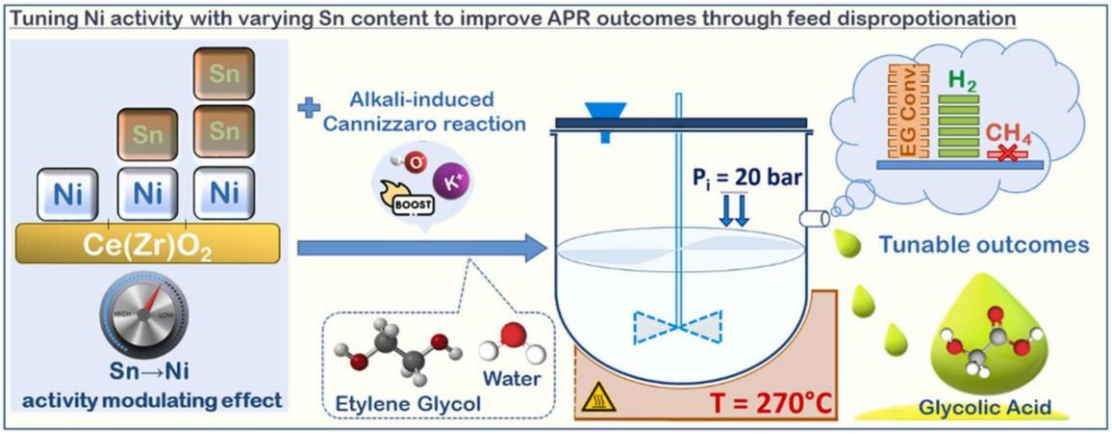
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Product distribution in aqueous phase reforming (APR) of polyols is closely related to the catalytically induced feed cleavage mechanism. Strategic variations in catalyst composition and synergistic effects prompted by reaction conditions, such as pH, can be utilized to tune product distribution of both liquid and gaseous phases. This study is aimed at comparing the physico-chemical properties of various $Ni_xSn_y/Ce(Zr)O_2$ catalysts and their performance in batch tests during aqueous phase reforming of a 6-wt.% ethylene glycol (EG) solution under both neutral and alkaline conditions. Results showed that progressive addition of tin strongly tuned catalysts activity and the nickel-induced methanation reaction under neutral conditions, albeit decreasing feed conversion. In synergy with tin tuning, alkaline environment boosts the process by increasing conversion and hydrogen yield while still minimizing methanation due to the alkali-induced process of Cannizzaro disproportionation of ethylene glycol into glycolic acid with subsequent reforming thereof [1].

In this study, three different intermetallic Ni-Sn compounds with different crystallographic arrangements, supported on cerium-zirconium mixed oxides were synthesized by reductive sintering. Samples textural, morphological, and physicochemical characteristics were studied throughout the entire synthesis process to correlate the differences with the catalytic results. $^{119}$Sn-Mössbauer and XRD analyses of 2.510SnNi-CZ_red and 510SnNi-CZ_red samples disclosed a crystallographic arrangement consisting of $Ni^0$ and the intermetallic $Ni_3Sn$ compound (IMCs), present in a distorted state with the 2.510SnNi-CZ_red sample, and of hexagonal geometry and well-defined crystallinity for the 510SnNi-CZ_red sample. On the other hand, the sample with the highest tin content, 1010SnNi-CZ_red, was shown to contain a modest relative abundance of $Ni^0$ and $Ni_3Sn$ and a conspicuous amount of $Ni_3Sn_2$. Investigation of the monometallic catalysts containing only tin on the CZ support showed that $Sn^{4+}$ had a strong interaction with the CZ, suppressing the reduction with loading dependency of tin. In the bimetallic catalysts although the reduction takes place completely, it was demonstrated through XPS, XAS, and TEM that exposure of IMCs to an oxygenated environment caused partial passivation, with the formation of an amorphous oxide layer. According to information gained

through analysis of the isomeric shifts of $^{119}Sn$ nuclei, aided by analysis of density variation of the occupied states at the Ni K-edge of samples containing IMCs, there appeared to be a Sn→Ni electron density donation capable of diminishing the intrinsic chemisorptive properties of nickel. Analytical studies of the chemisorption properties of bimetallic catalysts in comparison with the 10Ni-CZ_red catalyst used as a reference showed that the Sn-Ni combination significantly decreased the number of $Ni^0$ active sites for chemisorption. From catalytic point of view, tests carried out under standard conditions ($pH_i$=7) showed how the 'mitigating effect' of the Sn-mediated interaction with $Ni^0$ constrained the reaction pathways favoured over the monometallic nickel catalyst, suppressing the methanation reaction but also limiting feed conversion as the tin content increases in the IMCs involved. On the other hand, tests conducted under alkaline conditions ($pH_i$=14) showed a considerable increase in EG conversion, increased selectivity for $H_2$-producing pathways and thus high hydrogen yields, especially for the 510SnNi-CZ-red catalyst. The reason for the found increased conversion of ethylene glycol together with a higher hydrogen yield under initial alkaline conditions was attributed to competitive conversion of the feed into glycolic acid via the hydrogen-producing Cannizzaro reaction.




Further decarboxylation of glycolic acid with a related production of $CO_2$ and methanol would allow continuation of the reforming process via WGS or methanation reactions. Therefore, tin presence in the bimetallic catalysts indicated to be essential in tuning the cleavage properties and the selective suppression of the methane productive properties found for the monometallic nickel catalyst. Hence, in synergy with the Cannizzaro reaction induced by the alkaline environment, a positive and tunable combination of effects is obtained in terms of conversion and hydrogen selectivity and yield. Hydrogen high yields combined with negligible values of methane produced make the metallic and intermetallic arrangement found in the 510SnNi-CZ_red catalyst a promising initial point for simultaneous production of hydrogen and a fine chemical such as glycolic acid starting from aqueous solution of ethylene glycol at alkaline conditions [1].

Acknowledgments: This project has received funding from Marie Skłodowska-Curie Action – International Training Network (MSCA-ITN), grant agreement 813748 and the European Regional Development Fund within the Operational Programme 'Science and Education for Smart Growth' 2014–2020 under the project 'Center of Excellence: National center of mechatronics and clean technologies - BG05M2OP001-1.001-0008'.

References

1. C. Rosmini, M. P. Urrea, E. Tusini, S. Indris, D. Kovacheva, D. Karashanova, H. Kolev, A. Zimina, J. D. Grunwaldt, M. Rønning, M. Dimitrov, M. Popova, 'Unveiling the synergistic effects of pH and Sn content for tuning the catalytic performance of $Ni^0/Ni_xSn_y$ intermetallic compounds dispersed on Ce-Zr mixed oxides in the aqueous phase reforming of ethylene glycol', Appl. Catal. B: Environ. Energy, 350 (2024) 123904. https://doi.org/10.1016/j.apcatb.2024.123904.

# sO4. Alkaline fuel cell HOR catalyst evolution from noble to non-noble, from idea to a scale-up product

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Alkaline fuel cells (AFC) gain much attention in the last ten years as an alternative to acidic fuel cells. AFC advantage is usage of non-precious metal catalysts like nitrogen-doped carbon material on the cathodic side while anodic side is still dominated by platinum group metals (PGM) such as Pt and Pd. The significant increase of PGM prices and AFC commercialization require intensive research on anodic catalyst cost reduction. In 2012, GenCell Ltd. started a project with Institute of Catalysis of the Bulgarian Academy of Sciences aimed to replace existing Pt catalyst by cheaper catalyst composition with the same electrochemical performance. During this period a NiPd catalyst was developed and employed for (liquid electrolyte) AFC [1].

Nowadays a completely non-noble, trimetallic, Ni-based anode catalyst was designed and developed of the same electrochemical performance as NiPd catalyst under 6.6M KOH @ 70°C (Fig. 1). The achieved potential of the non-noble Ni-based catalyst at 100 mA/cm$^2$ current density was 50–54 mV *vs* 61 mV of NiPd catalyst (red baseline).

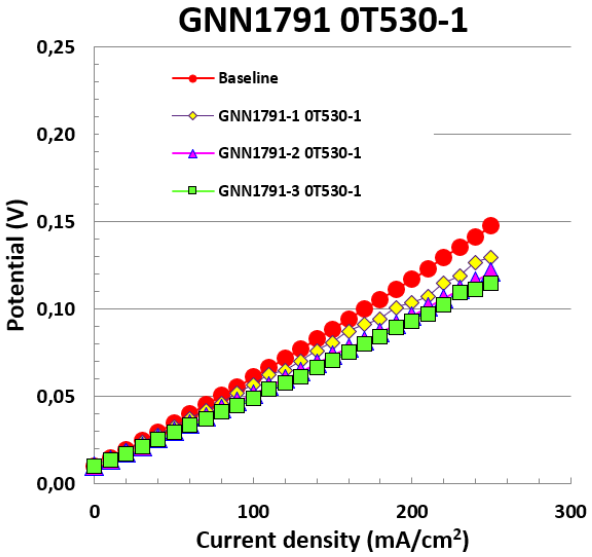



Fig. 1. Electrochemical performance of non-noble Ni-based catalyst at 400 g batch synthesis *vs* NiPd catalyst (red baseline) (Synthesis number: 0T530, anode number: GNN1791).

Several compositions and ratios were tested as well as preparation approaches and reduction conditions until reproducible results were obtained. The successful composition was scaled up and tested in a fuel cell module with projected area of 6480 cm$^2$ showing a stable anodic potential over the operation period including several start-ups and shutdowns. Ni-based catalyst reached over 1500 operating hour's module operation at a constant current of 100 amperes until reaching targeted end of life (EOL) at 375 W (Fig. 2).

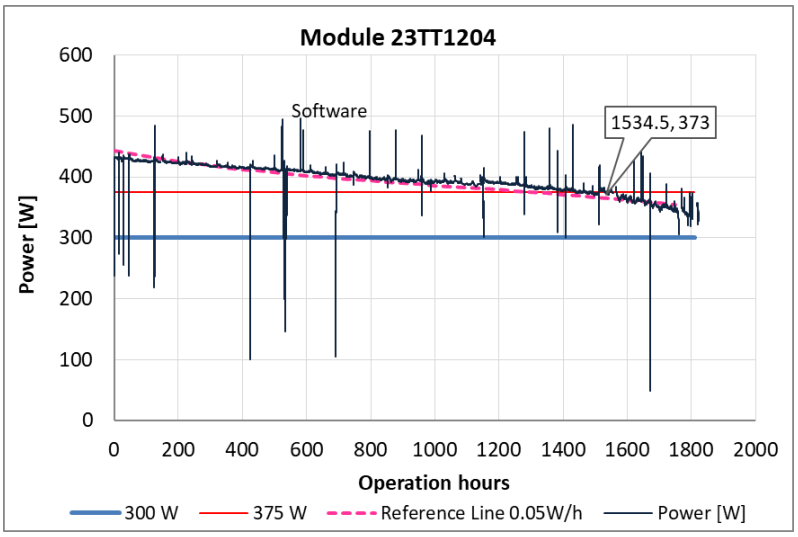



Fig. 2. Power profile of non-noble trimetallic Ni-based fuel cell module tested at 100 mA/cm$^2$ @ 70°C, 6.6 M KOH.

GenCell's non-noble catalyst manifested a stable operation and low degradation rate for three months of module work. The composition and synthesis are patent pending [2,3].

Acknowledgement: Financial support is due to funding from project between Institute of Catalysis, Bulgarian Academy of Sciences, and GenCell Ltd., Israel, for the period of 2012–2023.

References

1. N. Borchtchoukova, V. Feldman, G. Finkelshtain, S. Rakovsky, M. Gabrovska, D. Nikolova, L. Bilyarska, Nickel-based catalyst for fuel cell, US 10,522,844 B2 / 31.12.2019.
2. N. Borchtchoukova, Y. Wijsboom, G. Finkelshtain, M. Gabrovska, D. Nikolova, Nickel-based catalyst for fuel cell anode, EP4046217A1 / 24.08.2022.
3. N. Borchtchoukova, Y. Wijsboom, G. Finkelshtain, M. Gabrovska, D. Nikolova, Nickel-based catalyst for fuel cell anode, US2024/0128472A1 / 18.04.2024.

# sO5. Selectivity optimization of cobalt-based catalysts for $CO_2$ utilization by alkali promotion: atomic scale insights from molecular modelling

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$CO_2$ reduction based on green hydrogen is a promising long-term approach that can aid decarbonisation of the heavy industry and provide negative emissions to combat climate change. Cobalt-based catalysts, which are industrially applied in CO-based Fischer-Tropsch synthesis (FTS), were shown to be also active for $CO_2$-FTS. Unfortunately, (mono)metallic cobalt catalysts produce predominantly $CH_4$ with >90% selectivity. Several studies were able to tune the selectivity of cobalt catalysts for CO2-FTS to valuable products, mainly by using bimetallic catalysts [1] and promoters [2]. Although commonly pointed out that surface $CO_x$/H ratio modification is the main reason for the changed selectivity of Co catalysts due to alkali promotion [1-3], molecular level understanding about active phases/sites and mechanistic pathways that are responsible for the altered selectivities are still lacking, which limits rational design of selective catalysts for $CO_2$-FTS.

Here, we report an investigation based on molecular modelling to provide atomic scale understanding for alkali induced effects on $CO_2$ hydrogenation. The results indicate that alkali promotion changes both the mechanistic pathways for $CO_2$ activation and hydrogenation reactions kinetics, in addition to the surface coverages of $CO_x$ and hydrogen, providing key descriptors for optimization of mono- and bimetallic cobalt catalysts.

Periodic spin-polarized DFT calculations were conducted using the Vienna ab initio simulation package (VASP) with the revised Perdew-Burke-Ernzerhof (revPBE) functional incorporating non-local vdW-DF correlation. Electron-ion interactions were modelled with the PAW method, using a (3x3x1) k-points grid and a cut-off energy of 500 eV. Surface structures of fcc-Co nanoparticles were represented by Co(111) slabs with 4 atomic layers. Na-promoted Co surfaces were modelled as highly dispersed $Na_2O$ units adsorbed on Co(111), in accordance with experimentally characterized structures [3]. Both clean and alkali-promoted surfaces were modelled with a p(3x3) unit cell, corresponding to an adsorbate/Na coverage of 0.11 ML. Transition states were optimized using the CI-NEB method and verified by vibrational analysis.

Alkali promotion of Co(111) resulted in major changes of both adsorption energies ($E_{ad}$) of surface species and elementary reactions kinetics. $Na_2O$ promotion led to significant increase in both $CO_2$ and CO $E_{ad}$ due to the coordination of O atom of $CO_x$ with Na cations as shown in figure 1a for $CO_2$. Conversely, this bonding structure is not favourable for H, $CH_x$, and $C_2$ species, and therefore, $E_{ad}$ for these species is reduced. The results indicate that $Na_2O$ increases $CO_2$ coverage while decreasing those of H and $C_2$ species. The effect of alkali promotion on the kinetics was investigated by modelling elementary reactions for $CO_2$-FTS as shown in figure 1b. The results indicate two main mechanistic changes on the promoted surface: (i) $CO_2$ dissociation is shifted from direct to H-assisted pathway, leading to increased H consumption on the surface; (ii) hydrogenation of O species is promoted while $CH_x$ hydrogenation and CH coupling are hindered.

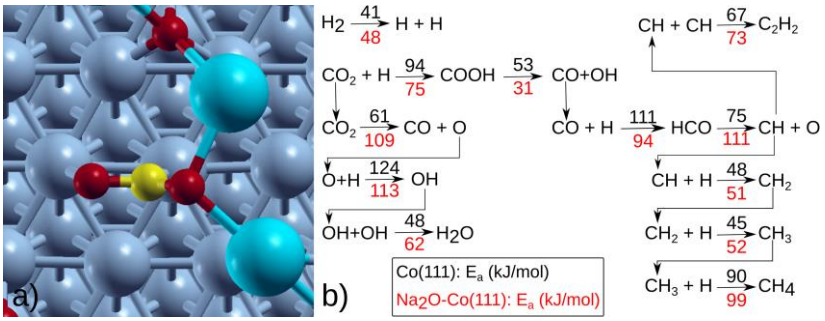



Fig. 1. a) Adsorption structure of $CO_2$ on $Na_2O$-Co(111), b) Energetically favoured reaction network showing the activation energies ($E_a$) for elementary reactions in $CO_2$-FTS for Co(111) (black) vs $Na_2O$-Co(111) (red).

Overall, these findings indicate that $Na_2O$ promotion boosts $CO_2$-FTS activity on Co catalysts by increasing the $CO_2$ coverage and promoting the rate limiting step of OH formation. In terms of selectivity, alkali promotion reduces the selectivity to $CH_4$ and saturated hydrocarbons, while selectively tuning the hydrocarbon formation to short chain species. These insights compliment recent findings on the effect of K promotion on cobalt-based $CO_2$-FTS [2] while the acquired mechanistic understanding provides useful design principles, in particular for the bimetallic FeCo catalysts, which were reported to hinder oxygen removal [1]. The results are currently further embedded in kinetic Monte Carlo simulations to investigate the effects of alkali promotion on product selectivity as a function of temperature, pressure, and surface coverage. This study provides novel atomic scale insights for alkali induced effects on Co-based $CO_2$-FTS catalysts, which can guide the rational design of catalysts with tunable selectivity.

References

1. D. Tuncer, A. C. Kizilkaya, Catalysts, 13 (2023) 1390.
2. W. Li, X. Nie, H. Yang, X. Wang, F. Polo-Garzon, Z. Wu, J. Zhu, J. Wang, Y. Liu, C. Shi, C. Song, X. Guo, AppL. Catal. B-Environ., 315 (2022) 121529.
3. K. Jeske, A. C. Kizilkaya, I. López-Luque, N. Pfänder, M. Bartsch, P. Concepción, G. Prieto, ACS Catal., 11(8), (2021) 4784–4798.

# sO6. Dual system for $CO_2$ capture and hydrogenation to methane based on modified mesoporous silica prepared from rice husks

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Increasing the high standard of living together with intensive industrialization, lead to the high consumption of energy and natural resources, which in turn exacerbates environmental problems related to climate change and deterioration of atmospheric air quality. This is mainly due to acid and greenhouse gas emissions in the atmosphere, depletion of fossil fuels, waste disposal on soil terrains, generation of polluted wastewater, etc. [1]. Environmental protection and climate change management set high challenges for developing efficient low-carbon and waste-free energy technologies while imposing the principles of circular economy in key industrial productions. A leading concept in the transition to green energy and achieving carbon neutrality are the technologies for capturing and utilizing carbon emissions (carbon capture and utilization, CCU) through their conversion into synthetic fuels (syngas), as well as obtaining fuels or precursors for their production via chemical transformation of waste biomass [2]. Reducing energy intensity of these processes to achieve economic and technological expediency, along with ensuring a high degree of conversion of the raw material to fuels require the application of catalysts.

In this study, dual adsorbent/catalyst system was developed based on N-(hydroxymethyl)-piperazine- and 1-methylpiperazine-modified mesoporous silicas and Mg-doped bimetallic Ni-Co modified mesoporous silicas, all of which obtained from rice husks, for $CO_2$ capture and hydrogenation to renewable methane, respectively.

Initial mesoporous silica (MS) was prepared by citric acid treatment of rice husks followed by calcination at 500°C without using organic template. This procedure is environmentally friendly and economically efficient. Cyclic amine (N-(hydroxymethyl)-piperazine or 1-methylpiperazine) modified mesoporous silicas were developed by post-synthesis procedure. The latter procedure did not affect significantly structural characteristics of the initial mesoporous silicas. $CO_2$ adsorption on the obtained materials was tested under dynamic conditions. A higher $CO_2$ capacity was reached in the case of N-(hydroxymethyl)-piperazine modified MS (Table 1). The materials are reusable and their $CO_2$ adsorption capacities were slightly lower in three adsorption/desorption cycles.

Table 1. Content of the formed functional groups in the prepared MS materials and their $CO_2$ capacity

| Sample | Content of organic functional groups[1], wt.% | $CO_2$ adsorption from $CO_2/N_2$, mmol/g |
|---|---|---|
| MS-N-(hydroxymethyl)-piperazine | 16.3 | 2.3 |
| MS-1-methylpiperazine | 14.6 | 2.1 |

[1] determined by TG analysis

The catalysts were prepared by incipient wetness impregnation technique with nickel and cobalt loading of 10 wt.% and 5 wt. % of metal, respectively.

Mg-doped Ni-Co modified mesoporous MS catalysts were prepared by a two-step procedure in which Mg salt was added either before or after modification with Ni and Co. XRD patterns of the Ni/Co bimetallic and Mg-doped Ni/Co modified catalysts after reduction at 400°C showed formation of $Ni^0$ and NiO nanoparticles. Material exposing a high specific surface area (364 $m^2/g$) and mesopores of narrow size distribution with a maximum at around 3.5 nm distinguish initial mesoporous silica. The impregnation procedure resulted in a decrease of the specific surface area of the modified mesoporous silicas, proportional to the amount of added metals. The influence of Ni and Co content, Mg adding, and sequence of Mg addition on catalysts reduction properties were followed by temperature-programmed reduction (TPR) analysis. TPR results showed that doping with Mg after the modification with Ni and Co led to a stronger interaction of the metals with the support. XPS study revealed that the surface became rich in nickel for silica-supported Mg-doped Ni-Co catalysts. The obtained catalysts were tested for carbon dioxide hydrogenation to methane. Non-doped samples exhibited lower activity than the Mg-doped entities.

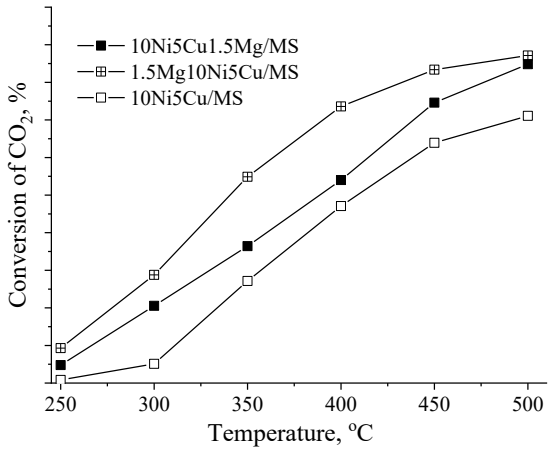



Fig. 1. Catalytic activity vs. temperature for the catalysts at $H_2$:$CO_2$ ratio of 4:1 and GHSV of 60 000 $mL g_{cat}^{-1} h^{-1}$).

The selectivity to methane followed the same trend as the activity, which is due to the stepwise reaction in which CO was an intermediate in the process of $CH_4$ formation. The highest activity and high selectivity for methane formation were registered for 1.5Mg10Ni5Co/MS material, reaching equilibrium conversion and 100% selectivity at 400°C. Stability and re-usability of the latter catalyst in three reaction cycles indicated that it is appropriate for practical application.

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References

1. D. Lüthi, M. Le Floch, B. Bereiter, T. Blunier, J.-M. Barnola, U. Siegenthaler, D. Raynaud, J. Jouzel, H. Fischer, K. Kawamura, Th. F. Stocker, High-resolution carbon dioxide concentration record 650 000–800 000 years before present, Nature, 453 (2008) 379–382.
2. M. F. Hasan, M. S. Zantye, M.-K. Kazi, Challenges and opportunities in carbon capture, utilization, and storage: a process systems engineering perspective, Comput. Chem. Eng., 166 (2022) 107925, https://doi.org/10.1016/j.compchemeng.2022.107925.

# sO7. Catalytic combustion of volatile organic compounds over cobalt supported on different porous materials

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Global environmental protection is the topic of research works for over two decades. Abatement of volatile organic compounds (VOCs) in the waste gases is an important task in the areas of environmental protection. The European Commission presented the so-called Green Deal in December 2019, also known as the Green Pact, which is a set of policies aimed at making Europe climate neutral by 2050. The design of a catalytic system for complete oxidation of hydrocarbons is an important problem of environmental catalysis. Cobalt oxide is reported as quite promising among the metal oxides used for preparation of supported catalysts for VOCs removal. Deactivation is the main drawback of the transition metal oxides catalysts as result of aggregation. The problem could be tackled by application of supports with new properties as those of nanostructured porous oxides.

New highly active and stable catalysts for complete oxidation of volatile organic compounds and carbon monoxide based on transition metals ($Co_3O_4$, MnOx) and microporous carriers like zeolite type ZSM-5 with Si/A varying ratio and ZSM-5 with second-level porosity, mesoporous silica type SBA-15, and macro-mesoporous silica were designed. Zeolite ZSM-5 was chosen because of its properties, namely high hydrothermal structural stability and high surface mass to volume ratio. Zeolite ZSM-5 exhibiting a second-level porosity was obtained by treatment with a buffer solution of hydrofluoric acid and ammonium fluoride. SBA-15 was used as the mesoporous carrier due to greater pore wall thickness and higher hydrothermal stability relative to MCM-41. The advantage of the hierarchically porous materials is that the large macro pores combined with the mesoporous structure give the materials large transport channels accompanied by high active surface area, which is beneficial for catalytic activity.

Samples were prepared by impregnation of the porous supports with cobalt acetate, manganese acetate, and cobalt nitrate precursors. Catalysts were characterized by different instrumental methods as SAXS, BET, TEM, XRD, XPS, EPR, SEM, $H_2$/TPR, $O_2$-TPD, $C_3H_8$/TPR, UV-Vis, and IR before and after catalytic measurements.

The catalytic properties were tested in complete oxidation reactions of methane, ethane, propane, butane, *n*-hexane, and CO. A stability examination was performed with selected catalysts that showed the highest activity.

ZSM-5 materials having different Si/Al ratio (23, 40, and 100) were modified by cobalt deposition from aqueous solution of $Co(C_2H_3O_2)_2.4H_2O$. Different cobalt oxide species were formed on the surface of Co–ZSM-5 samples: bulk-like $Co_3O_4$ phases, $Co^{2+}$ in ion exchange positions (α and γ sites), oxo cations containing $Co^{2+}$, $[Co–O–Co]^{2+}$, and/or CoOx stabilized inside the zeolite, and silicate like phases. Co-existence of two types of $Co_3O_4$ particles could be assumed: large supported $Co_3O_4$ particles and small particles strongly interacting with the support [1].

Zeolites ZSM-5 treatment with a buffer solution of HF and NH4F led to obtaining a material with secondary mesoporosity. Cobalt deposition from $Co(C_2H_3O_2)_2.4H_2O$ aqueous solution on the surface of treated samples generated the formation of different cobalt oxide species: bulk-like $Co_3O_4$ phases strongly interacting with the support, $Co^{2+}$ in ion-exchange positions (γ and β sites), and silicate like phases. A mechanism of cobalt silicate-phase formation was proposed, including replacement of silanol groups, bridging hydrogens by cobalt, and Co atom inclusion in tetrahedral framework positions [2].

The catalysts, prepared through use of ZSM-5 zeolites treated with HF and $NH_4F$, demonstrated a higher activity in the reactions of propane and *n*-hexane complete oxidation compared with catalyst samples containing untreated zeolite. Both higher metal particle dispersion on the hierarchical sample and presence of secondary mesoporosity played a positive role in increasing catalytic activity. Creation of additional porosity improved reagents access to the active sites.

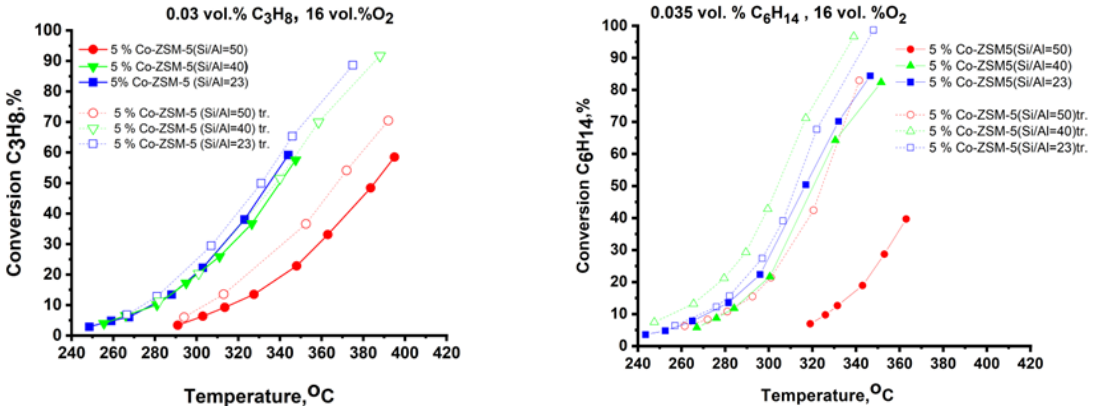



Fig. 1. Temperature dependence of (a) propane oxidation and (b) *n*-hexane complete oxidation on parent and treated Co-ZSM-5 catalysts of different Si/Al ratio (23, 40, and 50) [2].

Cobalt modification of SBA-15 and macro-mesoporous silica (MMS) led to a decrease of specific BET surface area and pore volume, and modification of the adsorption-desorption curve shape. This might be due to partial pore blocking by Co particles. Finely divided and weakly interacting with the support $Co_3O_4$ and $CoSiO_3$ species were formed on the surface of both precursor supports.

Highly developed surface of the porous carriers favoured the formation of finely dispersed metal oxide particles preventing agglomeration. The highly developed network of channels promoted diffusion of the reagents to the catalytically active centres. It was found that the reaction mechanism of VOCs complete oxidation was dependent on hydrocarbon type.

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References

1. R. Velinova, B. Grahovski, H. Kolev, G. Ivanov, S. Todorova, A. Naydenov, React. Kinet. Mech. Catal., 135 (2022) 83–103.
2. B. Grahovski, R. Velinova, P. Shestakova, A. Naydenov, H. Kolev, I. Yordanova, G. Ivanov, K. Tenchev, S. Todorova, Catalysts, 13(5), (2023) 834.

# sO8. Recycling and reuse of spent automotive catalysts: challenges and solutions

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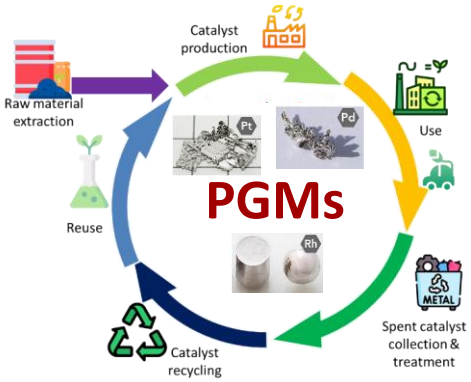
Recently, the high demand and hindered supply of critical raw materials (CRMs) for EU industry motivated the development of environmentally friendly recycling technologies of end-of-life products. Currently, the preparation of heterogeneous catalysts is strongly related to the use of one or more CRMs, being the main consumer of platinum group metals (PGMs) together with high consumption of rare earth elements (REEs) as well as other strategic materials.

This investigation presents research activities on understanding mechanisms associated with PGMs recovery from spent automotive catalysts (SACs) and further reuse of the recovered materials for synthesis of new catalysts in order to secure the PGMs value chain and achieve carbon neutrality. Research team ambitious goal was focused on attaining higher recovery rates, but also on increasing cost efficiency and environmental friendliness.

In parallel, the investigation revealed that application of mechanochemistry for PGMs recovery allows optimising the processing technology, enhancing the PGMs recycling rate, and increasing the sustainability. Mechanochemistry involves the use of mechanical energy to induce chemical reactions, typically through grinding, milling, or other mechanical processes. Mechanical treatment is widespread as a technique utilized to improve metal extraction or recycling rate. However, mechanochemistry is a branch of chemistry concerned with chemical and physicochemical changes of substances of all states of aggregation due to the influence of applied mechanical energy. Therefore, the term ‘mechanochemistry’ addresses the effects of mechanical energy on treated materials and the resulting mechanochemical reaction induced by direct absorption of mechanical energy. Thus, mechanochemistry complements conventional methods of chemical reactions activation by heat, irradiation, and electrochemistry. Despite recent interest in mechanochemistry, it remains far less completely studied and understood in comparison with conventional methods of energy input. Mechanochemical methods are mainly solvent free and thus their application leads to improved sustainability metrics, having signify-cant differences in the reaction outcomes, reaction selectivity, and reduced reaction time, which makes this technique a focus of interest for PGM recovery. Herein, we provide mechano-chemistry reaction examples, directly compared to respective solvent-based reactions. Appro-priate mechanochemical treatment can be applied to reach reduced reaction time, different reaction outcomes in product selectivity and in some cases different reaction products, in-cluding inaccessible products in solution chemistry. In such cases, PGM recovery process, i.e., PGMs oxidation/reduction pathways could be completely changed under mechanical treatment.

The possibilities to apply mechanochemical reactions as a main or single step of PGM recovery were investigated. Thus, a wasteless, energy saving, and room temperature methodol-ogy for direct PGM activation and recycling was obtained in consideration with green and sus-tainable principles. Numerous mechanochemical treatment conditions were tested in order to

optimize PGM recovery processing. Characterization methods, exploited to analyse treated materials include X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), and Fourier-transform infrared spectroscopy (FTIR). Detailed analyses of obtained results revealed the optimal conditions for mechanochemical treatment. Under these conditions, a higher PGMs concentration was observed on the surface of considered samples. This indicates that mechanochemical processing could effectively enhance metals accessibility from the studied waste materials by creating new fresh surfaces. Thus, PGMs become more accessible for future extraction.




This investigation highlighted the role of mechanochemistry in improving PGM recycling technology toward more efficient, environmentally friendly, and sustainable expertise, indicating the potential for scalability and further industrial application. In this way, the growing demand for PGMs in various high-tech and industrial sectors can be addressed by closing the loop of their life cycle.

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# sO9. Photoelectrochemical and photocatalytic activity of photodeposition-functionalized Ag/$TiO_2$ and $MnO_x$/$TiO_2$ thin films

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Heterogeneous semiconductor photocatalysts like titanium dioxide ($TiO_2$) absorb light energy above their bandgap ($E_g \approx 3.2$ eV, $\lambda \leq 388$ nm) generating electron-hole pairs (excitons) that drive redox reactions. Applications include oxidation of organic contaminants and solar energy conversion. However, recombination of electron-hole pairs in $TiO_2$ leads to over 99% loss of absorbed light energy [1]. This can be mitigated by decorating titania with metal (Me) or metal oxide ($MeO_x$) clusters, forming Schottky-type (Me | $TiO_2$) or pn-type ($MeO_x$ | $TiO_2$) heterojunctions, which enhance quantum efficiency by preventing recombination [2]. Cocatalyst decoration is achieved via (i) wet impregnation with a $Me^{n+}$ precursor salt and thermal decomposition, or (ii) photodeposition, where UV illumination forms Me/$MeO_x$ cocatalysts, expected to result in higher quantum efficiency heterojunctions [3].

This study compares thermal- and photodeposition-based Me/$MeO_x$ functionalization in $TiO_2$ thin films regarding photoelectrochemical (PEC) and photocatalytic efficiency. $TiO_2$ films, 250 nm thick and pure anatase, were deposited on ITO substrates via sol-gel dip-coating titanium tetraisopropoxide-based sol. Functionalization involved photodeposition in 5 mM $AgNO_3$ for Ag or 5 mM $MnSO_4$/$KIO_3$ for $MnO_x$, using a 365 nm UV LED at varying doses (2.5, 5, and 10 J $cm^{-2}$). Thermally functionalized layers were prepared by soaking substrates in the same for 1-h electrolytes followed by annealing at 350°C for an additional 1 h. PEC measurements in 0.5 M $Na_2SO_4$ (+0.5V bias vs. Ag/AgCl) determined the photocurrent ($j$) for pristine and modified $TiO_2$ layers via chronoamperometry, using pulsed UV LEDs with intensity ($I_{UV}$) varied from 0.69 to 3.65 mW $cm^{-2}$. Quantum efficiency was assessed using the power law: $j = \alpha \times I_{UV}^{\beta}$, where $\alpha$ reflects $I_{UV}$-agnostic PEC activity and $\beta$ indicates the $I_{UV}$ reaction order.

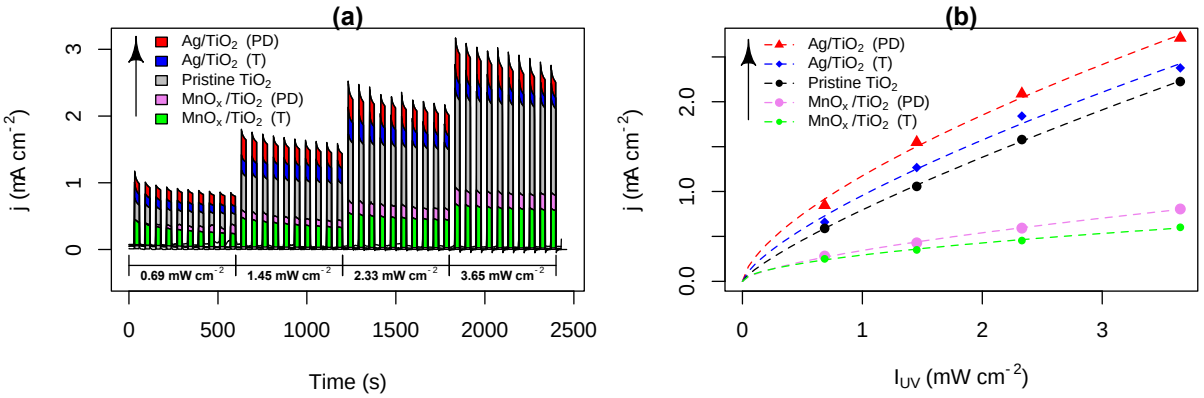



Fig. 1. Chronoamperometry results for pristine $TiO_2$ and Ag / $MnO_x$ functionalized $TiO_2$ via thermal decomposition (T) or photodeposition (PD) functionalization **(**a**)**; $j$-$I_{UV}$ dependence plots (b**)**.

Figure 1 compares $j$-$I_{UV}$ dependence for pristine $TiO_2$, thermally (T) functionalized, and photodeposition (PD) functionalized (example for 5 J $cm^{-2}$) Ag/$TiO_2$, and $MnO_x$/$TiO_2$ photoanodes. Compared to pristine $TiO_2$ ($\alpha$ = 0.80), $MnO_x$ functionalization reduced activity

by about 60% in both thermal ($\alpha$ = 0.29) and photodeposition ($\alpha$ = 0.34) cases while Ag/$TiO_2$ samples showed approximately 50% higher photocurrents ($\alpha$ = 1.17 for photodeposition and $\alpha$ = 0.95 for thermal application).

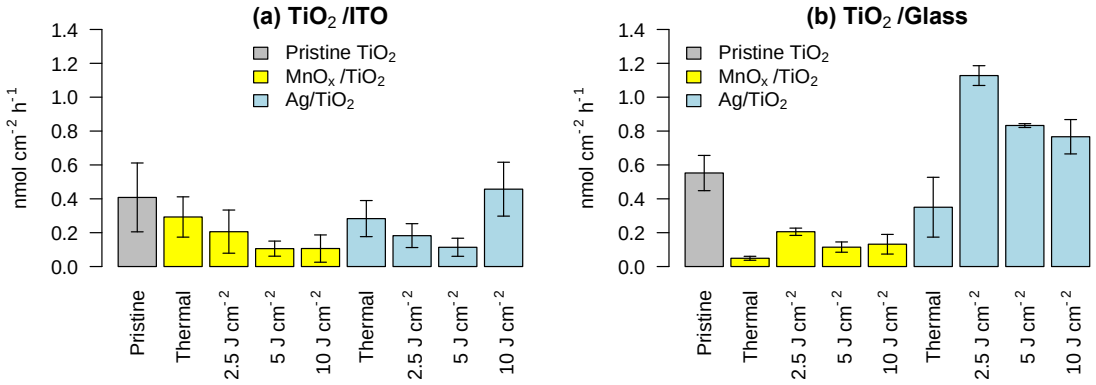



Fig. 2. Methylene blue removal rates for pristine and Ag/$MnO_x$ functionalized $TiO_2$ layers on ITO substrate **(**a**)** and glass substrate **(**b**)**.

PEC results did not directly translate to photocatalytic oxidation (PCO) activity. Figure 2a shows Methylene blue (MB) PCO rates. Ag/$MnO_x$ decorated $TiO_2$/ITO samples performed worse than the pristine catalyst, possibly due to the already existent $TiO_2$|ITO heterojunction accumulating photogenerated electrons inaccessible for PCO activity without an external bias. However, reference samples on uncoated glass aligned better with PEC activity results (Fig. 2b).

In conclusion, this work demonstrates that photodeposition is a superior method for Me/$MeO_x$ decoration of $TiO_2$, offering greater flexibility in parameter adjustment and yielding heterojunctions with higher activity in both PEC and PCO applications compared to thermal impregnation.

Acknowledgement: This work was possible through financial support from Bulgarian National Science Fund under project КП-06-Н59/11 ‘Photocatalytic activity of thin films with selectively photodeposited cocatalysts’.

References

1. A. M. El-Zohry, L. Kloo, L. He, Understanding charge dynamics in $TiO_2$ using ultrafast mid-infrared spectroscopy: trapping versus recombination, J. Phys. Chem. C, 128 (2024) 4192–4199.
2. Y. Zhao, Y. Shu, X. Linghu, W. Liu, M. Di, C. Zhang, D. Shan, R. Yi, B. Wang, Modification engineering of $TiO_2$-based nanoheterojunction photocatalysts, Chemosphere, 346 (2024) 140595.
3. M. Okazaki, Y. Suganami, N. Hirayama, H. Nakata, T. Oshikiri, T. Yokoi, H. Misawa, K. Maeda, Site-selective deposition of a cobalt cocatalyst onto a plasmonic Au/$TiO_2$ photoanode for improved water oxidation, ACS Appl. Energy Mater., 3 (2020) 5142–5146.

# sP1. Effect of mechanical activation on processing of alumina-supported CoPd catalyst precursors for CO hydrogenation

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Impregnation is the most often used method for catalyst synthesis but wastewater and harmful gas emissions are produced. Cobalt-based catalyst preparation via drying, calcination, and reduction is a time and energy consuming process. As a catalyst treatment, mechanical activation has low impact on environment. Activated system is in metastable condition that is transformed into equilibrium state by heating, sorption, chemical reaction, defects, and aggregation. Thus, excessive energy is decreased. Energy rich systems can release extreme energy in a suitable moment ensuring easy running of some processes associated with catalyst formation as well as to affect chemical processes proceeding on the surface. Application of mechanical activation in a number of cases makes technology easier by decreasing included number of stages.

Bimetallic catalysts were prepared by deposition of $Co(NO_3)_2.6H_2O$ and $Pd(NO_3)_2.2H_2O$ salts from aqueous solution, matching 10%Co and 0.5%Pd, on alumina support. The suspensions were dried in vacuum. Decomposition of supported salts comprised a 6-hour heating treatment in air or argon flow at $T \leq 300°C$ to prepare catalyst precursor. Aiming to replace this step in technology, mechanical activation of dry catalyst precursors was performed in a planetary ball mill with $ZrO_2$ milling instruments. IRS, XPS, TG-DTG, and TPR techniques were used for characterization of all synthesized materials.

Infrared spectra of $Co(NO_3)_2.6H_2O$, CoO, $Co_3O_4$, and $Al_2O_3$ as prepared and mechanically treated systems were recorded and compared. Results showed that $Co_3O_4$ was the most probable oxide phase existing in the catalyst precursors. Band intensity ratio of $NO_3$ group at 1385 $cm^{-1}$ to $Al_2O_3$ at 548 $cm^{-1}$, $I_{1385}/I_{548}$, was used for tentative calculation of supported nitrate salts decomposition during milling.

X-ray photoelectron spectroscopy study of milled samples registered contamination with zirconia which was 28.8% Zr calculated toward Al. Probably it was due to partial polymorphous transformation of the alumina from 'δ/γ' into 'α' crystal modification that is characterized with high hardness and contributed to increased abrasion of the milling instruments. Analysis of O1s spectra by deconvolution showed a decrease in nitrates amount, i.e. mechanical treatment initiated decomposition of some part of the supported salts. Peak area corresponding to nitrates decreased from 19 to 9% of the complex O1s peak area.

Supported salts decomposition process was followed by TG-DTG. As prepared dry samples using inert gas flow were subjected to transformation by three stages of chosen 6-h preparation procedure from room temperature to 300°C. In the first decomposition stage at $T \leq 100°C$ partial dehydration of $Co(NO_3)_2.6H_2O$ and decomposition of $Pd(NO_3)_2.2H_2O$ to Pd were realized with sample mass decrease about 60% from total sample mass loss during entire treatment. During the second stage within 100–200°C, the process continued with cobalt nitrate dehydration and conversion to cobalt oxide phase(s) accompanied by $NO_x$ emission. Additional process of lower intensity occurred at $T > 200°C$ and assigned to partial decomposition of carbonate-carboxylate species on the carrier.

Decomposition of mechanically activated samples was studied in argon or airflow. A decrease of peak area was found with samples treated in argon compared with mechanically untreated precursor material. This result showed partial decomposition of the supported nitrate salts under the influence of mechanical activation. Decomposition processes were facilitated by mechanotreatment as seen by signals shifted toward lower temperatures. Duration of the decomposition stage was shortened to 2.5 h. Possibility should not be excluded that a peak positioned at 200°C resulted from sample contamination with $ZrO_2$. Mechanical activation in airflow revealed that the gas phase affected significantly dehydration and decomposition processes with the palladium salt.

Decomposition of the supported nitrates was about 50–53% due to mechanical impact as proved by IRS, XPS, and TG-DTG studies.

TPR of milling-unprocessed samples, which passed a 6-hour decomposition procedure, showed that the reduction was realized in two temperature ranges. Comparison of the obtained curves with TPR profile of $Co_3O_4$ confirmed this finding by IR study that $Co_3O_4$ had been formed in the sample and then reduced. Part of the $Co_3O_4$ was reduced under Pd promotion. Another part was reduced independently. It could be assumed that during low-temperature reduction formation of bimetallic particles might occur, the surface being enriched or entirely covered by cobalt. Presence of high-temperature peak due to cobalt oxide reduction could be explained by suggesting that at a definite moment of the reduction process no accessible Pd existed at the surface, which could participate in $Co_3O_4$ reduction. TPR of mechanically treated samples, which passed a 2.5-h decomposition procedure in air or Ar atmosphere, also disclosed two regions. Milling did not affect position of the main maximum in the low-temperature range. A characteristic of high-temperature reduction range was the presence of three maxima at 266/276, 333, and 418/425°C. Comparison indicated that under the influence of mechanical activation the amount of reduced oxide phase was increased relative to that in unprocessed precursor. Most probably, this special feature was due to reduction of zirconia contaminant. Overlapping of both running reduction processes of cobalt oxide and $ZrO_2$ resulted in increased peak area, with hydrogen consumption seeming higher. Another possible reason could be cobalt oxide reduction in contact with zirconia, which was somehow hindered.

DTG and TPR results showed that complete decomposition of the supported nitrates in argon or air had no substantial effect on oxide composition and precursor properties.

Briefly, mechanical treatment could lead to the following advantages: decomposition of large part of the supported salts; decrease of chemical transformation temperatures; shortened duration of the preliminary thermal treatment stage; increase of the low-temperature reducible oxide(s) amount.

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# sP2. Heterogeneity of adsorption and reaction sites of oxide-supported (10%Co+0.5%Pd) catalyst surfaces in the course of the CO hydrogenation reaction

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During reaction adsorption sites may function as reaction ones if they have appropriate properties like energy, strength, and stability. Physical, chemical, and physicochemical factors affect functions, which adsorption site performs in reaction.

Two component catalyst precursors were prepared by deposition of metal nitrate salts from aqueous solution on non-porous oxides as $Al_2O_3$ (A), $TiO_2$ (T), and $SiO_2$ (S) and then were decomposed in hydrogen (red), air (ox), or argon/nitrogen (inert) medium. Materials were reduced in $H_2$ successively at 300, 400, and 450°C. The catalysts were studied by chemisorption of $H_2$ and CO, catalytic activity in CO hydrogenation by infrared spectroscopy for stability of activity in the reaction with time on stream (TOS) at 250°C for 5 h, and temperature-programmed desorption of $H_2$ and CO (TPD) using a flow reactor of differential scanning calorimeter.

Hydrogen adsorption revealed that metal surface heterogeneity was similar as deduced from Freundlich isotherms showing close values of 1/n exponent, and adsorption sites were of the same type. Regressive analysis of experimental hydrogen isotherms based on Langmuir equation and reverse proportion between $K_L$ constant and $\Delta H_{ads}$ ($E_a$) allowed conclusion that hydrogen adsorption and CO hydrogenation, accordingly, were the most difficult in the case of A(red) catalyst and most facilitated on S(red) catalyst. $K_L$ values from the isotherms of titania-supported samples were almost the same but quite different from those of the other two groups of catalysts and a relatively higher $E_a$ was inherent to them. This explained a 30–42% decrease in methane yield although as a whole it was higher in comparison with $CH_4$ obtained with other catalysts.

Comparative analysis of infrared band intensity of linearly adsorbed CO species (2027–2042 $cm^{-1}$) showed the following order of catalyst adsorbents: T(inert) < T(red), A(red), A(inert) < A(ox), T(ox) < S(red) < S(ox) < S(inert). Further, a conjoint analysis of infrared bands for linearly adsorbed CO and TPD-CO peaks in the low-temperature region was made. Alumina-supported catalysts gave rise to low intensity IR bands, increasing with time on stream, which were more characteristic of $Co^{\delta+}$ sites. Low-temperature desorption peaks had a mean position of $T_{max}$ and their intensity was rather low to medium compared with those of other catalysts. Thus, large amount of linear CO intermediates was not formed on the surface of alumina-supported catalysts. Adsorption site strength was moderate; however, the sites were not much active as reaction centres for CO dissociation and hydrogenation. $CH_4$ band intensity increased with TOS. Domination of these centres and their properties were not an obstacle the reaction of CO hydrogenation to proceed on other active sites. Bands of linearly adsorbed CO species on silica-supported catalysts were of the highest intensity, which nearly did not change with time. TPD desorption was higher and the peaks were of the highest intensity compared with the other catalysts. These observations showed that (i) many intermediate compounds of the linear type were formed on the surface, (ii) adsorption sites were somewhat stronger than

those on catalysts with alumina support were, and (iii) adsorption, dissociation, and hydrogenation processes on the metal surface were in large part balanced. Methane bands slightly decreased with TOS and those of carbonate species increased at a relatively constant CO conversion, which showed that adsorption sites working as reaction centres gradually decreased activity with time in CO hydrogenation, thus favouring advantageous conditions for water-gas shift (WGS) reaction. Bands of linearly adsorbed CO on (10%Co+0.5%Pd)/$TiO_2$ catalysts were of low to medium intensity and decreased with TOS. Concerning amount of linear CO species it should be noted that it was similar to those of (10%Co+0.5%Pd)/$Al_2O_3$ catalysts. $T_{max}$ of desorption in the low-temperature region took the lowest values and desorption peaks were of the lowest intensity relative to other catalysts. The results showed that adsorption sites for linear CO species formation were of the lowest strength compared with matching samples of $Al_2O_3$ and $SiO_2$ carriers. Highly intensive bands characteristic of $CH_4$ as reaction product showed that these adsorption sites have changed into moderately active reaction centres for CO hydrogenation. On the other hand, decreased intensity of the $CH_4$ bands and weak but well-resolved bands of $CO_2$ were registered with time on stream. Thus, it could be speculated that similarly to silica-supported catalysts a certain part of reaction sites for hydrogenation acquire qualities, which made them more favourable for WGS reaction to proceed. It is known that $CO_2$ formation requires less contact time with a catalyst than necessary for hydrocarbon formation.

Comparative analysis of TPD-CO and *in situ* diffuse-reflectance infrared spectroscopy study during catalytic measurements for activity and stability in CO hydrogenation concerning carbonate-like species was also made. It showed that adsorption sites in the case of A(inert) and S(ox) catalysts were weak with unstable complexes. T(red), A(red), and S(inert) samples had adsorption sites of medium strength to form carbonate-like complexes of mean stability. T(red), T(ox), A(ox), and A(inert) catalysts exposed adsorption sites of high strength, and the carbonate-like species were of high stability.

It should be noted that a relatively large amount of desorbed carbonate-like species in TPD-CO was observed together with the least increase of carbonate-like intermediate infrared bands in the spectra of A(inert) sample. On the other hand, spectra of the latter sample detected a higher absorption in the region below 1600 $cm^{-1}$ as a whole in comparison with A(ox) and A(red) samples. These findings allow to presume that during work many stable and unstable carbonate-like compounds were formed on the surface of A(inert) catalyst, which originate on strong and weak adsorption sites, respectively. In this connection, unstable carbonates prevailed on the weak sites.

Bearing in mind T(red), T(ox), and T(inert) catalysts, changes in the infrared region below 1600 $cm^{-1}$ and desorption around 250°C in the TPD-CO profiles suggest that on the surface of the samples significant amount of weakly bonded carbonates at 250°C, most probably bidentate species, was formed and readily decomposed to carbon dioxide.

Performed investigations allowed detailed analysis of adsorption and reaction site dynamics. An idea was suggested that is concerned with transformation of adsorption sites into reaction sites for hydrogenation. In addition, the reaction centre should attain qualities with time favouring realization of WGS reaction. However, in terms of adsorption, the reaction centres were of high strength in relation to $CH_x$ species.

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# sP3. Enhancing alkaline oxygen evolution reaction performance through comparative N-doping of a waste fossil-derived Ni-Fe/activated carbon

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In recent years, earth-abundant transitions metals, such as Ni, Fe-based oxides, alloys, hydroxides, or carbides have been demonstrated as potential catalysts for oxygen evolution reaction (OER) considering the most energy consuming semi-reaction of electrochemical alkaline water splitting [1]. Compared to single metal oxides, studies revealed that bimetallic oxides and alloys like Co-Fe, Ni-Co, or Ni-Fe, have superior catalytic activity toward OER due to different redox potential, synergistic effect, and adjustable electronic structure. However, electrochemical performance of the most reported bimetallic-based electrocatalysts is still unsatisfactory for sustainable water splitting applications. This is caused by the fact that bimetallic oxides and alloys possess a relatively low surface area, poor electrical conductivity, and tendency for particle aggregation during preparation as well as leaching during the electrolysis, which inevitably affects their performance [2]. One of the best strategies to circumnavigate these concerns is to integrate bimetallic species with carbon materials such as activated carbon, carbon nanotubes, or carbon fibres, to promote their conductivity and electrocatalytic stability and to facilitate charge transfer of the hybridized system, thus boosting the overall OER performance. Carbon materials are an interesting option to disperse metals, preventing nanoparticle leaching and aggregation, minimizing the electrical resistance, and increasing the number of active sites. A combination of doped carbon and metal oxides/alloys results in a favourable synergism, which can remarkably stimulate interfacial electron transfer between catalyst surface and intermediate reactants.

An activated carbon (AC-$HNO_3$) derived residual coal-tar fossil, originally obtained with the method described by Tsyntsarski et al. [3], was doped by nitrogen functionalization using thermal methods in which impregnation of the matrix with urea or ethylenediamine or hydrazine was followed by heat treatment at 800 °C in inert atmosphere. A low-temperature reactive method using citric acid and NaOH was also adopted using hydrazine as n-dopant named hydrazine AC. At the same time, original carbon matrix was modified with different percentage of Ni-Fe for choosing the best one to be impregnated later to the modified carbon supports. In order to determine the activity of the catalysts in OER, a linear sweep voltammetric curve between 0.7 and 1.8 V vs. RHE (a positive going scan) was recorded at 0.005 V/s and rotation speed of 1800 rpm with a 1M KOH solution in water.

Information obtained through the combined use of X-ray photoelectron spectroscopy, HR-TEM, TEM-EDX, $^{57}$Fe-Mössbauer spectroscopy, $N_2$ physisorption, electrochemical impedance spectrometry, and cyclic voltammetry, made possible to follow sequential evolution contributing to the various modified carbon matrices. Thus, it was shown that the carbonaceous matrix treated with different nitrogen compounds substantially affected material's intrinsic electrocapacitive properties and electron transfer impedance by giving it reactivity according to the order: ethylenediamine < urea < hydrazine. Similarly, heat treatment in hydrazine seems

less effective than chemical treatment at a low temperature (Fig. 1). Addition of mixed metal oxides of nickel-iron, found to be optimal at 40 wt.%, seems to 'normalize' the effective activity in the alkaline OER reaction of the samples modified with urea, hydrazine, and hydrazine AC (Fig. 1, right panel).

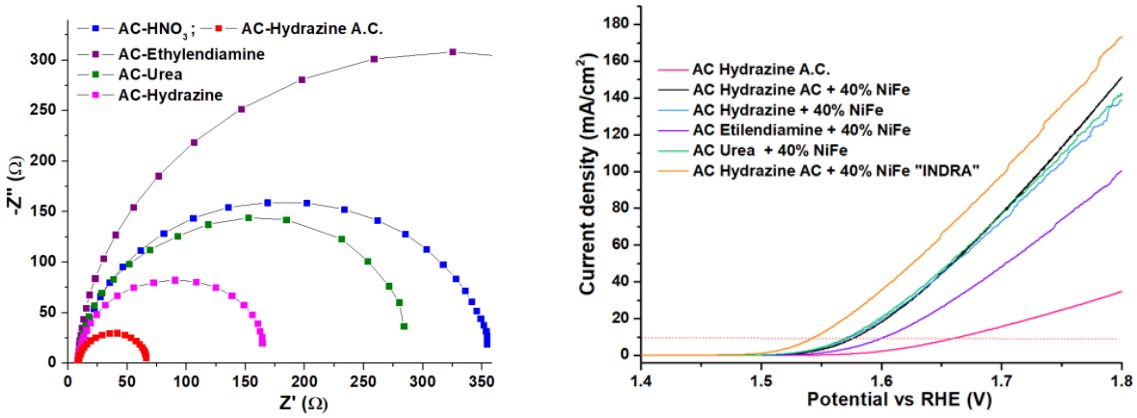



Fig. 1. Nyquist plots of electronic impedance spectroscopy (left panel) of modified carbonaceous supports, and voltammetric linear sweep curves related to OER conducted by modified activated carbon doped with 40 wt.% Ni-Fe (right panel).

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References

1. C. Rosmini, T. Tsoncheva, D. Kovacheva, N. Velinov, H. Kolev, D. Karashanova, M. Dimitrov, B. Tsyntsarski, D. Sebastián, M. Jesús Lázaro, Mesoporous Ce-Fe-Ni nanocomposites encapsulated in carbon nanofibers: synthesis, characterization and catalytic behaviour in oxygen evolution reaction, Carbon, 196 (2022) 186−202, https://doi.org/10.1016/j.carbon.2022.04.036.
2. P. Stelmachowski, J. Duch, D. Sebastián, M. J. Lázaro, A. Kotarba, Carbon-based composites as electro-catalysts for oxygen evolution reaction in alkaline media, Materials, 14(17), (2021) 4984, https://doi.org/10.3390/ma14174984.
3. B. Tsyntsarski, S. Marinov, T. Budinova, M. Ferhat Yardim, N. Petrov, Synthesis and characterization of activated carbon from natural asphaltites, Fuel Process. Technol., 116 (2013) 346–349, https://doi.org/10.1016/j.fuproc.2013.07.020.

# sP4. Initial exploring of Ni- and Co-based coatings in hydrogen evolution reaction electrodeposited on different supports

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Hydrogen evolution reaction (HER) in aqueous solution is one of the most studied electrode reactions not only from scientific point of view but also in terms of hydrogen production as the cleanest fuel:

$$2H^+ + 2e^- \rightarrow H_2\uparrow .$$

In alkaline electrolysis, materials that have a low overvoltage of the hydrogen reaction are used as electrodes. Noble metals, such as platinum, are characterized by the best catalytic behaviour toward HER, but their rarity and high cost prevent widespread use. To overcome these drawbacks, the energy industry and the scientific community are turning to base metals, such as nickel and cobalt, which present good electrocatalytic behaviour at a reasonable cost.

Current studies present estimation of the electrocatalytic HER activity of NiCo alloys in 1.0 MKOH related to Ni and Co single. Nickel and cobalt were electrodeposited as coatings on two different types of supports, as Ni-foam net and Fe-steel, at different Ni/Co mass ratios as 30/70, 50/50, and 70/30 wt.% and the same duration of 30 min.

Results of the electrochemical measurements are shown in figure 1. Catalytic activity of the NiCo coatings was different from those of Ni-foam and Fe-steel supports. Ni/Co mass ratio of 30/70 was most active in HER at Ni-foam net (Fig. 1a). However, the most active NiCo coating on Fe-steel was Ni/Co of 50/50 ratio (Fig. 1b).

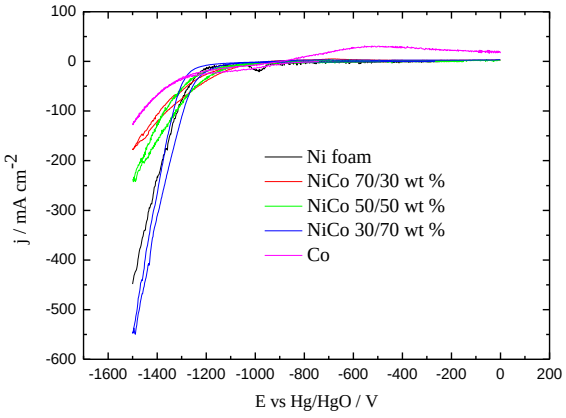



Fig. 1a. HER activity: Ni-foam net support.

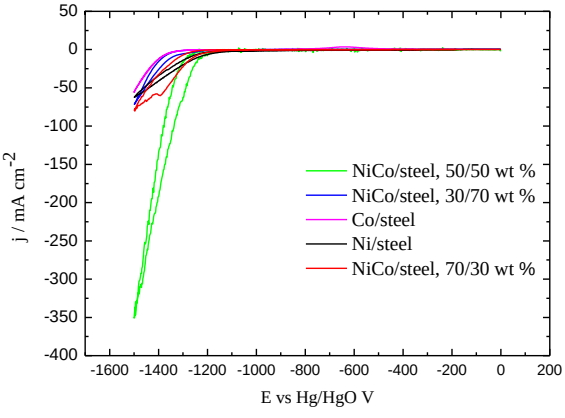



Fig. 1b. HER activity: Fe-steel support.

Composition, structure, and morphology of the as-deposited coatings were characterized by X-ray fluorescence spectrometry (XRF) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS).

SEM image of Co/foam presented in figure 2b shows spherical shape of the Co particles on the Ni-foam surface and homogenous deposition.

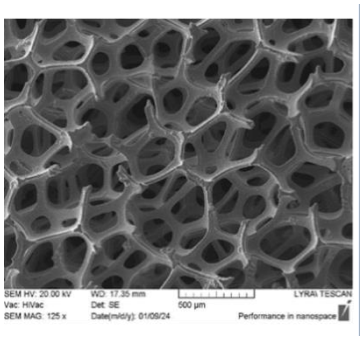


Fig. 2a. SEM image of Ni-foam.

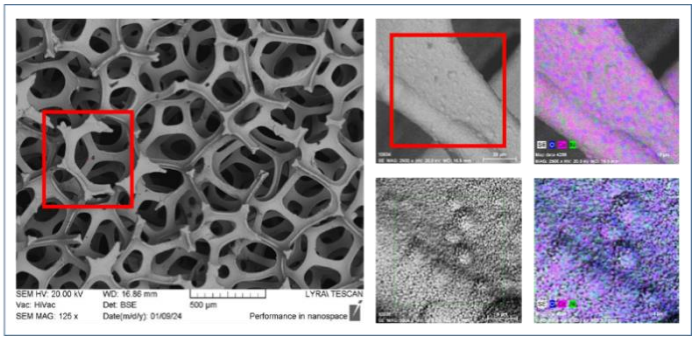


Fig. 2b. SEM-EDS images: elemental mapping of the Co/foam surface.

In summary, NiCo/foam catalyst with mass ratio of Ni/Co=30/70 demonstrated a promising performance in hydrogen evolution reaction upon initial exploring of nickel- and cobalt-based coatings applying supports as Ni-foam and Fe-steal. Further studies of the CoNi compositions on nickel foam net will clarify the origin of the observed HER activities depending on Ni/Co mass ratio.

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# sP5. Hydrogenation of renewable levulinic acid to γ-valerolactone on Ni-Cu sodalite zeolite catalysts prepared from fly ash

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Lignocellulosic biomass is applied as a promising alternative for fossil fuel sources because of the increased demand of energy and decrease in fossil fuel resources [1]. Hydrolysis of lignocellulosic biomass into a mixture of cellulose, hemicellulose, and lignin, and further transformation of hemicellulose and cellulose to C5 and C6 monosaccharides are important steps of biomass valorization. Among platform molecules that are produced from biomass, levulinic acid (LA) is one of the most important entity for further production of valuable products, such as biofuels, solvents, intermediates for pharmacy, etc. Hydrogenation of levulinic acid to γ-valerolactone (GVL) is important process because the latter can be used as a solvent, fuel additive, and intermediate in the production of diverse value-added chemicals [1-3]. Among applied catalysts, supported noble metals (Ru, Ir, and Pd) as well as transition metals such as Co, Cu, and Ni show the best catalytic results. However, metal leaching under severe reaction conditions together with high price limit the application of noble metals in the studied processes. Development of active and cheap catalysts for GVL production by hydrogenation of levulinic acid requires optimization of some reaction parameters like temperature, pressure, space velocity, and reaction time as well as choice of type and number of supported metals and carrier itself. Zeolites modification with low-cost transition metals is a promising way to prepare catalysts requiring both metallic and acidic function.

In the present study, Ni (5 wt.%) and Ni-Cu (5 wt.% Ni and 1.5, 2.5, and 5 wt.% Cu) modified sodalite zeolites obtained by hydrothermal synthesis from fly ash were prepared by post-synthesis incipient wetness impregnation. *Ex-situ* reduced catalysts were investigated in a batch reactor under pressure and static conditions (150°C and 30-bar hydrogen pressure for 4 hours) in the hydrogenation reaction of levulinic acid to γ-valerolactone.

The catalysts were characterized by X-ray powder diffraction, $N_2$ physisorption, NMR, Mössbauer, and UV-Vis spectroscopies, TEM, and $H_2$-TPR methods. Finely dispersed NiCu alloy and $Cu^0$ nanoparticles were detected after decomposition of the impregnating salt and performed reduction on the modified sodalite zeolite samples.

Table 1. Crystalline phases formed in the reduced catalysts

| Sample | NiCu alloy, nm | $Cu^0$, nm |
|---|---|---|
| 5Ni/sodalite | – | – |
| 5Ni1.5Cu/sodalite | 17 | undetectable |
| 5Ni2.5Cu/sodalite | 21 | 43 |
| 5Ni5Cu/sodalite | 21 | 43 |

TEM images reveal the formation of metal nanoparticles on the sodalite support after reduction (Fig. 1). The results are in good correspondence with XRD data (Table 1).

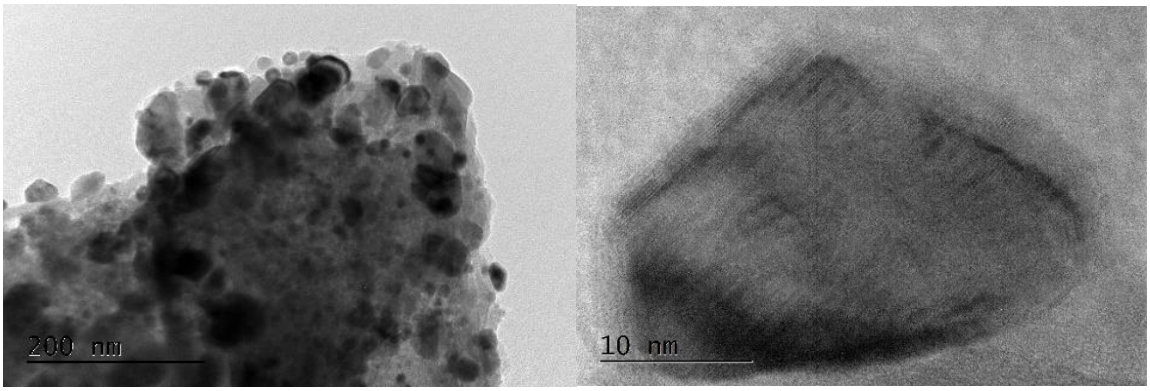



Fig. 1. TEM images of the 5Ni2.5Cu/sodalite catalyst.

The catalysts were studied in the reaction of upgrading lignocellulosic biomass-derived levulinic acid to γ-valerolactone. Bimetallic 5 wt.% Ni-1.5, 2.5, 5 wt.% Cu/sodalite catalysts manifested a moderately high catalytic activity in the studied catalytic reaction (Table 2).

Table 2. Data about catalytic conversion of levulinic acid to γ-valerolactone

| Sample | LA conversion, % | GVL, % | 4-hydroxy valeric acid (HVLA), % | GVL/HVLA ratio |
|---|---|---|---|---|
| 10Ni/sodalite | 37 | 31 | 6 | 5.2 |
| 5Ni1.5Cu/sodalite | 23 | 18 | 5 | 3.5 |
| 5Ni2.5Cu/sodalite | 72 | 59 | 13 | 4.5 |
| 5Ni5Cu/sodalite | 33 | 28 | 5 | 5.3 |

Among the studied catalysts, 5Ni2.5Cu/sodalite exhibited the highest activity and high selectivity to GVL as well (Table 2). Registered high levulinic acid conversion and GVL yield could be attributed to the formation of finely dispersed Ni-Cu alloy on the sodalite zeolite that stabilizes the metallic nickel in highly dispersed state, the optimum Ni/Cu ratio being 2.

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References

1. L. T. Mika, E. Cséfalvay, Á. Németh, Catalytic conversion of carbohydrates to initial platform chemicals: chemistry and sustainability, Chem. Rev., 118 (2018) 505–613, doi: 10.1021/acs.chemrev.7b00395.
2. K. Alper, K. Tekin, S. Karagöz, A. J. Ragauskas, Sustainable energy and fuels from biomass: a review focusing on hydrothermal biomass processing, Sustain. Energy Fuels, 4 (2020) 4390–4414, doi: 10.1039/D0SE00784F.
3. Sh. Dutta, I. K. M. Yu, D. C. W. Tsang, Y. H. Ng, Y. S. Ok, J. Sherwood, J. H. Clark, Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: a critical review, Chem. Eng. J., 372 (2019) 992–1006, doi:10.1016/j.cej.2019.04.199.

# sP6. Catalytic properties of selenium and phosphorus ionic liquids heterogenised on algae-based biochar

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Ionic liquids (ILs) are widely investigated compounds in recent years due to their unique properties such as high thermal stability and low volatility. Another reason for the significant use of ionic liquids in various spheres of industrial and academic importance is the various nature of the cations and/or anions in their structure. Based on the above, ILs are applied as environmentally friendly solvents, materials for supercapacitors production, electrochemistry, analytical chemistry, and extraction [1]. Apart from aforementioned applications, ionic liquids have been extensively studied as efficient catalytic systems under heterogeneous conditions, where a number of carriers like zeolites, resins, metal oxides, and activated carbon have been used for ionic liquid immobilization. Recently, biochar has been gaining more and more popularity as a catalyst carrier. Hence, aluminium-based ionic liquid grafted on biochar as a heterogeneous catalyst for the selective synthesis of tetrazole and 2,3-dihydroquinazolin 4(1H)-one derivatives were reported [2]. In light of this, biochar-based graphitic carbon nitride adorned with IL containing acidic polymer was applied as a non-metallic catalyst for Knoevenagel condensation [3]. Although catalytic systems based on selenium- and phosphorous-containing ionic liquids could be found in the literature, supported ILs based on hydrogen selenate and hydrogen phosphate anions are practically missing.

Encouraged by these findings, catalytic performance of pyridinium hydrogen selenate (PHSe) and pyridinium dihydrogen phosphate (PH2P) ionic liquids immobilized on algae-based biochar (AC) was studied in this work. For that purpose, acetic acid esterification with butanol was used as a test reaction. Surface phenomena, textural properties, and thermal behaviour for PHSe/AC and PH2P/AC were studied via X-ray powder diffraction (XRD), nitrogen adsorption-desorption isotherms ($S_{BET}$), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). $S_{BET}$ and SEM measurements revealed that all of the samples (AC, PHSe/AC, and PH2P/AC) obtained were mixed microporous-mesoporous materials. XRD and XPS data showed better dispersed PH2P particles (15.86 nm) than PHSe (41.62 nm) on the carrier surface due to stronger surface ionic liquid-support interaction for PH2P/AC in comparison with PHSe/AC. The latter was responsible for a higher thermal stability of PH2P/AC with respect to PHSe/AC. In addition, more evident PH2P sites (than PHSe) on the biochar surface favoured ester production in the presence of PH2P/AC than PHSe/AC. It was confirmed by both the registered ester yields and the rate constants for PH2P/AC (77.4% and $53.26\times10^{-4}$ l/mol×min) and PHSe/AC (58.1% and $28.82\times10^{-4}$ l/mol×min) after 70 min reaction time.

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References

1. J. L. Shamshina, P. Berton, Int. J. Mol. Sci., 24(9), (2023) 7866.
2. M. Norouzi, P. Moradi, M. Khanmoradi, RSC Adv., 13 (2023) 35569–35582.
3. S. Sadjadi, F. Koohestani, M. Heravi, Molecules 25 (2020) 5958.

# sP7. Conversion variation in a commercial vacuum residue hydrocracker investigated by intercriteria analysis and pilot plant tests

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LUKOIL Neftohim Burgas refinery (LNB) has made a transition from processing of predominantly the design crude oil – Urals mixed with up to 30% Middle East crudes (Arabian Medium, Basra Medium, Arabian Light, Basra Light, Arabian Heavy, Basra Heavy, Kuwait Export Blend, etc.) to refining of 100% non-Russian crude oils [1]. Initially, LNB has experienced hardship to find the right non-Russian crude oils to process and determine appropriate blending ratio of the latter oils. Then, by using the suitable blending ratio, refinery operation was stabilized. However, the conversion level of the most profitable process 'H-Oil vacuum residue hydrocracking' in the LNB refinery has shown variations within the range of 10 wt.%. Moreover, calculated conversion of the vacuum residue based on data of throughput, reaction temperature, and a plug flow reactor model with an activation energy of 215 kJ/mol and a reaction order of 1.59 as established in Ref. 2 has been found about 4–6 wt.% lower than observed conversion. This supposed no optimal performance of the H-Oil unit. The reason for observed lower conversion than that of the model developed during processing vacuum residues from Urals and Middle East crude oils was unclear. Some doubts have appeared that the crude blend refined in the LNB might be the culprit for lower vacuum residue conversion. In order to understand the root cause for this finding hydrocracking pilot plant tests were performed with six vacuum residues derived from diverse crude oils at the same operating conditions. A regression was developed to relate vacuum residue properties to the conversion that was called 'feed reactivity'. Then this regression was put as a variable accounting for quality of the commercial hydrocracker to assess its impact on conversion level. Intercriteria analysis evaluation of the commercial hydrocracker data was performed and the factors having the highest coincidence with conversion were identified. Then a multiple regression with these factors was developed and as a result, it was found that the reason for lower H-Oil vacuum residue conversion was quality level of the mixed vacuum residue feed, and vacuum residue content in the H-Oil feed. The higher the 'feed reactivity' and the vacuum residue content in H-Oil feed, the higher the conversion in the H-Oil unit was. Developed model allows optimization of crude oil blend composition and H-Oil mixed feed composition.

References

1. D. Stratiev, I. Shiskova, V. Toteva, G. Georgiev, R. Dinkov, I. Kolev, I. Petrov, G. Argirov, V. Bureva, S. Ribagin, et al., Experience in processing alternative crude oils to replace design oil in the refinery, Resources, 13 (2024) 86, https://doi.org/10.3390/resources13060086.
2. D. Stratiev, V. Toteva, I. Shishkova, S. Nenov, D. Pilev, K. Atanassov, V. Bureva, S. Vasilev, D. D. Stratiev, Industrial investigation of the combined action of vacuum residue hydrocracking and vacuum gas oil catalytic cracking while processing different feeds and operating under distinct conditions, Processes, 11 (2023) 3174, https://doi.org/10.3390/pr11113174.

# sP8. Methane conversion to add-value compounds over transition metal cations in zeolites

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Transition metals are known to be active catalysts for selective oxidation of highly stable organic compounds, such as methane. Selective four-electron reduction of oxygen, which occurs in zeolite channels, is achieved through the collaborative efforts of two Fe(II) cations working together to efficiently break the O−O bond via oxygen intermediates. In this study, activation of molecular oxygen and subsequent oxidation of methane over Fe sites in CHA, FER, MOR, and BEA zeolites with different Si/Al ratio, 8.4 and 14.6, and transition metal ions (TMI) content within 0.1–5 wt.% were studied under continuous treatment in the temperature regime from room temperature to 450°C.

Reactivity tests of methane oxidation by molecular oxygen over iron mordenite zeolites were combined with FT-IR spectroscopy to study reagents transformation on the zeolite surface. Mass spectrometry analysis of gaseous products of the simultaneous interaction of methane and oxygen or carbon dioxide with TMI-exchanged zeolites revealed the formation of methanol and other add-value compounds. The spectroscopic studies provided direct evidence of involvement of methoxy groups ($CH_3O$-TMI) in methanol formation. Specifically, the $Fe^{2+}$ cations were active sites at the first stage of the reaction while isolated $Fe^{2+}$ sites and $Fe^{3+}$-OH species participated in the following reaction course. Differences in the reaction pathway of methane oxidation over Fe-MOR compared to Fe-FER and Fe-*BEA catalysts reflect unique properties of MOR topology providing isolated α-oxygens in individual mordenite pockets, although formed by molecular oxygen splitting by two cooperating iron ions and considering the nature of adsorption sites in the mordenite matrix.

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# sP9. MCR-ALS analysis for active species identification in alcohol to hydrocarbon process

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FT-IR spectroscopy has played a major role in identifying reaction intermediates in catalytic processes since the first detection of surface-adsorbed species. In this study, ethanol conversion process was carried out over protonic chabazite (Si/Al=8) zeolite. Advanced FT-IR operando spectroscopic techniques were employed, along with simultaneous mass spectroscopy and gas chromatography analysis of products.

The spectroscopic investigation provided information about the species formed on the surface of catalysts. Mass spectrometry and gas chromatography methods were used to identify desorbed products. The studies were also supported by spectroscopic, chromatographic, and thermogravimetric analyses of the coke species formed on the catalyst surface during alcohol conversion. Experimental spectroscopic data was analysed using multivariate curve resolution by alternating least squares (MCR-ALS) algorithms. This allowed for identifying concentration profiles for specific species found in complex spectra.

FT-IR spectra (Fig. 1) registered during ethanol conversion showed extensive formation of species involved in hydrocarbon pools (HCP) in chabazite cages. This was confirmed by the rapid formation of propylene and C4+ hydrocarbons upon contact with the SSZ-13 catalyst and ethanol. The bands at 1602 and 1617 $cm^{-1}$ can tentatively be attributed to aromatic compounds as highly methylated (ethylated) benzenium cations. The m/z = 70 fragmentation ion observed may come from divinyl ether formed over the acid sites of SSZ-13 in trace amounts during the first 25 minutes of the reaction. The band observed at 1505 $cm^{-1}$ was identified in the methanol-to-hydrocarbon process as due to alkyl-substituted cyclopentenyl cations.

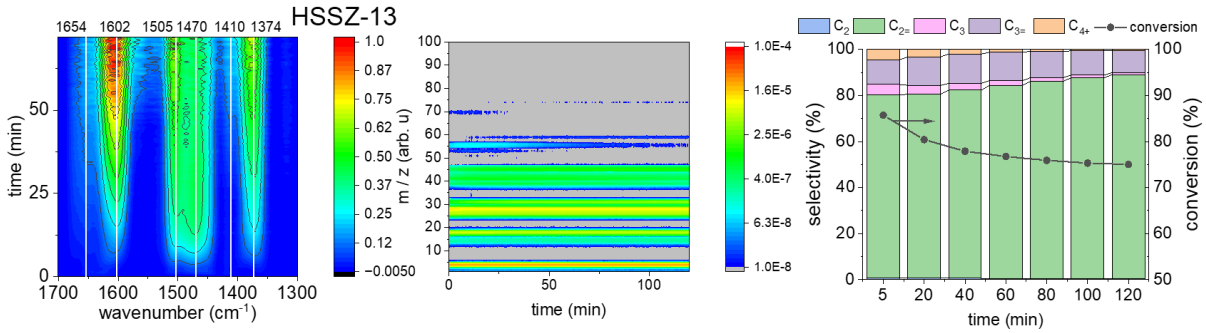



Fig. 1. Top-down projection of FT-IR spectra (left), mass spectrometry results (middle), and gas chromatography selectivities and conversions collected during ethanol conversion over HSSZ-13 (right).

Further analysis using MCR-ALS of the obtained results helped in identifying three distinct species formed during ethanol dehydration over SSZ-13 zeolite. Concentration profiles provided information on their formation timing. Species A, represented by bands specific for alkyl-substituted cyclopentenyl cations (band at 1505 $cm^{-1}$), was identified as the one formed at the very beginning of ethanol conversion. Species B and C were formed in the later stages of the reaction. Species B is expected to be a gas phase product (ethylene) formed only in part of the reaction and then prone to oligomerize to aromatics represented by species C.

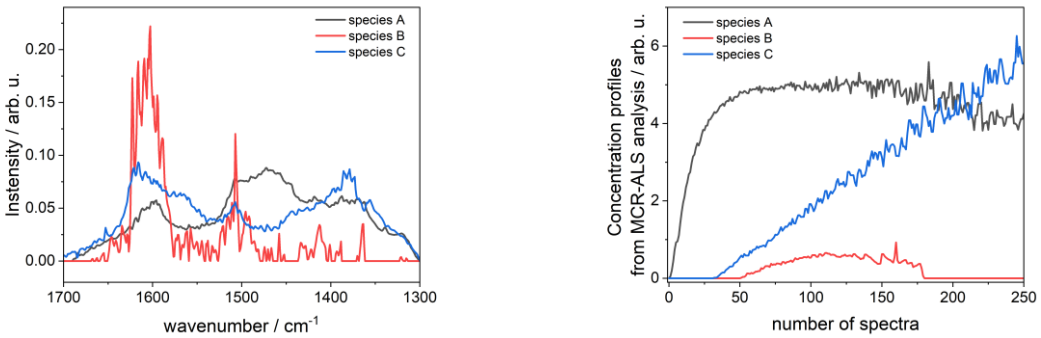



Fig. 2. MCR-ALS results analysis of FT-IR spectra recorded during ethanol conversion over SSZ-13 zeolite.

Overall, MCR-ALS allows for resolution of the complex spectra of a mixture of species into pure-component contributions. At the same time, the component profiles are constrained by physical or chemical objectives, for instance, non-negativity and unimodality.

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References

1. M. J. Wulfers, F. C. Jentoft, ACS Catalysis, 4 (2014) 3521–3532.
2. S. Zeng, W. Zhang, J. Li, S. Lin, S. Xu, Y. Wei, Z. Liu, J. Catal., 413 (2022) 517–526.
3. E. D. Hernandez, F. C. Jentoft, ACS Catalysis, 10 (2020) 5764–5782.

# sP10. Coke assessment in spectroscopic and chromatographic studies of spent zeolite catalysts for ethylene oligomerization

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Activity of zeolite-catalysed hydrocarbon transformation decreases over time due to the formation of unwanted heavy carbon-derived substances that poison the catalysts. Nature and location of the formed carbon deposits might block access to active sites, thus reducing catalyst effectiveness. Understanding the type and location of these carbon deposits is essential for designing catalysts with the desired properties. It is crucial to understand properly how catalyst deactivation occurs to design zeolitic catalysts with targeted performance. Research is focused on identifying the relationship between specific types of carbon deposits and zeolite catalysts properties to control formation of these deposits.

Coke nature was assessed during IR and UV-Vis temperature-programmed oxidation experiments supported by mass spectrometry in the temperature range of 200 to 550°C in synthetic airflow. For quantitative analysis, thermogravimetric (TG) experiments of total coke removal were performed. Qualitative study was further supported by GC-MS analysis of coke extracted from the catalyst by dissolving in HF and extracting with $CH_2Cl_2$. The spent catalysts were examined after ethylene conversion into higher hydrocarbons (ZSM-5, CBV2314E, Zeolyst, 325°C, 5000 ml/(g·h), 15 h). The catalysts were modified by sequential desilication (0.6 M or 0.8 M NaOH, 65°C, 30 min) and dealumination (0.1 M or 0.2 M $HNO_3$, 65°C, 2 h) procedures to alter their acidic and textural properties.

Parent ZSM-5 and modified analogues displayed differentiated textural and acidic properties (Table 1). Mild modification of the *m*-deSi&deAl sample could preserve sample microporosity and acidity without extensive formation of mesopores. A harsher treatment in the *s*-deSi&deAl sample could bring about the development of the external surface area at the expense of micropore volume and acid site concentration.

The catalysts were used to convert ethylene to higher hydrocarbons with the preferable formation of propene. The most increased activity and fastest deactivation were found for microporous ZSM-5 catalysts, from 100% to 45% within 15 h, while modified *m*-deSi&deAl manifested a slower deactivation rate from 100% to 70% within 15 h. The *s*-deSi&deAl sample exhibited constant conversion at a moderate level without a significant drop in activity (60–55% during 15 h).

Total oxidation during TG analysis of spent catalysts provided information that the lowest amount of coke was found for *s*-deSi&deAl (Fig. 1). Mild dealumination did not significantly influence coke content. GC-MS analysis of extracted coke gave evidence that the highest content of naphthalenes was found for the parent catalyst, which is characterised by the highest concentration of Brønsted acid centres ($c_B$, Table 1). It is with these centres that aromatisation reactions are mainly associated.

FT-IR spectroscopic analysis of the coke oxidation process over spent catalysts provided information on the nature of coke species. A complex IR band at around 1640–1550 $cm^{-1}$ identifies the coke species formed during ethylene oligomerization over a series of ZSM-5.

Table 1. Chemical composition, acidic and textural properties of micro/mesoporous zeolites

| Catalyst | Si/Al | $S_{BET}$ $m^2/g$ | $S_{EXT}$ $m^2/g$ | $V_{micro}$ $cm^3/g$ | $c_B$ $\mu mol/g^{-1}$ | $c_L$ $\mu mol/g^{-1}$ |
|---|---|---|---|---|---|---|
| ZSM-5 | 11.3 | 346 | 27 | 0.16 | 559 | 111 |
| *m*-deSi&deAl | 11.7 | 387 | 67 | 0.16 | 509 | 109 |
| *s*-deSi&deAl | 11.1 | 377 | 157 | 0.11 | 227 | 228 |

The bands centred at 1615 and 1575 $cm^{-1}$ are indicative of species formed by condensation reactions producing $C_6H_7^+$ olefinic cations, $CH_2{=}CH{-}CH[CH{=}CH]CH^+$, or cyclic alkenyl carbenium ions, $C_6H_9^+$, and poly-methylbenzenes as coke forming compounds, e.g., 1,2,4- or 1,2,3-trimethylbenzene due to the 1615 $cm^{-1}$ band. Modified *s*-deSi&deAl zeolite demonstrated lower coke amounts and was less aromatic with a higher olefins content, thus making it more prone to removal. Moderate catalytic activity and low coke content of the modified *s*-deSi&deAl could provide a proper balance between catalyst activity and catalyst lifetime.

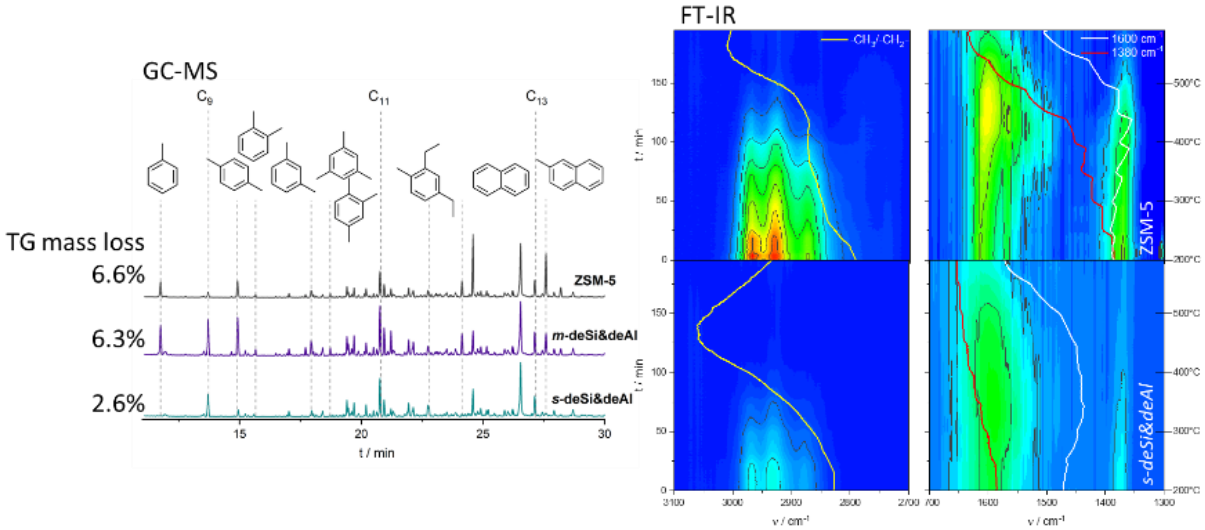



Fig. 1. GC-MS patterns of coke extracted from spent catalysts (left), and a top-down view of spectra recorded during coke oxidation over parent catalyst and modified *s*-deSi&deAl analogue in the range of C–H stretching (3100–2700 $cm^{-1}$) and C–C stretching (1700–1300 $cm^{-1}$) bands (right).

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# sP11. Polystyrene cracking over commercial zeolites Y

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The well-defined microporosity combined with tunable properties of acidic sites and exceptional stability make zeolites, already well-proven catalysts in oil refining and petrochemistry, promising catalysts for polyolefin conversion to higher value petrochemicals and transportation fuels. The relationship between zeolite properties and their catalytic performance is still well researched, mainly focusing on the impact of acid site density and pore structure on catalytic performances (activity, selectivity, stability). Catalytic solutions to waste polyolefin upcycling could benefit from the vast experience of existing processes and units (e.g., fluid catalytic cracking, hydrocracking) currently used to upgrade heavy oil fractions. Therefore, a better understanding of the relation between catalyst properties and catalytic performances is required to fine-tune the design of higher-performance catalysts in the chemical upcycling of waste polyolefins.

A series of commercially available 12-MR zeolites Y like CBV-100, CBV-500, CBV-720, and CBV-760 of various acidity and textural properties were used as catalysts for polystyrene cracking. IR monitoring of adsorbed probes as CO and pyridine was applied to determine catalyst acidic features. Catalytic cracking of polystyrene performance and coke combustion were assessed in thermogravimetric and IR-GC&MS *operando* studies.

Commercially available zeolite differs in protonic functionality due to diverse mesoporous and acidic functions. Both micropore topology and acidic properties are recognised to rule the catalytic performance of each zeolitic structure [1-3]. Results show that less confined microporosity in mesoporous zeolite catalysts as CBV-720 and CBV-760 improves polystyrene conversion and avoids overcracking, thus offering a higher share of $C_{6+}$ fraction. The secondary mesoporosity, therefore, provides a less restricted accessibility of acid sites to pre-cracked polymer fragments. The mutual dependence of speciation and accessibility of the acidic sites, which are either inherent to the microporous structure or located on newly developed mesoporous surface, is seen on comparing purely microporous and free of extra-framework species zeolite CBV-100 and mesoporous CBV-500 possessing a considerable quantity of extra framework aluminium species. Hierarchical zeolites exhibit a higher catalytic activity and suffer from less deactivation due to their secondary porosity

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References

1. K. A. Tarach, J. Martinez-Triguero, S. Valencia, K. Wojciechowska, F. Rey, K. Góra-Marek, Appl. Catal. B: Environ., 338 (2023) 123066, https://doi.org/10.1016/j.apcatb.2023.123066.
2. K. A. Tarach, M. Akouche, K. Pyra, V. Valtchev, G. Jajko, J.-P. Gilson, K. Góra-Marek, Appl. Catal. B: Environ., 334 (2023) 122871, https://doi.org/10.1016/j.apcatb.2023.122871.
3. B. Reiprich, K. A. Tarach**,** K. Pyra, G. Grzybek, K. Góra-Marek, ACS Appl. Mater. Interfaces, 14 (5), (2022) 6667–6679, https://doi.org/10.1021/acsami.1c21471.

# sP12. Highly resistible RGO-supported Pd catalyst to sulphur dioxide and water vapour for low-temperature VOCs oxidation

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Volatile organic compounds are principal air pollutants among which low molecular weight hydrocarbons and oxygen-containing compounds are mostly widespread. They are precursors to ozone formation in the ground layer of the atmosphere and both with particulate matter are the main cause of air pollution. Smog brings about serious damage to human health and has a harmful effect on vegetation. In addition, volatile organic compounds influence oxidation processes and the formation of greenhouse gases in the troposphere. Several ways are known to eliminate harmful emissions among which catalytic oxidation has some advantages over other methods. Supported palladium catalysts are considered effective for complete oxidation at low temperatures. However, the presence of water vapour deactivates many of the hydrophilic catalytic systems. For this reason, we presume that the use of hydrophobic support could be useful for VOCs complete oxidation at lower temperatures in wet medium as the hydrophobic surface would restrict water vapour adsorption and protect the catalyst against deactivation.

This work deals with the catalytic behaviour of palladium deposited on reduced graphene oxide (RGO) in the complete oxidation of several volatile organic compounds with or without presence of water.

The catalyst was prepared in two steps by incipient wetness impregnation using palladium acetate on a previously obtained RGO material with a binder alumina hydrogel on ceramic granules. The Pd/RGO catalyst was characterized by powder XRD, SEM-EDS, TEM, CO chemisorption, XPS, and $N_2$ physisorption. The tests on complete catalytic oxidation of CO, propane, butane, hexane, dimethyl ether, toluene, and propylene were carried out in a fixed bed reactor at GHSV of 30 000 $h^{-1}$.

Complete oxidation to $CO_2$ and $H_2O$ was observed for all VOCs. CO oxidation proceeded at the lowest temperature while VOCs complete oxidation (except propane) occurred within 150–400°C with the lowest $T_{50}$ observed for propylene. Among the examined compounds propane was the most difficult to oxidize, and the increase in reaction temperature from hexane through butane to propane correlated well with the strength of the C–H bond of the studied n-alkanes. It is noteworthy that the Pd/RGO catalyst retained its activity for 200 h without decrease in activity in both the presence and absence of additional water vapour in the feed gas. In practice, the catalysts manifested no deactivation during all stability and activity measurements.

In order to determine regenerability of the catalysts used, regeneration experiments were performed after $SO_2$ poisoning. Tests were carried out with samples containing Pd/RGO designated as surface or volume entity. The former was obtained by sputtering Pd/RGO and a binding gel containing Al on a ceramic support while the latter was prepared by mixing Pd/RGO with Al-containing gel. For the first 40 hours, the catalysts were treated in the absence of water vapour until a stabilized plateau was reached. After reaching stabilization, the stability test continued in the presence of water vapour and $SO_2$ for 75 hours. In the presence of water vapour, however, the activity of the catalysts decreased.

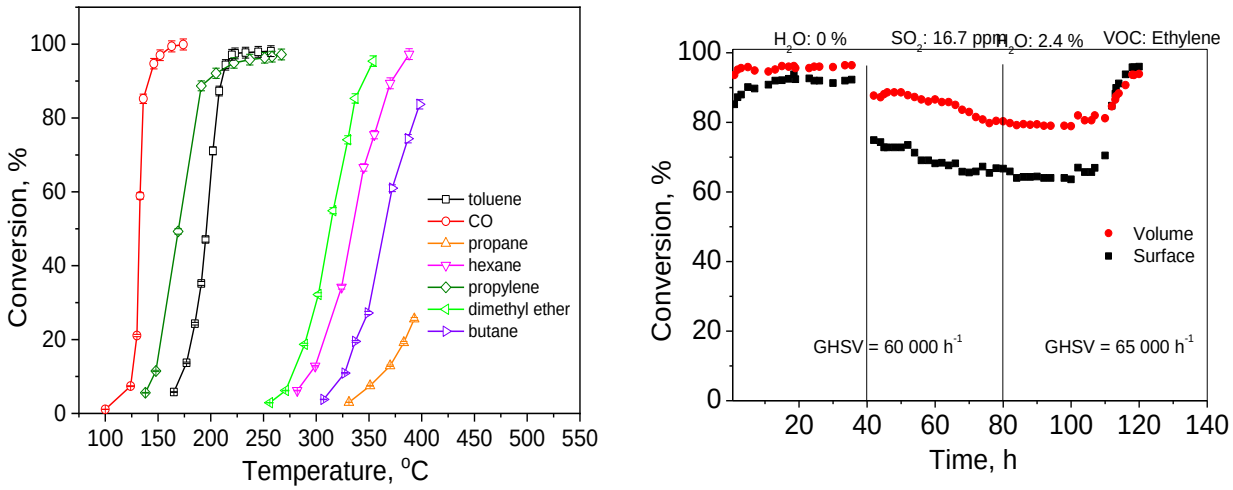



Fig. 1. Temperature dependence of VOCs and CO conversion degree on Pd/RGO catalyst. Dependence of ethene conversion on time in the presence and absence of water and $SO_2$.

After stabilization in the presence of water vapour, an experiment was conducted to regenerate the catalysts. It was found that upon switching off $SO_2$ and water vapour supply the activity of the material was fully restored. XRD pattern of the catalyst after poisoning indicated a higher amount of palladium metal and a reduced amount of PdO. After regeneration, palladium metal was not detected due to increased amount of PdO. Traces of $Pd_4S$ were also observed. Probably, formation of the latter phase was a result of easy-going decomposition of finely dispersed amorphous sulphate phases formed during impact with $SO_2$ and influence of the reducing carbon support. It is worth noting that the $Pd_4S$ phase is reported in the literature as highly efficient in the complete oxidation of methane.

Acknowledgement: The authors are grateful to Bulgarian National Science Fund for financial support via project KP-06-H 59/8 ‘Porous 3D graphene-based hierarchical materials for environmental protection’.

# sP13. Catalytic oxidation of VOCs over Co and Co-Mn oxides supported on hierarchically macro-mesoporous silica

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Volatile organic compounds (VOCs) are identified as major contributors to global air pollution. These compounds are precursors for ground-level ozone formation, photochemical smog, and secondary aerosols. They are released to the environment by a variety of methods such as industrial processes, transportation, and domestic activities. There are many different techniques for VOCs removal, such as adsorption, absorption, biofiltration, and thermal and catalytic combustion. The choice of technique depends on VOC nature, its concentration, and waste gas flow rate. Catalytic combustion is a competitive abatement technique for VOCs removal especially when the organics cannot be recycled or are present at low concentrations [1]. Different types of catalysts, such as supported noble metals, metal oxides, or supported metal oxides, and mixtures of noble metal and metal oxides were used. Among them cobalt and manganese containing catalysts are less expensive and demonstrate high activity for VOCs oxidation [2,3]. Although the catalytic activity of transition metal oxides is not as good as noble metal catalysts so far, it has drawn increasing attention and deemed to be dominant in the future.

Cobalt-based catalysts offer the best balance between cost and catalytic activity, since their behaviour is often very close to that of noble metals and the selectivity to $CO_2$ is higher if compared with other catalysts based on oxides of transition metals. A combination between $Co_3O_4$ and other oxides often affects textural, morphological, redox, acidic, and basic properties as well as catalytic activity.

Hierarchically porous catalysts are of recent scientific and technological interest due to their improved diffusion performance and high specific surface area. The hierarchically porous silica has a positive effect compared with common silica supports. An advantage of the hierarchically porous materials is that the large macro-pores combined with the mesoporous structure attribute to the materials large transport channels accompanied by a highly active surface area [4]. Macro-mesoporous silica was synthesized by the soft templating method using emulsions as templates. Structural and catalytic properties of series of mono-component cobalt and bicomponent Co-Mn catalysts were studied. Samples were prepared by incipient wetness impregnation method using acetate precursors. The obtained materials were characterized by SAXS, $N_2$ adsorption-desorption, XRD, UV-Vis, XPS, and $H_2$-TPR methods and TEM microscopy. SAXS pattern of bare material exhibited a reflection at 7.4 nm characteristic of wormhole-like mesostructure. Modification of macro-mesoporous (MM) silica with Co and Mn brought about a decrease of the specific BET surface area, pore volume, and modification of the adsorption-desorption curve shape. This might be due to partial pore blocking by Co and/or Mn particles. Cobalt oxide lines were not observed for the studied catalysts thus pointing to $Co_3O_4$ fine dispersion. XPS results indicated that only $Co^{2+}$ and $Mn^{4+}$ species were present on the surface.

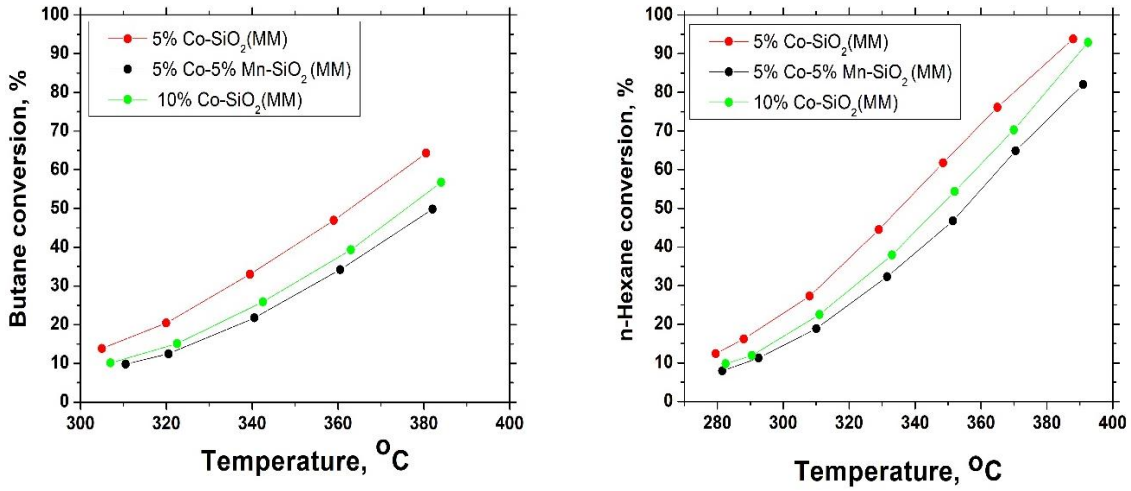



Fig. 1. Temperature dependence of butane and *n*-hexane conversion over Co-$SiO_2$(MM) and Co-Mn-SiO2(MM) catalysts.

Low intense peaks characteristic of $Co_3O_4$ weakly interacting with the surface were observed in the TPR profile of 5%Co-$SiO_2$(MM) sample. Catalyst behaviour was examinated in the complete oxidation of butane and *n*-hexane. It was found that in both cases the 5%Co-$SiO_2$(MM) sample exhibited the best catalytic performance. However, it should be pointed out that an increase in cobalt content and introduction of Mn on using acetate precursor caused a decrease in activity. Reduced activity of the two-component Co-Mn catalyst obtained from a mixed solution of acetates is most likely due to the fact that cobalt forms inactive silicate-like phases, whereas manganese gives rise to a separate phase of manganese oxide the activity of which is lower in the studied reactions.

Acknowledgement: The authors thank Bulgarian National Science Fund for financial support by contract КП-06-Н49/4.

References

1. A. Kołodziej, J. Łojewska, Catal. Today, 105 (2005) 378.
2. M. Baldi, E. Finocchio, F. Milella, G. Busca, Appl. Catal. B: Environ., 16 (1998) 43.
3. P.-O. Larsson, A. Andersson, L. R. Wallenberg, B. Svensson, J. Catal., 163 (1996) 279.
4. J. L. Blin, B. Bleta, J. Ghanbaja, M. J. Stébé, Microporous Mesoporous Mater., 94 (2006) 74.

# sP14. Bimetallic Pd-Au and Pd-Ag nanoparticles supported on MCM-41, MCM-22, and Beta-11 as catalysts for BTEX complete oxidation

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Benzene, toluene, ethylbenzene, and xylenes are commonly referred to as BTEX. They are volatile organic compounds (VOCs) that are found in vehicle emissions, petroleum, and petroleum products, such as gasoline, coal, and wood tars. BTEX are used in the manufacture of a variety of consumer goods, including chemicals, rubber, leather, plastics, cleaners and paints, and paint thinners. BTEX compounds are toxic for bone marrow, central nervous system, immune system, liver, and kidneys. They can get into human body through contaminated air by cigarette smoke and vehicle exhaust, drinking water from groundwater and through skin. Benzene is a known human carcinogen, which may cause leukemia and impacts on red and white blood cells. In this connection, BTEX removal by catalytic combustion to harmless products has been investigated over mesoporous and zeolite catalysts modified with noble metals such as palladium, gold, and silver.

Various types of zeolites as Beta-11, MSM-22 (Si/Al 30), and mesoporous molecular sieves MCM-41 (Si/Al 20 and 50) were synthesized and modified with different metals (Pd, Au, Ag, Ce, and Ba) by deposition-precipitation, impregnation, and ion-exchange methods. Obtained catalysts were characterized by ICP, XRD, XRF, XPS, HRTEM, SEM/EDX, and nitrogen physisorption techniques, and tested in heterogeneous catalytic decomposition of benzene and toluene.

The obtained results revealed that activity is dependent on carrier type and acidity, and type of deposited metal. For both palladium- and gold-modified MCM-22 and MCM-41 samples in the reaction of toluene combustion, a 50%-conversion ($T_{50}$) took place at a temperature of 205°C whereas complete oxidation was observed at 220°C. The highest catalytic activity during benzene combustion over the studied catalysts was detected over two silver containing catalysts, Pd-Ag-Ba-Ce/MCM-22-30 and Pd-Ag/Beta-11, with $T_{50}$ at 200°C and 230°C, respectively. At a temperature of 300°C, total conversion of benzene combustion was observed for MCM-22 and Beta-11 samples modified by both palladium and silver.

In conclusion, it can be summarized that zeolites and mesoporous materials exhibiting high total surface area, large volume, and wide pore distribution are suitable for carriers of small amounts of highly dispersed nanosized metals. Applying a bimetallic active phase containing palladium and silver on such supports led to production of active catalysts for BTEX complete oxidation at relatively low temperatures.

# sP15. Structural and catalytic properties of $MnO_x$-$CeO_2$ oxides supported on SBA-15

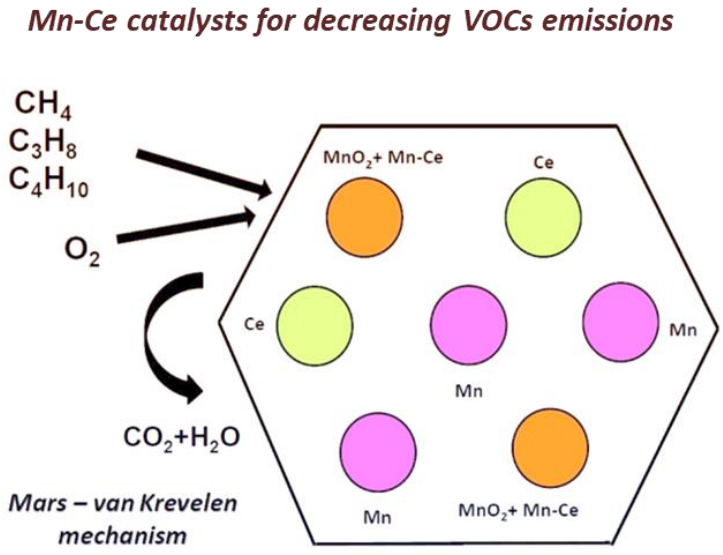
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An important problem of environmental catalysis is the design of a catalytic system for complete oxidation of hydrocarbons. Among the metal oxides, manganese oxide is reported to be quite promising for preparation of supported catalysts for removal of volatile organic compounds (VOCs).

Cerium has high oxygen storage capacity associated with fast $Ce^{4+}/Ce^{3+}$ redox process making more oxygen available for the oxidation process. Mesoporous silica materials have attracted much attention exhibiting high surface area, uniform pore-size distribution, large pore size, and wide potential applications in the fields of separation, adsorption, and catalysis. Among the different types of mesoporous silicas, SBA-15 has received considerable interest by manifesting thicker pore walls and higher hydrothermal stability.

This work is focused on a study of the structural and catalytic properties of a series of SBA-15-supported monocomponent manganese and bicomponent Mn-Ce catalysts before and after VOCs catalytic oxidation. Single component (Mn) and bicomponent Mn-Ce samples of different Mn/Ce ratio were prepared using SBA-15 according to the 'two-solvent' technique. The obtained materials were characterized by $N_2$ adsorption-desorption, XRD, SEM and TEM microscopy, EPR, XPS, $H_2$-TPR, propane-TPR, and $O_2$-TPD. The catalytic properties were tested in the reactions of complete oxidation of *n*-hexane, toluene, and propane.




SBA-15 modification with Mn caused a decrease of BET specific surface area, pore volume, and modification of the adsorption-desorption curve shape. This might be due to a partial pore blocking by manganese or Mn-Ce particles, which was confirmed by TEM images

revealing Mn and Ce clusters location inside the channels of SBA-15. According to XRD data $MnO_2$ (pyrolusite) and $Mn_2O_3$ (bixbyite) formation was visible from the XRD patterns of single Mn deposited on the SBA-15 support. No crystalline phase was detected in the case of bicomponent Mn-Ce on SBA-15 owing to high dispersion of the manganese and cerium oxides. This could be explained by mixed Mn-Ce oxide formation, which was confirmed by EDX-TEM analysis. $Mn^{3+}$ was predominant species on the surface of all catalysts. However, an EPR analysis showed presence of isolated $Mn^{2+}$ ions in the samples. In contrast to X-ray photoelectron spectroscopy, which found presence of $Ce^{3+}$, EPR analysis did not confirm this. This could be due to very rapid reduction of $Ce^{4+}$ under the X-rays because of ceria fine dispersion.

Monocomponent manganese samples demonstrated the highest activity in all the studied reactions, which is explained by higher reducibility because of weak interaction between manganese oxide and the SBA-15. Manganese and cerium oxide fine dispersion and strong interaction in the channels of the SBA-15 molecular sieve brought about the formation of hardly reducible oxide phases and, consequently, lower catalytic activity.

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# sP16. Co-modified SBA-15 catalysts for waste gases purification processes: effect of precursor

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In recent years, volatile organic compounds (VOCs) are the main source of air pollution. Typically, VOCs origin is associated with industrial processes. Catalytic combus-tion is one of the most effective techniques for removing VOCs from industrial gases of low concentration [1]. Various catalysts have been used in practice like transition metal oxides and supported noble metals. Among the metal oxides, cobalt oxide is reported as quite promising for preparation of supported catalysts for VOCs removal [2]. Primary limitation of transition metal oxide catalysts is the propensity for deactivation due to aggregation. This issue could be addressed by employing supports with novel characteristics, such as nano-structured porous oxides.

Among these classes of oxides, mesoporous silicas such as SBA-15 has received notable attention due to thicker pore walls and enhanced resistance to hydrothermal conditions when compared with MCM-41 materials [3].

Novel data on structural and catalytic properties of a series of monocomponent cobalt and bicomponent Co-Mn samples supported on SBA-15 prepared by different precursors are reported. The catalysts were characterized by SAXS, $N_2$ physisorption, XRD, TEM, TPR, XPS, UV-Vis, and FTIR methods. Further, they were tested in butane and *n*-hexane combus-tion reactions. It was established that Co-SBA-15 catalyst preparation by different precursors did not significantly change the mesoporous structure. Cobalt species were located in the mesopores and their shrinkage occurred after calcination to decompose cobalt precursor.

Depending on the precursor used, different types of oxide phases were formed on the surface of the mesoporous support. Finely divided and weakly interacting with support $Co_3O_4$, CoO, and $CoSiO_3$ were formed on cobalt samples surface prepared from both precursors.

Bicomponent Co-Mn samples exhibited the highest activity in both reactions. This is in line with our previous studies [4] according to which bicomponent CoMn samples supported on $SiO_2$ or SBA-15 showed higher activity than monocomponent counterpart did. It is well known that in most cases VOCs oxidation over oxide catalysts proceeds through Mars-van Krevelen reaction mechanism [4]. The latter mechanism states that the solid oxidizes VOCs and that organic molecule's introduction of oxygen species comes from the crystal lattice. As a result, lattice oxygen mobility and catalyst reducibility could be associated with catalytic behaviour.

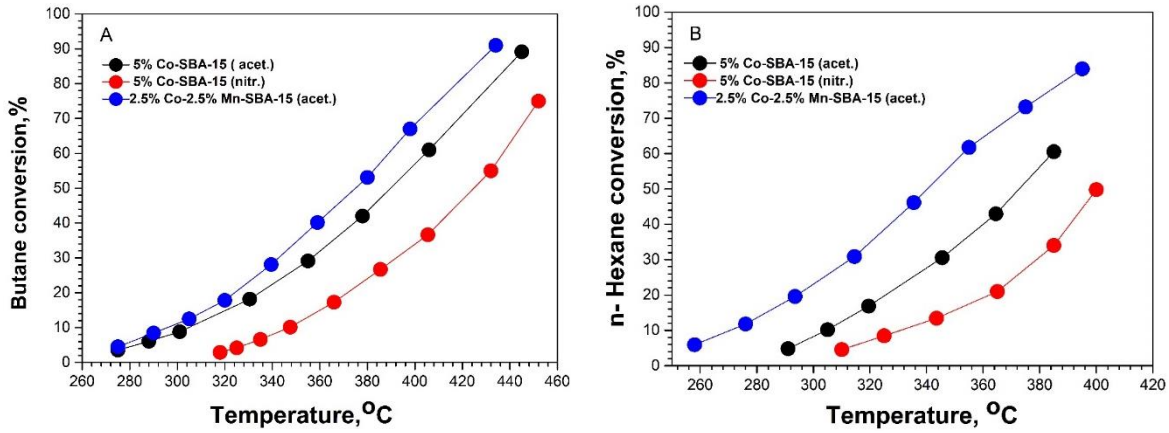



Fig. 1. Temperature dependence of butane (A) and *n*-hexane combustion (B).

Data from TPR measurements demonstrated the lowest reduction temperature of Co-Mn sample.

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References

1. H. Huang, Y. Xu, Q. Feng, D. Y. C. Leung, Low temperature catalytic oxidation of volatile organic compounds: a review, Catal. Sci. Technol., 5 (2015) 2649–2669.
2. S. J. Jiang, S. Q. Song, Enhancing the performance of $Co_3O_4$/CNTs for the catalytic combustion of toluene by turning the surface structures of CNTs, Appl. Catal. B-Environ., 140–141 (2013) 1–8.
3. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, Science, 279 (1998) 548–552.
4. S. Todorova, J.-L. Blin, A. Naydenov, B. Lebeau, H. Kolev, P. Gaudin, A. Dotzeva, R. Velinova, D. Filkova, I. Ivanova, L. Vidal, L. Michelin, L. Josien, K. Tenchev, $Co_3O_4$-MnOx oxides supported on SBA-15 for CO and VOCs oxidation, Catal. Today, 357 (2020) 602–612.

# sP17. Effect of preparation method on cobalt-modified SBA-15 catalysts for waste gas purification processes

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Volatile organic compounds (VOCs) have been the primary cause of air pollution in recent years. One of the best methods for eliminating volatile organic compounds from industrial gasses at low concentrations is catalytic combustion. In practical applications, a range of catalysts has been employed, such as supported noble metals and transition metal oxides. Among the metal oxides used to produce supported catalysts for VOCs elimination cobalt oxide is supposed to be very promising. Transition metal oxide catalysts' main drawback is their tendency to deactivate because of aggregation. Use of supports with unique properties, like nanostructured porous oxides, could help solving this problem. Among these classes of oxides, mesoporous silicas such as SBA-15 has received notable attention due to its thicker pore walls and enhanced resistance to hydrothermal conditions.

Novel data on structural and catalytic properties of monocomponent cobalt samples supported on SBA-15 prepared by different methods were collected. The samples were characterized by different instrumental methods as SAXS, $N_2$-physisorption, XRD, TPR, XPS, UV-Vis, and FTIR. Catalyst performance was evaluated by tests on butane, *n*-hexane, and CO combustion. It was established that preparation of the Co-SBA-15 catalysts by different methods did not change mesoporous structure significantly. Cobalt species were located in the mesopores and shrinkage occurred after calcination to decompose cobalt precursor. X-ray patterns disclosed wide and very weakly intense reflexions for $Co_3O_4$ and CoO with samples obtained by impregnation demonstrating development of finely divided oxide particles. No diffraction bands were observed in XRD pattern of sample obtained after cobalt deposition by the 'two solvents' method, thus showing that finely dispersed oxide particles were formed on the surface of these samples as well. The highest activity of Co-SBA-15 catalyst prepared by the latter method was observed with all the studied reactions.

Based on detected activity of the prepared Co–SBA-15 materials, one could expect further development of these new catalytic systems for real application in greenhouse gas emissions abatement.

Acknowledgements: The authors are grateful to Bulgarian National Science Fund for financial support under contract КП-06-Н49/4. Research equipment of distributed research infrastructure INFRAMAT, part of the Bulgarian National Roadmap for Research Infrastructure supported by Ministry of Education and Science of Bulgaria, was used in this investigation.

# sP18. Catalytic combustion of VOCs and CO over noble metals supported on MCM-22 zeolite

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Volatile organic compounds (VOCs) represent one of the main groups of environmental pollutants, which are detected in exhaust gases released in the process of burning organic materials. A number of industrial chemical processes as well as because of various decay developments also emit VOCs. All VOCs are greenhouse gases, most being toxic, and the removal is based on complete catalytic combustion. Among volatile hydrocarbons, methane is most difficult to oxidize, especially at a temperature below 350°C. VOCs catalytic oxidation is most successfully carried out with catalysts containing supported noble metals, such as palladium and platinum, which are expensive. Therefore, it is interesting to investigate the effect of combination between noble metals of small amount and cheaper metals, such as Ce and Ba, known for stabilizing and activating properties.

Various types of MSM-22 zeolites modified with noble metals, such as palladium, gold, and silver of low concentration were synthesized by different methods like deposition-precipitation, impregnation, and ion exchange. Additionally, metals as Ba and Ce were applied to enhance catalytic activity by stabilization of the catalyst surface and improve oxygen storage capacity. The catalysts were characterized by the following methods: ICP, XRD, XRF, XPS, HRTEM, SEM/EDX, $O_2$-TPD, $CH_4$-TPR, and low-temperature nitrogen adsorption. Synthesized catalysts were tested in the reactions of CO oxidation and VOCs complete catalytic oxidation using methane, ethane, and propane for this purpose. Effect of reaction conditions, reagents initial concentration, and water vapour and oxygen presence on the catalytic performance was investigated and model predictions were proposed.

Methane ignition temperature $T_{10}$, $T_{50}$, and total conversion for the most active Pd-Au-Ce-MCM-22-30 catalyst was found to be 255, 325, and 430°C, respectively. For the reaction of CO oxidation, the temperature at 50% and 90% conversion, $T_{50}$ and $T_{90}$, over the same catalyst was 98 and 140°C, accordingly. In the presence of water vapour (2 vol.% $H_2O$) and absence of oxygen, the most active catalyst showed excellent thermal stability and the activity remained almost unchanged. Investigated noble nanostructured materials have a strong potential for practical applications due to their high activity and stability for CO and VOCs complete oxidation.

# sP19. Application of graphene oxide as adsorbent for the removal of toluidine blue from aqueous solutions

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Organic dyes play a pivotal role in various industries including textiles, cosmetics, and food processing. However, their indiscriminate use often leads to water pollution posing a significant threat to aquatic ecosystems and human health. Toluidine blue is such an organic dye commonly used in laboratories as a biological stain and in the textile industry for dyeing cotton, wool, and silk.

Contaminated wastewater containing toluidine blue exhibits a vivid blue hue, which is not pleasant to look at and can harm aquatic life because it is toxic. Utilizing adsorbents for dye removal not only aids in water quality restoration but also presents a sustainable approach to combating dye pollution. Effective treatment of organic dye-polluted waters, such as those contaminated with toluidine blue, necessitates the selection of appropriate adsorbents being crucial for dyes successful removal from polluted environments.

Graphene oxide (GO) has been gaining significant attention in recent years because of its impressive electronic, thermal, optical, and mechanical characteristics. Numerous studies have highlighted its potential as a nano adsorbent due to large specific surface area, complex aromatic structure, and plentiful oxygen-containing functional groups. Moreover, GO has been found to be effective in adsorbing cationic dyes, making it a promising material for dye removal applications.

The aim of the present work was to investigate efficiency of the prepared hierarchical graphene oxide as adsorbent for the removal of toluidine blue dye from aqueous solutions.

Studied material was prepared by the Tour method from synthetic graphite with the use of appropriate amounts of concentrated sulphuric acid, phosphoric acid, and potassium permanganate. The material was washed to pH 6.5 and sonicated for effective exfoliation. Final graphene oxide was obtained by freeze-drying.

As prepared graphene oxide was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and low-temperature nitrogen adsorption.

XRD results showed successful preparation of GO with a crystallite size of 6 nm. SEM and TEM methods revealed a porous material that consists of typical graphene sheets of relatively small size, which are crumpled, plicated, and broken (Fig. 1). Nitrogen adsorption-desorption isotherms (Fig. 1) are typical of graphene materials being of II type with H3 hysteresis evidencing non-rigid aggregates of plate-like particles or pore network of macropores not completely filled with condensate. Specific surface area was 165 $m^2/g$ with a total pore volume of 0.26 $cm^3/g$ and average pore diameter of 6.2 nm. GO isotherm exposed a mixed-type micro-mesoporous texture. Hence, the prepared material was micro-mesoporous with a hierarchical pore structure.

Determination of the most effective factors affecting toluidine blue removal, such as solution pH, duration of contact, temperature, and initial dye concentration, was carried out using batch technique.

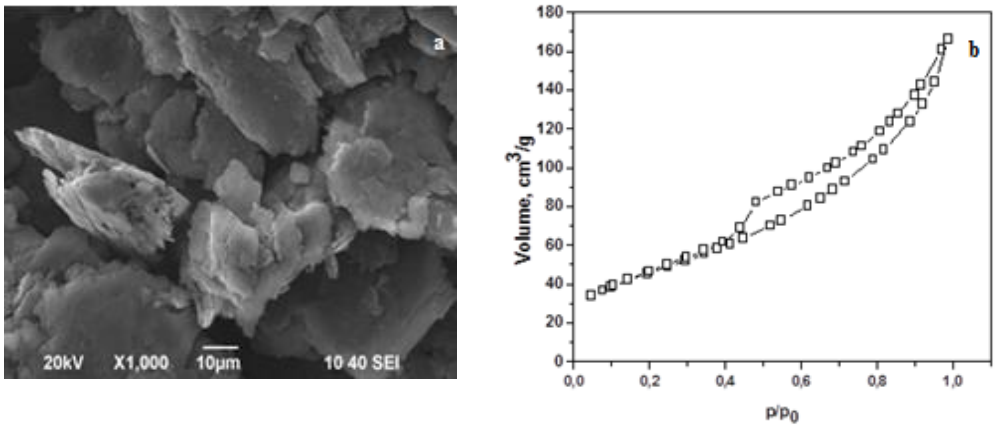



Fig. 1. SEM micrograph and adsorption-desorption isotherm of graphene oxide.

The removal of this dye proved to be rapid by attaining equilibrium within thirty minutes, and indicated a strong affinity of the tested material for toluidine blue in aqueous solution. Experimental equilibrium data were analysed using linear Langmuir, Freundlich, and Dubinin-Radushkevich models. Resulting isotherm constants and correlation coefficients for these models are summarized in table 1.

Table 1. Isotherm constants and correlation coefficients for the three models for toluidine blue adsorption

| Langmuir parameters | | | Freundlich parameters | | | Dubinin-Radushkevich parameters | | |
|---|---|---|---|---|---|---|---|---|
| $Q_0$ mg $g^{-1}$ | $K_L$ L $mg^{-1}$ | $r^2$ | $k_F$ $mg^{1-n}L^ng^{-1}$ | n L $mg^{-1}$ | $r^2$ | $Q_m$ mg $g^{-1}$ | E kJ $mol^{-1}$ | $r^2$ |
| 254.45 | 0.130 | 0.9922 | 88.50 | 5.16 | 0.9564 | 186.79 | 32.60 | 0.7931 |

With correlation coefficient ($r^2$) exceeding 0.99, it is evident that the Langmuir model describes adsorption process in the best way. Toluidine blue adsorption increases as medium pH rises. Pseudo-second-order model effectively characterizes the adsorption process. Increasing temperature leads to a higher number of adsorbed dye molecules. Negative values for changes in Gibbs free energy and enthalpy indicate spontaneous and exothermic adsorption of toluidine blue onto the tested material with a negative change in entropy.

Maximum adsorption capacity of the studied material was determined as 254.45 mg $g^{-1}$. This finding suggested that investigated nanomaterial holds promise as a potential adsorbent for efficient removal of toluidine blue from contaminated aqueous solutions.

Acknowledgement: The authors are grateful to Bulgarian National Science Fund for financial support via project KP-06-H 59/8 ‘Porous 3D graphene-based hierarchical materials for environmental protection’.

# sP20. Combined purification of methylene blue from aqueous media by adsorption and photocatalysis using 3D graphene-based material

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Methylene blue (MB) is a widely used dye in industry, microbiology, diagnostics, etc., and can be harmful if released in water. Therefore, its removal from aqueous media is of research interest. A common approach to effective MB elimination from contaminated water is adsorption using various advanced materials. Many materials have been synthesized and applied for this purpose. However, achieved results of adsorption capacity of predominant part of materials are not as satisfactory as required for complete removal of aforementioned dye. One possible approach to enhance activity of the solid material is to combine its removal efficiency with simultaneous photocatalytic degradation.

Initial studies were conducted to determine the photocatalytic activity of monolithic 3D-RGO material (RGO – reduced graphene oxide). The monolith was prepared by gelation of pre-synthesized graphene oxide (GO) suspension under basic conditions followed by hydrothermal treatment at 160°C for 15 h. The monolith was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), low-temperature nitrogen adsorption, and FTIR and XPS spectroscopies.

XRD results showed that hydrothermal treatment led to successful reduction of GO to RGO although with increased crystallite size. SEM and TEM techniques disclosed a porous 3D monolith that consisted of typical graphene sheets of relatively small size, which are crumpled, plicated, and broken. Nitrogen adsorption isotherm of 3D-RGO revealed a mixed-type micro-mesoporous texture. Hysteresis loop type and position also indicated appearance of macropores. Hence, the prepared 3D-RGO monolith material was micro-meso-macroporous with a hierarchical pore structure. XPS C1s spectrum of 3D-RGO confirmed C=C $sp^2$ graphitic carbon and presence of $sp^3$ carbon bonds as well as oxygen-containing functional groups.

Photocatalytic activity of the material was evaluated by studying the process of methylene blue degradation in aqueous solution under UV light irradiation. Sample adsorption capacity toward MB of different concentration was investigated to select suitable concentration of MB for the photocatalytic studies. It was established that for initial concentration of 100 and 300 mg/L MB adsorption was 100% and 35%, respectively. MB solution of 120 mg/L was prepared and added to the 3D-RGO material. The suspension was irradiated with a 6W or 18W 252 nm UV lamp. Absorbance of the clear supernatant aliquots was measured using a spectrophotometer at a wavelength of 650 nm. Then the photodegradation degree (% Cdeg) was calculated. Results of the combined study are presented in figure 1.

Photodegradation degree was 51% upon irradiation with 6W lamp and increased to 63% when applying 18W UV lamp.

The photocatalytic degradation reaction was modelled using a pseudo-first-order kinetic equation of the Langmuir-Hinshelwood kinetic model, $-\ln(C_t/C_0) = k.t$, where $C_t$ is the instantaneous dye concentration during irradiation time t, $C_0$ is the initial concentration after the end of the dark period, and $k$ is the reaction rate constant.

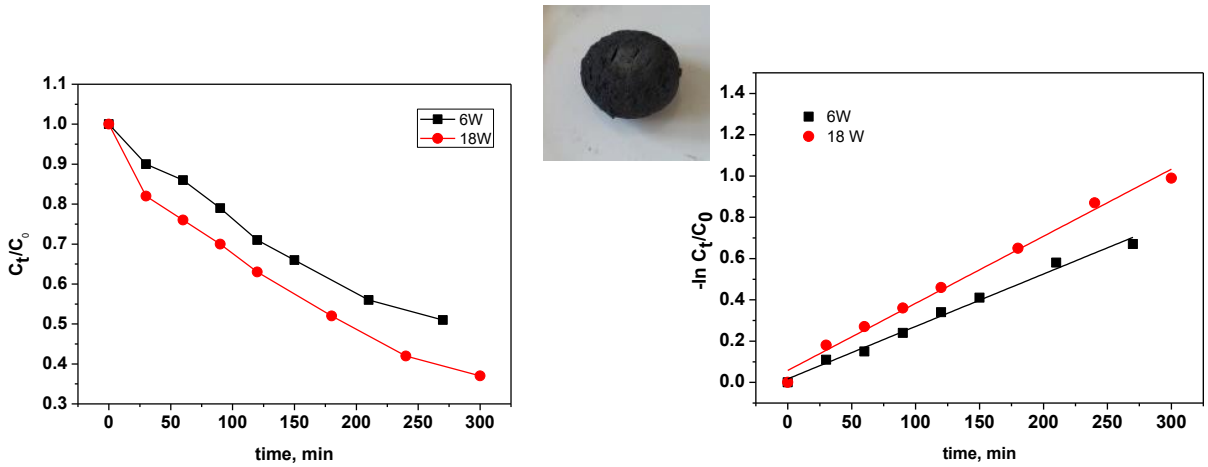



Fig. 1. Photocatalytic activity of 3D-RGO (a) and kinetic curves of photocatalytic decolorization (b) for MB removal during irradiation with 6 and 18 W UV lamp.

Graphic expression of this equation is a line passing through the origin of the coordinate system, from the slope of which *k* could be determined. Determination of the 'apparent' rate constant was used to model and describe the rate of the degradation process.

Calculated values of the rate constants *k* were $2.5\times10^{-3}$ and $3.3\times10^{-3}$ $min^{-1}$ for the photocatalytic process using 6 and 18 W UV lamps, respectively.

The material studied is perspective for application in dye removal from contaminated waters after optimizing the conditions to conduct the photocatalytic process: pH of the starting solution, sample amount, UV lamp power, dye concentration of the starting solution, dye type, and others in further experiments.

Acknowledgement: The authors are grateful to Bulgarian National Science Fund for financial support via project KP-06-H 59/8 'Porous 3D graphene-based hierarchical materials for environmental protection'.

# sP21. Photocatalytic activity of $TiO_2$ particles, obtained by *Mentha Spicata*-mediated green synthesis

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Titanium dioxide nanoparticles were obtained using phyto-synthesis by means of *Mentha Spicata* (MS) leaf extract combined with hydrothermal treatment. Titanium precursor solution was prepared by dissolving Ti isopropoxide, $Ti(OPr)_4$, and complexing agents in isopropanol. The mixture of Ti solution and plant extract (in three different concentrations) was transferred into an autoclave at 150°C. The so-obtained precipitates were washed, dried and finally treated at 400°C for 3 h. Prepared powders from solution with 40 ml MS, 70 ml MS, and 100 ml MS are denoted as M0, M1, and M2, respectively.

Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM/EDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS).

Further the samples were tested using Reactive Black 5 as a model pollutant dye (5 ppm) under polychromatic UV-A illumination ($\lambda_{max}$ = 365 nm, 18W BLB lamp). Oxidative discoloration reaction was monitored by a UV-1600PC UV-visible absorbance spectrophotometer in the wavelength range 200–800 nm. The samples were left under dark conditions for 30 min followed by irradiation for 90 minutes.

Anatase phase of the titania particles was revealed from the XRD patterns. BET analysis showed that the specific surface area of the M0, M1, and M2 samples was 123, 121, and 126 $cm^2/g$, respectively. Sample pore sizes were in the range 7–8 nm.

XPS analysis disclosed peaks of C1s, O1s, and Ti2p on the surface of the powders. Oxygen spectra were wide, asymmetric, and deconvoluted by Lorentzian-Gaussian curve fitting into three components. The first one at ~529.9 eV is attributed to lattice oxygen in $TiO_2$, the second peak at ~530.6 eV is described to a C=O bond, and the third one at ~531.9 eV is assigned to adsorbed hydroxyl groups. An increase of MS concentration in the $TiO_2$ solution gave rise to increased area of the peaks matching C=O bond and hydroxyl groups. Titania nanoparticles manifested irregular particle structure. Optical bandgap was estimated using Tauc equation. Optical bandgap values were 3.24, 3.19, and 3.19 eV for the M0, M1, and M2 samples, respectively.

SEM analysis revealed that all investigated samples exposed randomly oriented plate-like particles. The M0 sample had many dense clusters, which consist of small particles of various size. SEM image of the M1 sample showed a different morphology relative to that of M0. The plate-like structures became larger with more clearly defined boundaries. It should be noted that the distance between them increased significantly, which is a prerequisite for increased number of catalytically active sites. This affected positively all steps of the photo-

catalytic reaction for dye degradation. The M2 sample had a similar morphology to that of M1 particles, but the clusters decreased in size and became slightly denser. TEM photograph of the M1 sample revealed asymmetric spherical particles of about 5-nm size. The M2 sample exposed particles with several types of morphology: spherical-like, elongated, and many clusters with different dimensions. The average particle size was about 20 nm. Both TEM and SEM analyses suggest that varying the plant concentration is the key to modify particle morphology.

M1 photocatalyst powder exhibited the best rate constant for complete decomposition of the RB5 azo dye under UV irradiation ($k = 6.13\times10^{-2}$ $min^{-1}$), while samples M0 and M2 demonstrated $k = 4.01\times10^{-2}$ $min^{-1}$ and $k = 4.4\times10^{-2}$ $min^{-1}$, respectively. The highest degree of discoloration of the model contaminant dye was achieved in the presence of the M1 photocatalyst prepared from Ti solution with 70 ml MS extract. The results confirm a positive effect of using the MS leafs as capping agent in the green synthesis procedure on the photocatalytic properties of $TiO_2$ nanoparticles.

Applying *Mentha Spicata* extract in optimal concentration followed by hydrothermal treatment led to formation of highly active $TiO_2$ nanophotocatalysts. Their morphological features ensure a high number of active catalytic sites, which are responsible for higher adsorption activity, electron-hole diffusion, and mass transportation bringing about outcomes as enhanced rate of the photocatalytic reaction in the presence of plant-mediated titania powders.

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# sP22. Photocatalytic degradation of azo dye using AB-PBI/plant-synthesized $TiO_2$ hybrid membranes

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Titania ($TiO_2$) is a promising material, which has been widely used in various fields of industry, medicine, etc., due to its unique properties like very high stability, no toxicity, low price, high photocatalytic activity, and photoelectric conversion efficiency [1]. Polymer membranes can be applied as a photocatalytic support to improve nanoparticle reusability and dispersion. Tight polymer-nanoparticle conjunction or heterojunction facilitates separation of photogenerated electron holes and as a result inhibits their recombination rate [2].

Novel AB-polybenzimidazole/$TiO_2$ nanocomposite membranes of 100-μm thickness were synthesized by film casting approach with subsequent anti-solvent inversion in order to obtain porous composites. Modified Eaton's reagent (methanesulphonic acid/$P_2O_5$) was used as both reaction medium for microwave-assisted synthesis of AB-PBI and efficient dispersant of partially agglomerated titania powders. Maximum content of achieved $TiO_2$ filler was 20 wt.%. Titanium dioxide particles were obtained by plant-extract-mediated synthesis using different amounts of Mentha Spicata (MS) aqueous extract and hydrothermal treatment at 150°C followed by calcination at 400°C.

Phase and surface composition, structure, thermal behaviour, morphology and paramagnetic characterization of the prepared AB-polybenzimidazole/$TiO_2$ nanocomposite membranes were studied by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis, and scanning electron microscopy (SEM).

Photocatalytic ability of the synthesized AB-polybenzimidazole/$TiO_2$ nanocomposite membranes was studied in the reaction of Reactive Black 5 dye (RB5) degradation as a model contaminant under UV light irradiation. Photocatalytic tests were performed at pH=3 adjusted by 1M HCl. Initial concentration of used RB5 dye solution was 5 ppm.

Both plant extract quantity in Ti solution and PBI matrix form, basic or acid doped, have influence on the photocatalytic activity of AB-polybenzimidazole/$TiO_2$ membranes. Acid and base forms of polymer membrane, containing $TiO_2$ particles, obtained with lower quantity of MS extract exhibit 89% and 96% degradation rate after 180 min UV illumination, respectively. Samples prepared on using a higher amount of Mentha Spicata extract possess lower photocatalytic efficiency, namely 55% and 88% for membrane acid and base form, respectively.

EPR data showed that $N_b^{\bullet}$, $O_2^{-\bullet}$, and $OH^{\bullet}$ radicals were formed in AB-polybenzimidazole/$TiO_2$. Relative concentration of the $N_b^{\bullet}$ species increased under UV light irradiation in the air, while sample illumination in inert atmosphere did not generate new $N_b^{\bullet}$ particles. In addition, $Ti^{3+}$ species on the surface was formed.

Acknowledgement: The authors express their gratitude to Bulgarian National Science Fund for financial support by project КП-06-Н69/8 'Novel polymer-hybrid materials containing (bio)synthesized metal oxide particles with improved photocatalytic and antimicrobial potential'.

References

1. B. Su, X. Liu, X. Peng, T. Xiao, Z. Su, Mater. Sci. Eng., A, 349 (2003) 59–62.
2. Z. Tian, S. Wang, Y. Wu, F. Yan, S. Qin, J. Yang, J. Li, Z. Cui, J. Alloys Compd., 910 (2022) 164887.

# sP23. Ti-zeolite Y nanocomposites modified with Au and $CeO_2$ and their photocatalytic activity

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The use of silica-based materials as photocatalysts for $CO_2$ photoconversion has proven to be a promising strategy because of their high surface area, structured framework, and ultraviolet radiation transparency [1]. At the same time, zeolites can promote interfacial proton and electron transfer reactions and show a high $CO_2$ capture capacity. Titania incorporation into zeolites decrease the surface area owing to partial pore blockage by the Ti species. However, the surface area is still greater than that of pure $TiO_2$. Addition of noble metals (Au, Pt, Ag) and lanthanide oxides improve activity and selectivity to $CH_3OH$ of these materials [2-4]. Herein, nanocomposites based on Ti-zeolite Y were modified with ceria and gold. Gold and ceria effects on the photocatalytic properties were evaluated in $CO_2$ reduction.

Ti was incorporated into zeolite Y framework (1% $TiO_2$) during synthesis from titanium (IV) acetylacetonate. The material thus obtained was modified by impregnation with 1% $CeO_2$ and/or Au (1%). Obtained samples were named TiY, TiYAu, and TiYCeAu and characterized by SEM microscopy, XRD, $CO_2$ adsorption-desorption, $H_2$-TPR, photoluminescence, and UV-Vis and Raman spectroscopy. The photocatalysts were tested in $CO_2$ reduction with $H_2O$ under visible light irradiation (525 nm). Photocatalytic activity of the materials was determined by monitoring variation of $CO_2$, $CH_4$, $C_2H_6$, and $CH_3OH$ concentration during the photocatalytic process by gas chromatography.

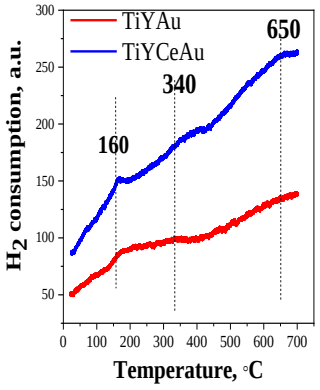



Fig. 1a. $H_2$-TPR

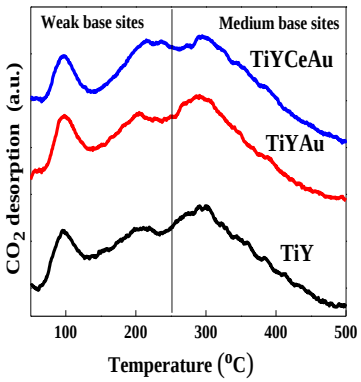



Fig. 1b. $CO_2$-TPD

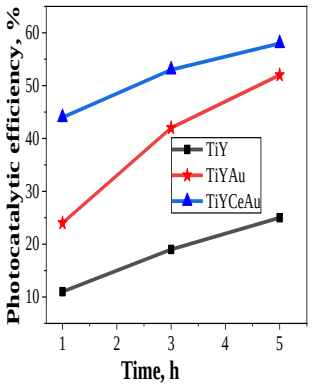



Fig. 1c. Photocatalytic results of $CO_2$ reduction with $H_2O$

Crystalline structure typical of zeolite Y was confirmed by X-ray diffraction and SEM images showing preservation of the zeolite Y morphology and a slight decrease of the zeolitic particles size. No significant variations of structure and morphology were evidenced after cerium or gold immobilization. Raman results demonstrated presence of $CeO_2$ with surface oxygen vacancies for $Ce^{4+}$ and $Ce^{3+}$ and of titanium into the silica zeolite.

$H_2$-TPR profiles (Fig. 1a) exhibited three steps for a sample with ceria that agree with $Au^+$ reduction, oxygen from surface, and $CeO_2$ reduction, accordingly. In the absence of cerium, hydrogen consumption was significantly lower. Ceria was added as a basic promoter for carbon dioxide chemisorption and to inhibit $e^-/h^+$ recombination and generation of oxygen vacancies. Photoluminescence spectra evidenced these effects of cerium loading. Gold and Ce presence did not significantly change ceria adsorption as well as the ratio of weak to medium basic sites (Fig. 1b).

UV-Vis diffuse reflectance spectra of synthesized photocatalysts showed a surface-plasmon resonance effect after Au immobilization and a red shift of the absorption spectra after cerium immobilization. This explained improved photocatalytic efficiency for the cerium containing sample (Fig. 1c). In addition, co-existence of the Au nanoparticles with titania and ceria favoured the photocatalytic activity due to injection of photo-excited electrons of the gold surface plasmon in the system.

New active nanocomposites were obtained for photocatalytic reduction of carbon dioxide with $H_2O$ under visible light irradiation. Gold and ceria impact as well as the local structure of the titanium species incorporated within the zeolite Y framework on $CO_2$ reduction and selectivity to $C_2H_6$ and $CH_3OH$ was evidenced.

References

1. M. B. Bahari, A. A. Jalil, C. R. Mamat, N. S. Hassan, H. D. Setiabudi, D.-V. N. Vo, Surf. Interfaces, 31 (2022) 102049.
2. J. Ji, R. Li, H. Zhang, Y. Duan, Q. Liu, H. Wang, Z. Shen, Appl. Catal. B-Environ., 321 (2023) 122020.
3. H. Tang, Z. A. Chen, M. Wu, S. Li, Z. Ye, M. Zhi, J. Colloid Interface Sci., 653 (2024) 316–326.
4. Y. Xia, J. Man, X. Wu, S. Huang, A. Lu, X. Shen, S. Cui, X. Chen, G. Fu, Ceram. Int., 49 (2023) 6100–6112.

# sP24. Investigation of $NiO/Pd/Al_2O_3$, $CuO/Pd/Al_2O_3$, and $CoO/Pd/Al_2O_3$ as catalysts for ozone decomposition and photocatalysis

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$NiO/Pd/Al_2O_3$, $CuO/Pd/Al_2O_3$, and $CoO/Pd/Al_2O_3$ samples were synthesised using deposition method and characterized by BET, IR, XPS, XRD, and SEM techniques. Activity for photocatalytic wastewater decolouration of three model textile dyes under UV light was then tested. Initial concentration of Reactive Orange 16 (yellow), Reactive Blue (blue) 19, and Reactive Red 180 (red) dyes in aqueous solutions was 20 ppm. Rate constants of the $NiO/Pd/Al_2O_3$ photocatalysts decreased in the order 30.4 (blue) >19.0 (yellow) >7.6 (red). For the CuO containing samples the rate constants were 22.6 blue) >17.4 (yellow) > 6.7 (red), while the $CoO/Pd/Al_2O_3$ catalysts demonstrated 13.1(blue) > 9.1(yellow) > 2.5(red). We could conclude that for all the three used pollutants $NiO/Pd/Al_2O_3$ manifested superior performance followed by the $CuO/Pd/Al_2O_3$ and $CoO/Pd/Al_2O_3$ samples. In addition, the catalysts were examined toward ozone decomposition at ambient temperature for 3 h with 23000-ppm concentration where the NiO containing sample yet again showed higher activity with practically full conversion. Meanwhile both the $CoO/Pd/Al_2O_3$ and $CuO/Pd/Al_2O_3$ samples attained about 90% conversion. No temporary loss of activity was observed during the test, which is a common problem due to accumulation of oxygen atoms on active sites of the different catalysts.

# sP25. Catalytic combustion of methane over Pd-modified La-Ce-Zr-Al catalyst

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Methane is the major component of natural gas and a powerful greenhouse gas. It has the potential to cause significantly more global warming than previously thought, according to recent research [1]. Catalytic combustion is one of the most promising technologies for reducing methane emissions [2,3]. Among the catalysts often used for methane combustion, palladium occupies an important place, separately or in combination with different metals or metal oxides, on alumina support. Various additives are used to improve the characteristics of palladium catalysts. Among these is lanthanum, which is typically used to retard catalyst deactivation by preventing PdO transformation into Pd and enhancing resistance against reduction of alumina surface area. Doping La into $CeO_2$ may reduce particle size, prevent sintering, and make ceria more reducible. Added $ZrO_2$ to $CeO_2$ significantly increases ceria thermal stability. It is known that inorganic materials, such as zeolites, ceramics, silicon dioxide, zirconia, and alumina find application as catalytic supports. Among them, ceramic catalyst supports possess good thermal stability and relatively low cost.

The present study aims to investigate a Pd-modified La-Ce-Zr-Al catalyst prepared by the sol-gel method for a possible use as an active phase in the preparation of catalysts from ceramic cylinder supports obtained by extrusion for methane abatement applications. Low-temperature $N_2$ adsorption, XRD, SEM, TEM, and XPS techniques were applied to characterize the catalyst. Nitrogen adsorption-desorption isotherms were found to manifest similar profiles, matching the type IV isotherm characteristic of mesoporous materials. Investigation using XRD analysis revealed that palladium deposition on the supports leads to the appearance of peaks that are typical of PdO. After the catalytic tests a new, highly crystalline cubic metal-Pd phase was observed. XPS analysis showed that palladium is present on the catalyst surface in different oxidation states. Catalyst morphology and microstructure was investigated by SEM and TEM.

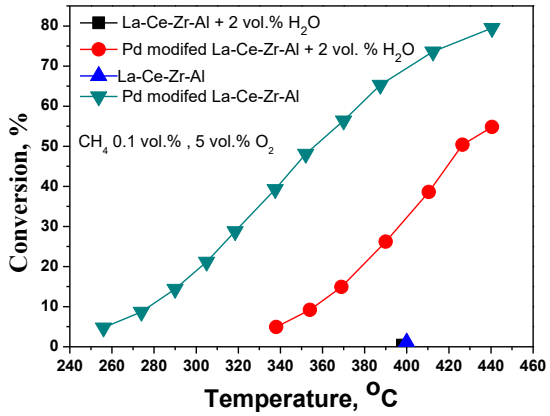



Fig. 1. Temperature dependence of methane oxidation over palladium-modified La-Ce-Zr-Al catalyst cylinders.

The reaction of complete oxidation of methane over Pd-modified La-Ce-Zr-Al catalyst cylinders proceeded above 250°C (Fig. 1). $T_{50}$ in dry gas feed was 356°C, while in the presence of 2% water vapour $T_{50}$ was 426°C with 5 vol.% oxygen content at GHSV of 30 000 $h^{-1}$).

Based on the obtained results it can be concluded that Pd-modified La-Ce-Zr-Al catalyst cylinders can be successfully used as promising catalysts for reduction of methane emissions.

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References

1. D. T. Shindell, G. Faluvegi, D. M. Koch, G. A. Schmidt, N. Unger, S. E. Bauer, Improved attribution of climate forcing to emissions, Science, 326 (2009) 716–718.
2. E. Arendt, A. Maione, A. Klisinska, O. Sanz, M. Montes, S. Suarez, J. Blanco, P. Ruiz, Structuration of $LaMnO_3$ perovskite catalysts on ceramic and metallic monoliths: physicochemical characterisation and catalytic activity in methane combustion, Appl. Catal. A-Gen., 339 (2008) 1–14.
3. A. Barrera, S. Fuentes, G. Díaz, A. Gymez-Cortes, F. Tzompantzi, J. C. Molina, Methane oxidation over Pd catalysts supported on binary $Al_2O_3$–$La_2O_3$ oxides prepared by the sol-gel method, Fuel, 93 (2012) 136–141.

# sP26. Composite carbon material with excellent adsorption properties toward $CO_2$ prepared by new one-step approach

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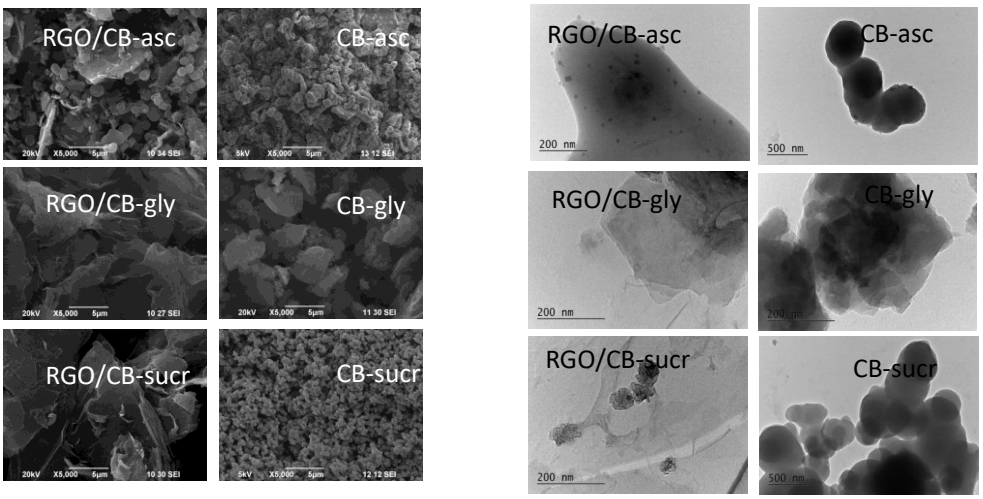
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Diverse materials have been considered in $CO_2$ capture. Recently, different classes of solid adsorbents have been studied for $CO_2$ adsorption. Due to low price and environmentally friendly nature carbon nanomaterials are considered one of the prospective adsorbents because of their physicochemical properties. It has been found that the performance of such materials in $CO_2$ sorption depends on morphology and specific chemical functionalization ensuring high porosity and presence of oxygen-containing surface groups. Graphenes and carbon dots represent some of the latest developed classes of non-traditional carbon materials. They are nanocarbon materials with specific morphological features and a high ability to expose different functional groups at the surface. Their $CO_2$ capture properties have not been much studied. Concerning the design of new material with improved adsorption ability toward $CO_2$ through intensified interactions of the different type of adsorption sites with the gaseous adsorbate, combining the properties of reduced graphene oxides and carbon dots seems a prospective approach. Synthesis method, initial compound type, and preparation conditions have a great influence on the chemical state and porous structure of the carbon-based materials. The goal of the present work is to achieve high $CO_2$ capture capacity using one-step prepared composite of reduced graphene oxide-carbon ball (RGO/CB) materials by different types of reducing agents.

RGO/CB composite materials were obtained by simultaneous preparation of RGO by the Tour method and carbon balls using as reducing agents L-ascorbic acid, sucrose, and glycine. The prepared composites were characterized by powder XRD, SEM-EDS, TEM, XPS, and $N_2$ physisorption. Carbon dioxide adsorption measurements were performed under static volumetric conditions at two temperatures to determine heats of adsorption. Different models including Langmuir, Freundlich, and Langmuir-Freundlich were used to fit the experimental data. Adsorption capacities were determined and the isosteric heats of adsorption Qst were calculated.

XRD analyses show predomination of the amorphous hump of the carbon balls over the RGO peaks. SEM and TEM micrographs revealed different morphological features depending on the reducing agent used. XPS high-resolution C1s spectra could be fitted to different peaks assigned to C–C, C=C, C–O, and C=O bonds, thus confirming various oxygen functional groups in the material.

Carbon dioxide adsorption on the obtained composites and porous carbon balls presented in figure 1 shows enhanced $CO_2$ capture capacity for the materials prepared by L-ascorbic acid. Adsorption capacity at 100 kPa and 273 K was 3.6 mmol/g for the composite and 2.6 mmol/g for the carbon balls. The values are higher than (or close to) literature reported performance of carbon materials. It was found that in the case of $CO_2$ adsorption, its uptake correlates with textural values of the micropore volume and size. Micropores with pore widths below 0.8 nm possessed the strongest affinity to $CO_2$ at low pressures, while larger micropores could be involved in adsorption upon increased pressure.




| Sample | S $m^2/g$ | V $cm^3/g$ | $D_{av}$ nm | $S_{mi}$ $m^2/g$ | $V_{mi}$ $cm^3/g$ |
|---|---|---|---|---|---|
| CB-sucr | 116 | 0.09 | 3.1 | - | - |
| RGO/CB-sucr | 13 | 0.02 | 2.4 | - | - |
| CB-asc | 493 | 0.27 | 2.2 | 367 | 0.15 |
| RGO/CB-asc | 487 | 0.24 | 2.0 | 430 | 0.17 |
| CB-gly | 10 | 0.02 | 6.4 | - | - |
| RGO/CB-gly | 12 | 0.04 | 20 | - | - |

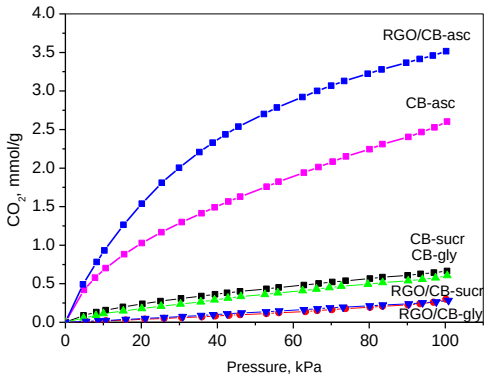



Fig. 1. Morphological, textural, and $CO_2$ adsorption characteristics.

The combination of two types of carbon materials such as porous carbon balls and graphene could bring out a new composite material with excellent adsorption properties toward target gases.

In summary, applying L-ascorbic acid to a one-step procedure resulted in the preparation of a composite of carbon balls and RGO. The latter is a carbon material with excellent adsorption properties toward $CO_2$ adsorption.

Acknowledgement: The authors are grateful to Bulgarian National Science Fund for financial support via project KP-06-H 59/8 ‘Porous 3D graphene-based hierarchical materials for environmental protection’.

# sP27. $Ni^0$ supported on biowaste-derived porous aluminosilicates for $CO_2$ methanation

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Currently, global warming and climate change are the most pressing issues worldwide. Carbon dioxide emissions have increased dramatically through the decades, and significant efforts are being made to minimize greenhouse gas releases and convert them into valuable products [1]. $CO_2$ conversion to methane would not only reduce effectively toxic emissions in the atmosphere but would also be able to fulfil partially the energy demand. The success of the so called 'power-to-gas' (PtG) idea is heavily reliant on the development of highly active and stable methanation catalysts derived from inexpensive but well-engineered materials [2]. Although manufactured methanation catalysts using noble metals (Pt, Ru, Rh, etc.) have already been investigated, their high price limits the large-scale development of this reaction [3]. Silicates and aluminosilicates are attractive among other supports due to their high surface area, scalable pore size distribution, high dispersion of a wide number of active sites, cation exchange capacity, mechanical and thermal resistance [2]. Utilizing agricultural and anthropogenic wastes as feedstocks to produce synthetic porous catalytic supports would contribute to alleviate the human-related carbon footprint inside a circular economy [4]. Employment of nickel as hydrogenating agent will further moderate the cost related to the catalyst production ensuring high $CO_2$ conversions and $CH_4$ selectivity.

The aim of this study is to synthetize and characterizes different biowaste-derived silicate and aluminosilicates with established meso-/microporosity to be used as catalytic support in combination with $Ni^0$ for the $CO_2$ methanation. For this purpose X-ray powder diffraction (XRD), temperature-programmed reduction (TPR), nitrogen physisorption, and solid-state NMR were employed to clarify the relation between the catalytic systems and the reaction outputs. $CO_2$ methanation was held in a flow-through tubular reactor at different temperatures and flow rates. Typically, 150 mg of meshed and prereduced catalyst (0.25–0.5 μm) where diluted between two layers of Pyrex beads. For the experiment an initial flow ratio $CO_2/H_2$=0.12 was employed in the temperature range of 260–460°C. Volumetric flow rates (GHSV) were varied at selected temperatures to optimize operating conditions. Gas products were analysed online by gas chromatography.

From morphological and textural point of view, silicates obtained by rice husks (Orice) are amorphous and mostly mesoporous with a relatively high surface area of 370 $m^2/g$ and an average pore size of 4 nm. On the other hand, the zeolites obtained by hydrothermal treatment of the silicon and aluminium coming from rice husks and food packaging, respectively, can be morphologically related to the family of faujasites and tschernichites with surface area higher than 600 $m^2/g$ and hierarchically structured pore sizes. Ni 5-wt.% impregnation of the supports generated slight changes in the surface area and a strong metal-support interaction able to diversify Ni reduction temperature in function of the used support. From the catalytic point of view (Fig. 1), the $CO_2$ conversion is strictly linked to the number of acid active sites present in

the catalytic support rather than those at the surface of the hydrogenating agent ($Ni^0$). Moreover, the presence of alkaline earth metals boosts methane production at lower temperatures. With exclusivity of Ni-faujasites a temperature dependent unusual selectivity ($CO/CH_4$ = 1) was observed explainable by a mechanism of partial oxidation of the nickel phase at low temperatures that limits hydrogen chemisorption and spillover.

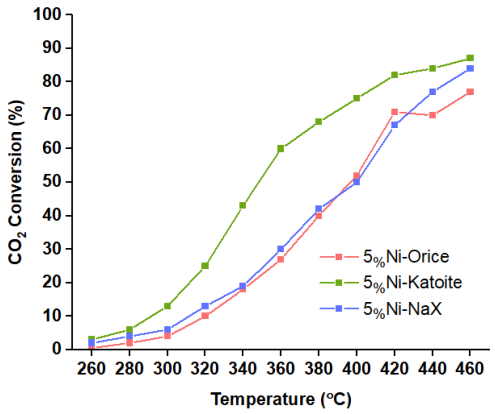



Fig. 1. $CO_2$ conversion vs. temperature over different Ni-aluminosilicates.

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References

1. P. Aragüés-Aldea, A. Sanz-Martínez, P. Durán, E. Francés, J. A. Peña, J. Herguido, Improving $CO_2$ methanation performance by distributed feeding in a Ni-Mn catalyst fixed bed reactor, Fuel, 321 (2022) 124075, https://doi.org/10.1016/j.fuel.2022.124075.
2. W. L. Vrijburg, G. Garbarino, W. Chen, A. Parastaev, A. Longo, E. A. Pidko, E. J. M. Hensen, Ni-Mn catalysts on silica-modified alumina for $CO_2$ methanation, J. Catal., 382 (2020) 358–371, https://doi.org/10.1016/j.jcat.2019.12.026.
3. M. C. Bacariza, I. Graça, J. M. Lopes, C. Henriques, Tuning zeolite properties towards $CO_2$ Methanation: An Overview, ChemCatChem, 11(10), (2019) 2388–2400, https://doi.org/10.1002/cctc.201900229.
4. S. Chernyak, V. Rodin, R. Novotortsev, I. Kaplin, K. Maslakov, S. Savilov, Family of biomass-derived Ni and Ni–Mn catalysts of $CO_2$ methanation, Catal. Today, 424 (2023) ,113846, https://doi.org/10.1016/j.cattod.2022.07.014.

# sP28. C-C coupling of 1-butanol over Mg- and Li-doped zeolite

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Synthetic liquid fuels based on waste biomass sources become topical issue to limit greenhouse effect of $CO_2$ coming from fossil fuels. Development of catalysts with optimized microstructure for Guerbet condensation of primary alcohols (bioethanol and biobutanol) into a mixture of liquid fuels (alkanes, alkenes) and higher alcohols is an important issue in sustainable chemistry studies [1]. Various catalysts with acid, base, or redox properties catalyse alcohol conversion reactions. A variety of catalytic materials have been studied for Guerbet coupling including solid base metal oxides such as MgO, Mg-Al, and Zr-Ce mixed metal oxides, basic zeolites, and hydroxyapatite [2,3].

In the present work, we explore the physicochemical properties and catalytic activity of Mg and Li containing samples supported on L type zeolite. Gas-phase coupling of 1-butanol was investigated in a flow reactor at 400°C and atmospheric pressure. Hydrothermal synthesis of the pure zeolite L was carried out from initial gel composition 20 $SiO_2$:$Al_2O_3$:10 $K_2O$:400 $H_2O$. Magnesium and lithium were applied by wet impregnation using $Mg(NO_3)_2.6H_2O$ (Mg/L sample) and $LiNO_3$ (Li/L sample), respectively. Metal loading in the supported catalysts was 0.6 mmol $g^{-1}$. After impregnation, the samples were dried and calcined at 400°C. Obtained samples were characterized by using a combination of $N_2$ adsorption-desorption isotherms, XRD, FTIR, XPS, TPD-$CO_2$, and TPD-$NH_3$.

BET surface area of the L zeolite was 274 $m^2/g$, $S_{mi}$ of 96 $m^2/g$, and a micropore volume of 0.05 $cm^3/g$. Attending to the Mg/L and Li/L samples, impregnation of Mg and Li decreased the surface area and significantly reduced the Smi, while total pore volume and pore size increased. XRD and FTIR results showed that there was no major change in crystal structure of the modified zeolite.

Li/L sample exhibited over 3-fold higher C-C coupling activity than Mg/L counterpart did. Moreover, this sample formed preferentially Guerbet derivatives and $C_8$ hydrocarbons and according to TPD-$CO_2$ had a higher concentration and strength of base sites. Likely, calcination at 400°C of Mg/L and Li/L samples resulted in the formation of a highly dispersed Mg and Li oxide phase with weak acidic properties. Thus, these exposed sites slightly enhanced the side reaction of butanol dehydration. During catalytic transformation of 1-butanol, small quantity of butanal, 4-heptanone, and $C_7$ hydrocarbons were detected in all reaction products.

Acknowledgements: This research was financially supported by Scientific Cooperation Funds of Bulgarian and Czech Academies of Sciences through contracts IC-CZ/02/2023-2024 and BAS-23-01, respectively. L.K. and J.M. also acknowledge funding by Technology Agency of the Czech Republic through grant No. TN02000044.

References

1. J. Sun, Y. Wang, ACS Catalysis, 4 (2014) 1078–1090.
2. T. W. Birky, J. T. Kozlowski, R. J. Davis, J. Catal., 298 (2013) 130–137.
3. C. Yang, Z. Meng, J. Catal., 142 (1993) 37–44.

# sP29. Ozone decomposition at ambient temperature over noble metals modified MCM-22 and MCM-41 catalysts

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Ozone in the atmosphere protects the earth's surface against UV radiation. On the ground level, ozone is a harmful air pollutant that causes respiratory and cardiovascular diseases to human beings, oxidative damage to living plants and even climate change [1]. Catalytic decomposition is the most promising method for ozone removal due to its safety, economy, and high efficiency.

Noble metals (Pd, Au, and Ag) modified mesoporous molecular sieves (H-MCM-41, Si/Al ratio 20 and 50) and zeolites (H-MCM-22, Si/Al ratio 30) were synthesized by different methods as deposition-precipitation, impregnation, and ion exchange. The obtained catalysts were characterized by a variety of techniques like ICP, XRD, XRF, XPS, HRTEM, SEM/EDX, and nitrogen physisorption. Further, they were examined in heterogeneous catalytic decomposition of ozone at ambient temperature.

All investigated catalysts containing silver active metal manifested a very high catalytic activity toward ozone decomposition at room temperature without showing any deactivation with time on stream. Both mesoporous and microporous gold containing catalysts exhibited lower activity and stability with time on stream. However, their activity could be enhanced by adding a second metal as palladium. Catalyst support acidity played a very important role in the reaction of heterogeneous decomposition of ozone. By decreasing carrier acidity and adding certain metal having basic properties, such as Ce and Ba, the catalysts could also enhance primary activity. The most active catalyst in the reaction of ozone decomposition, Ag-Ba-Ce-MCM-41-50, demonstrated a very high activity of about 90% at ambient temperature and remained stable with time on stream.

Reference

1. J. Maa, R. Caob, Y. Dangc, J. Wanga, Chin. Chem. Lett., 32(10), (2021) 2985–2993.

# sP30. $M_xO_y/CeO_2$ (M = Cu, Co, Fe, Ni) derived from Ce-MOFs as a highly efficient catalyst for light-assisted Fenton-like reaction for water purification

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Issues related to environmental pollution and multifaceted efforts to remove various impurities in air, soil, and water are among the current problems of scientific research in recent years. The problem of water contamination with organic chemicals is extremely serious as pollutant degradation is slow and ineffective. Advanced oxidation processes (AOPs) are appealing techniques to treat these toxic compounds. By leveraging diverse reactive oxygen species (ROS), AOPs are searched for to oxidize or even mineralize recalcitrant and toxic organic pollutants to $CO_2$, $H_2O$, and some ions. Persulphates have been introduced as an alternative to $H_2O_2$ and $O_3$ to generate sulphate radicals ($SO_4^{\bullet-}$), which show superiorities of a higher oxidizing capacity, better selectivity, wider pH applicability, and longer lifetime than hydroxyl radicals ($^{\bullet}OH$) do [1].

In this work, novel nanocomposites of $M_xO_y/CeO_2$ catalyst type derived from Ce-MOF was prepared and examined for catalytic degradation of organic pollutants in photo-Fenton-like reaction. For this reason, a series of highly ordered microporous Ce-based metal-organic frameworks (MOFs) were synthesized as precursors for catalyst preparation. Matching $M_xO_y/CeO_2$ nanocomposites were prepared by wet impregnation of M(II/III) on the Ce-MOFs surface followed by pyrolysis of the obtained materials. Two different Ce-MOFs samples were selected as ceria precursors having different morphological, structural, and porous features. A number of physicochemical methods were applied to characterise obtained nanocomposite catalysts and gain information about structural, optical, and morphological properties.

Catalytic activity of the prepared materials was evaluated by light-assisted Fenton-like reaction for antibiotics degradation in water. The composites exhibited superior activity compared to bare ceria and metal oxides. The effect of the different metal ion, oxide loading, light irradiation, and water matrix was evaluated. The main ROS involved in the catalytic reaction were determined by series of ROS scavenging experiments.

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References

1. C. Cheng. W. Ren, H. Zhang, X. Duan, S. Wang, Chin. J. Catal., 59 (2024) 15–37, https://doi.org/10.1016/S1872-2067(23)64611-X.

# sP31. Ruddlesden-Popper type perovskite $La_2CuO_4$ decorated active carbon as a Fenton-like catalyst for antibiotic degradation

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Peroxymonosulphate ($HSO_5^-$, PMS) is a well-known oxidant for water treatment. It needs to be activated to form strong oxidizing agents like sulphate radical ($SO_4^{\bullet-}$), hydroxyl radical ($^{\bullet}OH$), superoxide ion radical ($O_2^{\bullet-}$), and the non-radical singlet oxygen ($^1O_2$). Recently, antibiotics removal from wastewater by PMS upon homogeneous and heterogeneous catalysts has received a great research attention due to high effectiveness and oxidation rate of the latter determined by simple treatments centred at bench scale in the laboratory [1].

Mixed metal oxides like perovskites and spinels have gained increased attention as catalysts for peroxymonosulphate activation. Compared with $ABO_3$-type perovskites, $A_2BO_4$-type has a prominent redox ability due to its unique structure. However, few studies discussed the effect of $A_2BO_4$-type perovskites in heterogeneous Fenton-like process mostly for $H_2O_2$ and there is no information about catalytic activation of peroxymonosulphate.

In this work for the first time, we report the catalytic activity of $La_2CuO_4$ toward activation of peroxymonosulphate. The prepared catalyst was dispersed on activated carbon by simple ball milling in planetary ball mill in order to increase the specific surface area. All the composites were tested toward removal of antibiotics from water by activation of peroxymonosulphate. Both the effect of perovskite to activated carbon ratio as well as of water matrix was evaluated. Reaction mechanism was determined by a series of reactive oxygen species scavenging experiments.

Obtained results showed that the great potential of rare earth based Ruddlesden-Popper type perovskite toward highly efficient peroxymonosulphate is active for water remediation from organic pollutants.

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Reference

1. E. Brillas, J. Environ. Chem. En., 12(4), (2024) 113191, doi: https://doi.org/10.1016/j.jece.2024.113191.

# sP32. Enhanced heterogeneous photocatalysis for antibiotic degradation using ZnO nanostructured films co-catalytically modified with Pd/MnOx

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In the realm of environmental remediation, degradation of antibiotic pollutants presents a significant challenge. In this study, zinc oxide (ZnO) nanostructured films were fabricated via the sol-gel method followed by dip-coating technique, providing a high surface area and efficient light absorption properties. These films were further enhanced through photofixation with palladium (Pd) and manganese oxide (MnOx), forming Pd/MnOx-ZnO composite catalysts. Synthesized catalysts were systematically characterized using various analytical techniques including X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and UV-Vis spectroscopy to elucidate structural, morphological, and optical properties. Catalytic performance of Pd/MnOx-ZnO nanostructured films was evaluated in the degradation of the antibiotic doxycycline under UV light irradiation. Remarkably, the Pd/MnOx-ZnO composite catalyst exhibited superior photo-catalytic activity compared to pristine ZnO films, thus achieving efficient degradation of doxycycline. Enhanced catalytic performance was attributed to synergistic effects between ZnO nanostructures and Pd/MnOx nanoparticles by facilitating charge separation and promoting reactive species generation. This study underscores the potential of engineered ZnO-based nanostructured films photofixed with Pd/MnOx as promising catalysts for degradation of antibiotic pollutants, offering a sustainable solution for water purification and environmental protection.

# sP33. Structure engineering of $Ni/SiO_2$ vegetable oil hydrogenation catalyst via $CeO_2$

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Inspired by our finding that metallic Ni particles could be uniformly distributed on a reduced ceria surface and stabilized on $Ce^{3+}$ sites, we suppose a possible improvement in activity and selectivity of $MgNi/SiO_2$ vegetable oil hydrogenation catalyst by increasing surface metal Ni availability via modification by ceria. So far, no studies related to this approach of designing $Ni/SiO_2$ catalysts for partial hydrogenation of vegetable oil have been reported.

Proposed approach involved addition of ceria modifier to $SiO_2$ carrier and as a catalyst component. Commercial silica gel (SIG) of the mesoporous type was used as a silica support for Ni-based catalyst precursor synthesis. SIG was kindly provided by ALUSIL Ltd. (Sofia, Bulgaria). Precursors were prepared with identical composition as $SiO_2$/Ni=1.0 and Mg/Ni=0.1, applying two synthesis modes: (i) precipitation of Ni, Mg, and Ce nitrate solutions with $Na_2CO_3$ solution over bare SIG (named Ni, MgNi, and CeMgNi); and (ii) Ni and Mg precipitation over $CeO_2$-modified SIG (denoted as MgNi-Ce).

Evaluation of structure, reducibility, and surface and electronic state of the $CeO_2$-doped $MgNi/SiO_2$ catalyst was performed by means of powder X-ray diffraction (PXRD), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and X-ray photoelectron spectroscopy (XPS) combined with high-resolution transmission electron microscopy (HRTEM), temperature-programmed reduction with hydrogen ($H_2$-TPR), and $H_2$ chemisorption techniques. Prior to sunflower oil hydrogenation reaction, as-synthesized precursors were activated by dry reduction with hydrogen at 430°C for 5 h. Hydrogenation of commercial edible sunflower oil was performed in a glass reactor at constant temperature of 160°C under $H_2$ pressure of 0.2 MPa. Added ceria impact was elucidated by comparing fatty acid content obtained by the catalysts at iodine value of 80.

Applied strategy toward surface and bulk structure engineering via $CeO_2$ introduction to the MgNi configuration was aimed at $Ni^0$ phase distribution in reduced precursors and accessibility to the hydrogenation reaction. The expectation was to achieve enhanced $Ni/SiO_2$ catalytic performance and improved *cis/trans* selectivity. Figure 1 summarizes samples physicochemical properties and catalytic performance. Cooperating SEM-EDS, HRTEM, XPS spectroscopy, and $H_2$-chemisorption data reveal the reconstruction role of Mg and $CeO_2$ for morphology, microstructure, electronic properties, $Ni^0$ specific surface area, particle size, and dispersion in the active state of $Ni/SiO_2$ catalyst (Fig. 1). It was found that Mg provided more $Ni^0$ phase of smaller average particle size on the catalyst surface thus being accessible for hydrogen and big triglyceride molecule reagents. This structure designing reflects on a higher activity of the MgNi composition. $Ni^0$ specific surface area data correlates with SEM-EDS and XPS surface analyses and undoubtedly confirm a higher $Ni^0$ accessibility for most active Mg-doped $Ni/SiO_2$

catalyst. As well, calculated values of the $Ni^0$ particle size by $H_2$ chemisorption are in accordance with calculations based on HRTEM bulk structure analysis.

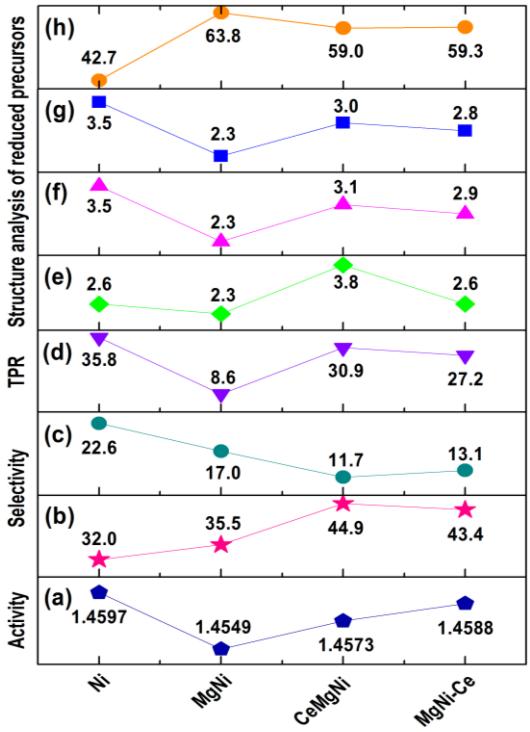



Fig. 1. Comparison among selected data on characterization of reduced precursors and catalysts: (a) refraction index $D_{50}$ at 70 min of hydrogenation; (b) C18:1-*cis* FA (mol.%); (c) C18:0 FA (mol. %); (d) unreduced structures after reduction at 430°C (%); (e) $Ni^{2+}/Ni^0$ ratio from XPS; (f) $Ni^0$ mean size (nm) from HRTEM; (g) Ni/Si ratio from SEM-EDS; (h) $SSA_{Ni}$ ($m^2/g$) from $H_2$ chemisorption.

Exploration of ceria designing of the MgNi structure using two modes: (i) modification of the silica gel support and (ii) $CeO_2$ introduction to Ni and Mg as third component also illustrates structure engineering via increased homogenous deposition of surface nickel in reduced CeMgNi and MgNi-Ce precursors. Both configurations exhibit similar structural features as is plotted in figure 1. The average $Ni^0$ particle size is higher relative to a reduced MgNi precursor. Obviously, these data are due to numerous $Ni^0$ particle sizes in the range of 1–6 nm in contrast to a higher uniform $Ni^0$ size of 1–4 nm in the MgNi. In addition, provided surface reconstruction led to a higher *cis/trans* selectivity, which was better pronounced with the CeMgNi catalyst. This fact clearly confirms a positive application of ceria as the catalyst dopant to maximize C18:1-*cis* oleic acid content accompanied by minimal formation of *trans*-fatty acids and C18:0 acid.

Observed hydrogenation behaviour of the CeMgNi and MgNi-Ce catalysts could be explained by possible reoxidation of active $Ni^0$ particles during the reaction owing to non-intimate Ce-Ni contact disturbed by Mg presence. Because of ceria's great oxygen storage capacity and possible existence of free CeOx species, the catalysts might readily lose activity.

This fact points to further search for a solution to achieve higher hydrogenation activity by improving dopant balance in the catalyst composition. This issue could offer the most stable $Ni^0$ particles through optimal bonding to $Ce^{3+}$ sites formed by lattice oxygen transfer during reduction/activation of the precursors, namely $Ni^{2+}$–$CeO_2 \rightarrow Ni^0$–$CeO_{2-x}$.

In summary, metallic Ni accessibility can be ensured via joint application of Mg and $CeO_2$ as components of $Ni/SiO_2$ catalyst. Design reconstruction of the structure and surface properties affects positively hydrogenation activity and *cis/trans* selectivity of the $Ni/SiO_2$ catalysts. Structure engineering of vegetable oil hydrogenation $Ni/SiO_2$ catalyst via $CeO_2$ could be achievable. Application of ceria dopant in $Ni/SiO_2$ catalyst is a promising approach to improve hydrogenation activity as well as *cis/trans* selectivity, and regulation of *cis* and *trans* fatty acids content in products of the partial sunflower oil hydrogenation process.

Acknowledgments: Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation. D.N., M.G., Ts.P-M., E.P., G.Z., J.K., and V.R. kindly acknowledge financial support by Bilateral Project between Bulgarian Academy of Sciences and Serbian Academy of Sciences and Arts. J.K. and V.R. are grateful to Ministry of Science, Technological Development, and Innovation of Republic of Serbia for financial support.

# sP34. Catalytic ability of K- and Co-promoted oxo-Re and oxo-ReMo nanosized compositions for water-gas shift reaction

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Water-gas shift (WGS) reaction (CO + $H_2O$ ↔ $CO_2$ + $H_2$) plays an important role in hydrogen economy because is an effective way to reduce carbon release to net zero-$CO_2$ emissions. The general goal of this research is development of nanosized oxo-rhenium catalyst formulations promoted by K and Co components for the WGS process. Rhenium as low-cost catalyst component is a good choice compared with platinum group metals. Surface density of 2 Re atoms/nm$^2$ on γ-$Al_2O_3$ support as well as 3 wt.% CoO and 5 wt.% $K_2O$ amounts were chosen to match the composition of own active sour WGS KCoRe catalyst developed some years ago. Initial evaluation of the impact of replacing half of rhenium with more affordable molybdenum was also studied. The purpose of this study is exploration of catalytic ability of CoRe, K-CoRe, CoReMo, and K-CoReMo formulations in WGS reaction and elucidation of the effect of CO/Ar reaction mixture used in activation-reduction pretreatment to form active catalyst structures. Oxo-K-Co-Re(Mo) entities formed in synthesized samples and reducibility were analysed by several physicochemical methods as $N_2$ physisorption, powder X-ray diffraction (PXRD), X-ray fluorescence spectrometry (XRF), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), and $H_2$ temperature-programmed reduction ($H_2$-TPR). Different testing modes were applied to evaluate WGS reaction activity and stability and performed within five consecutive days with the same catalyst portion in the 140–350°C range.

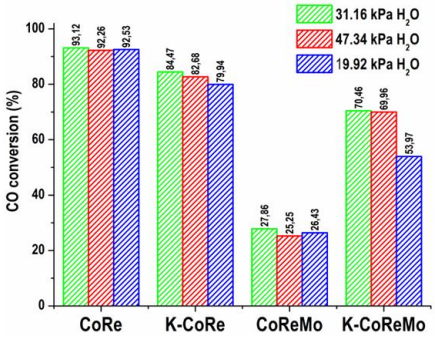



Fig. 1. CO conversion dependence on water vapour pressure at 350°C and GHSV of 4000 h$^{-1}$.

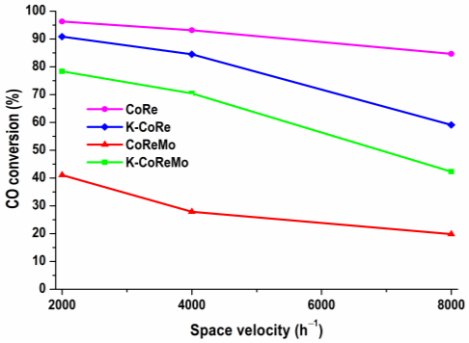



Fig. 2. CO conversion dependence on GHSV (2000, 4000, and 8000 h$^{-1}$) at 350°C and water vapour pressure of 31.16 kPa.

Estimation of catalytic WGS efficiency was carried out on testing day 4 by performing a further detailed examination via two consecutive experiments for catalytic behaviour stability after a 3-day testing period with equal catalyst charges for each composition while keeping the reaction temperature at 350°C. Express estimation of catalyst's deactivation behaviour started with a variation in water vapour pressure in the order 31.16 < 47.34 > 19.92 kPa at a GHSV of

4000 $h^{-1}$ (Fig. 1). Correlation between band gap energy (Eg) and catalyst activity was found as displayed in figure 3.

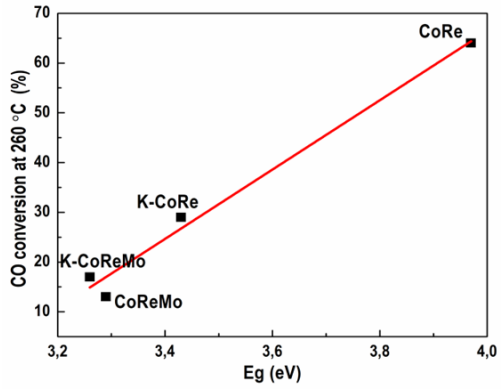



Fig. 3. Linear dependence of catalyst activity on Eg value.

Summarizing, at this stage of our fundamental research, we provide experimental evidence that the role of potassium and molybdenum to enhance ability of selected CoRe composition to promote WGS reaction is to not only attain higher CO conversion degree, i.e. larger amount of clean $H_2$, but also affect structural features of the CoRe system. Detailed analysis of WGS activity discloses impact on oxide nanostructures size as well as equilibrium in redox $Re^{4+}$–$Re^{7+}$, $Co^{2+}$–$Co^{3+}$, and $Mo^{4+}$–$Mo^{6+}$ structures. Parameters of reduction activation stage and WGS reaction demand a proper selection according to the specific features of the potassium- and cobalt-promoted Re(Mo) catalysts. Catalyst composition modelling is necessary as well for finding the best catalytically active oxo-rhenium formulation.

Acknowledgement: The authors kindly acknowledge financial support by project ‘Center of competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy’ (No. 794 BG05M2OP001-1.002-0014) funded by Operational Programme ‘Science and Education for Smart Growth’ 2014–2020, and co-funded by the EU from European Regional Development Fund.

# sP35. Synthesis and structural analysis of heat-generating cobalt-substituted magnetite nanoparticles with organic coatings

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Magnetic nanoparticles (MNPs) are a highly promising material for use in biomedicine. MNPs major advantage is their size, which is smaller or comparable with cells (10–100 μm), viruses (20–450 nm), proteins (5–50 nm), or genes (2 nm in width, 10–100 nm in length). Such small sizes allow for good tissue diffusion, which is beneficial for distributing the nanoparticles as close as possible to a site of biological interest. Their magnetic properties enable MNPs manipulation by applying an external magnetic field, which broadens the scope of applications.

Here, we present synthesis, surface modification, and structural analysis of magnetite-based nanoparticles, specifically $Co_{0.047}Fe_{2.953}O_4$ (S1) and $Co_{0.086}Fe_{2.914}O_4$ (S2). These nanoparticles were synthesized using co-precipitation method at 80°C for 2 hours.

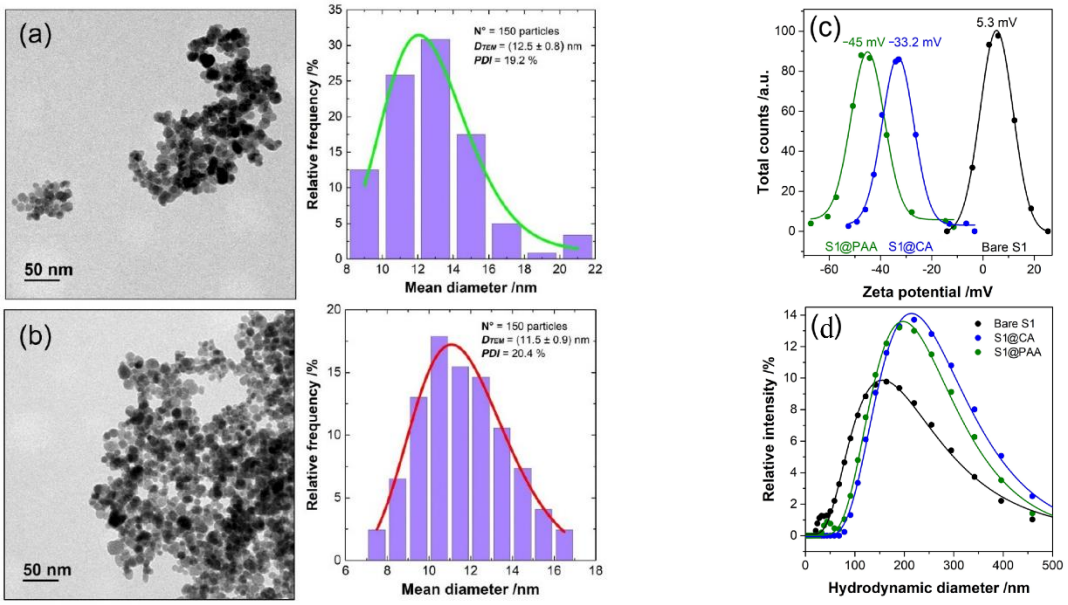
ICP-OES elemental analysis was conducted to investigate iron ions substitution for cobalt ions in magnetite structure ($Fe_3O_4$). The results indicated a little lower cobalt concentration compared with target values: $Co_{0.047}Fe_{2.953}O_4$(S1) and $Co_{0.086}Fe_{2.914}O_4$(S2).

Synthesized MNPs exhibited a single-phase nature to crystallize in a spinel-type structure of Fd$\underline{3}$m space group as confirmed by PXRD analysis. Transmission electron microscopy analysis revealed that the particles were quasi-spherical of approximately 11-nm size.

Co-substituted magnetic nanoparticles were coated with two organic ligands that stabilize colloidal dispersions electrostatically by utilizing unbound carboxyl groups on their surface. For this purpose, molecules of different molecular weight were selected: citric acid (CA) as a small molecule and poly(acrylic acid) (PAA) as a relatively large molecule.

Zeta potential measurements at physiological pH indicated successful implementation of coating protocols for the bare S1 nanoparticles. In contrast to the zeta potential of bare S1 (5.3 mV), both S1@CA and S1@PAA nanoparticles manifested a negative surface charge of −33.2 mV and −45.2 mV, respectively. Change in zeta potentials increases repulsion among nanoparticles due to Coulombic forces, thereby facilitating the electrostatic stabilization of the nanoparticle suspension. These results suggest existence of unreacted carboxyl groups on the nanoparticles' surface and robust coordination of certain carboxylic groups from CA and PAA with iron and cobalt cations.

Dynamic light scattering (DLS) method was used to determine hydrodynamic diameters of the nanoparticle aqueous suspension at pH 7. Intensity distribution on the graphs reveals particle size distribution within suspensions. In uncoated S1 suspension, a dominant peak at around 30 nm suggests presence of a large population of hydrated individual nanoparticles. Additionally, a smaller peak at about 170 nm indicates a minor presence of agglomerates. A similar trend is observed for S1@PAA, with primary particles centred at 50 nm and a smaller number of agglomerates at 210 nm. However, the S1@CA suspension exhibits a distinct feature. Absence of a peak of smaller particle sizes suggests a limited population of individual nanoparticles.




TEM micrographs: (a) $Co_{0.047}Fe_{2.953}O_4$ (S1); (b) $Co_{0.086}Fe_{2.914}O_4$ (S2) with statistical particle size distribution. (c) Zeta potential; (d) dynamic light scattering.

This observation might indicate a higher degree of agglomeration within the S1@CA suspension, leading to a larger average particle size. DLS results not only validate successful binding of CA and PAA but also indicate potential nanoparticle agglomeration.

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References

1. M. Ognjanović, M. Bošković, H. Kolev, B. Dojčinović, S. Vranješ-Đurić, B. Antić, Synthesis, surface modification and magnetic properties analysis of heat-generating cobalt-substituted magnetite nanoparticles, Nanomaterials, 14(9), (2024) 782, https://doi.org/10.3390/nano14090782.

# sP36. Electronic structure, magnetic properties, cobalt heating efficacy, and gadolinium-substituted magnetite nanoparticles

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Magnetic nanoparticles (MNPs) are a class of nanoparticles that can be manipulated using magnetic fields. These particles typically consist of magnetic material combined with a chemically functional component. MNPs physical and chemical properties largely depend on synthesis method and chemical structure with sizes ranging from 1 to 100 nm. This versatility in properties and size enables various applications in biomedicine including medical diagnostics, treatments, magnetic immunoassays, cancer therapy, enzyme immobilization, and biomedical imaging as well as environmental remediation, such as wastewater treatment, sensor and data storage technology, and catalysis.

In this work, we focused on the physicochemical characterization of previously synthesized cobalt-substituted magnetite and gadolinium-substituted maghemite nanoparticles, specifically $Co_xFe_{3-x}O_4$ (x=0.05; 0.1) and $Gd_xFe_{2-x}O_3$ (x=0.05; 0.10; 0.20; 0.50), with an average size of about 11 nm.

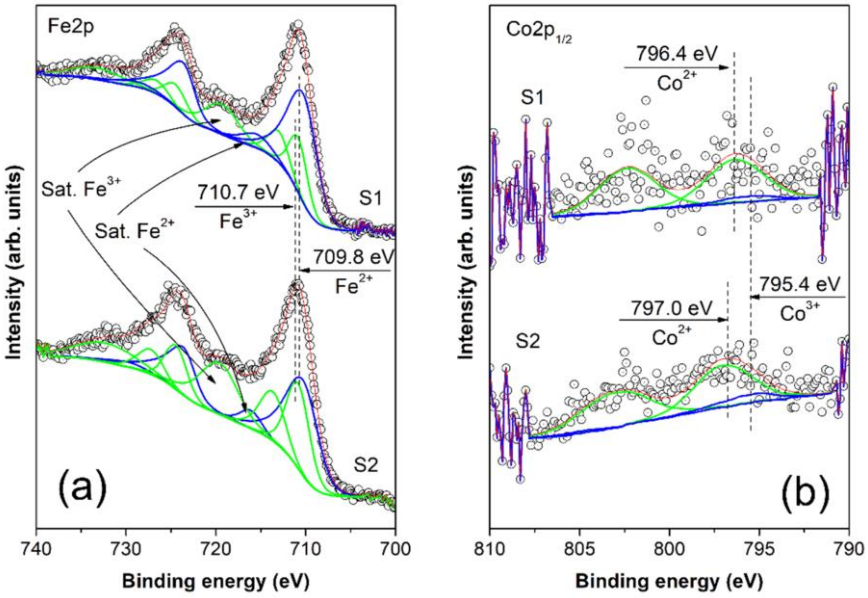
Isothermal magnetization measurements were conducted for both types of samples in a magnetic field ranging from −30 kOe to 30 kOe at room temperature (RT) using a SQUID magnetometer. The samples exhibited negligible coercivity and remanent magnetization. The observed increase in remanence and coercivity for MNPs of higher Co and/or Gd content could be attributed to increased magnetocrystalline anisotropy, making them slightly magnetically harder compared to samples of lower content. Acquired saturation magnetization of about 80 emu/g aligns with literature values commonly found for nanosized Co-substituted magnetite and Gd-substituted maghemite.

Efficiency of heat generation by MNPs is quantified by the specific loss power (SLP), often determined through calorimetric heating measurements. During the measurement, the samples were subjected to an AC magnetic field with an amplitude of 200 Oe and frequency of 252 kHz. Obtained SLP values reveal that samples of lower Co/Gd content show better heating efficacy. Therefore, they were coated with citric acid and polyacrylic acid to obtain stable colloids for further tests for magnetic hyperthermia applications in cancer therapy.

X-ray photoelectron spectroscopy was employed to probe the oxidation states and atomic concentrations of surface elements within the nanoparticles. Survey spectra data unveiled the core level peaks, encompassing iron (Fe2p), cobalt/gadolinium (Co2p/Gd3d), oxygen (O1s), and carbon (C1s) constituting the nanoparticles.

A meticulous examination of the Fe2p core level line shape, coupled with a comparative analysis against standard spectra measured for $Fe^{2+}$ and $Fe^{3+}$ oxidation states, suggests a combination of these two oxidation states for Co-substituted magnetite and only the $Fe^{3+}$ oxidation state for iron in Gd-substituted $Fe_2O_3$ MNPs. In the Co-substituted magnetite, XPS analysis showed that cobalt minor amount incorporated into the iron-oxide structure largely exists in the $Co^{2+}$ oxidation state with less than 10% of the total cobalt potential in the $Co^{3+}$ oxidation state.

In contrast, in Gd-substituted $Fe_2O_3$, gadolinium was registered only in the 3+-oxidation state.




High-resolution XP spectra of (a) Fe2p and (b) $Co2p_{1/2}$ core levels measured for magnetic nanoparticles of Co-substituted iron oxide.

Our study highlights $Fe^{2+}/Fe^{3+}$ and $Co^{2+}/Co^{3+}$ catalytically active centres on the particle surface, indicating that Co-substituted MNPs could facilitate redox processes on the surface. This suggests possible applications as heterogeneous self-heating catalysts in advanced oxidation processes under an AC magnetic field.

Acknowledgements: The authors thank Bulgarian National Science Fund and Ministry of Science, Technological Development and Innovation of Republic of Serbia for financial support by the project ‘Self-heating magnetic nanoconstructs for theranostic applications (Acronym: SeNaTa)’, as part of ‘Multilateral scientific and technological cooperation in the Danube region’ with contract numbers КП-06-Дунав/4 and 451-03-91/2022-05/11, DS 16.

Reference

1. M. Ognjanović, M. Bošković, H. Kolev, B. Dojčinović, S. Vranješ-Đurić, B. Antić, Synthesis, surface modification and magnetic properties analysis of heat-generating cobalt-substituted magnetite nanoparticles, Nanomaterials, 14(9), (2024) 782, https://doi.org/10.3390/nano14090782.

# sP37. Pt-modified iron oxide magnetic nanoparticles for catalytic applications

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Iron oxide magnetic nanoparticles have received significant attention for manifesting unique properties and possibilities for diverse potential applications. These entities exhibit superparamagnetism, high magnetic saturation, and biocompatibility making them ideal for drug delivery, magnetic resonance imaging (MRI), hyperthermia therapy, and environmental remediation. Additionally, their size, shape, and surface properties can easily be tailored allowing for straightforward functionalization and enhanced targeting, thereby maximizing their effectiveness in biomedical and environmental fields. However, producing iron oxide nanoparticles economically with desired characteristics for specific large-scale applications remains a challenge. While substantial progress has been made in understanding the basic science of nano-iron oxides, further evaluation of their catalytic properties and industrial applications is required. The unique properties of nanosized iron oxides, compared to their bulk counterparts, make them promising candidates as cost-effective and efficient catalysts, particularly in environmental processes.

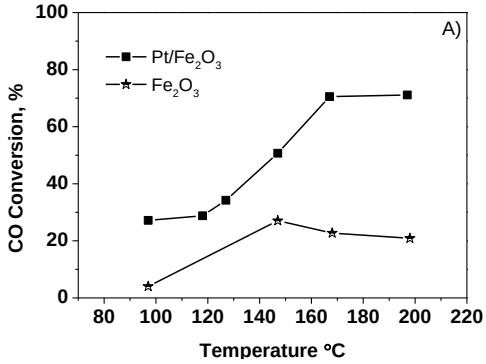
Our investigation was aimed at synthesizing iron oxide nanoparticles with controlled size and structure using the coprecipitation method. An aqueous solution of $FeSO_4.7H_2O$ and iron nitrate was mixed and purged with $N_2$ and then precipitated with NaOH (pH=13.5). The resulting black-brown precipitate was washed with doubly distilled water followed by ethanol, and dried at 70°C. Then the sample was calcined for 2 hours at 450°C. X-ray diffraction confirmed that the synthesized material was $Fe_3O_4$. Transmission electron microscopy images revealed the formation of rod-like particles of about 50–60 nm in length and 10–12 nm in diameter. Specific surface area determined by the BET method was approximately 97 $m^2/g$.

Given the high cost of precious metals, there is a growing interest in alternative catalysts. While metal oxides are relatively inexpensive, they often suffer from low activity and high operating temperatures. Based on literature data and our preliminary research, catalysts based on transition metal oxides, either alone or in combination with a noble metal, appear to be the most promising candidates for total oxidation reactions.

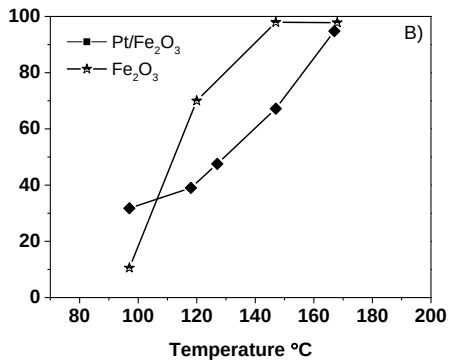
To enhance catalytic performance we deposited a noble metal onto nanosized $Fe_3O_4$ oxide via impregnation with an aqueous solution of $Pt(NH_4)_4Cl_2$. The goal was for the active platinum phase to cover uniformly metal oxide particle surface.

The catalysts were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, Mössbauer spectroscopy, and infrared spectroscopy. The catalytic behaviour of the samples was evaluated in the CO oxidation reaction.

Our intention was to establish the state of the catalytically active phases, metal oxide and noble metal particle size, interaction between noble metal and metal oxide nanoparticles, and the influence of these factors on catalytic activity.




Selective oxidation of CO in a hydrogen-rich mixture: CO conversion




Selective oxidation of CO in a hydrogen-rich mixture: $O_2$conversion

Data from various physicochemical studies indicated the formation of finely dispersed and strongly interacting platinum nanoparticles on the metal oxides surface. Demonstrated higher activity of $Pt/Fe_3O_4$ is likely due to oxygen adsorption on the magnetite surface as highly reactive oxygen species, which subsequently interacts with coadsorbed carbon monoxide on the Pt surface.

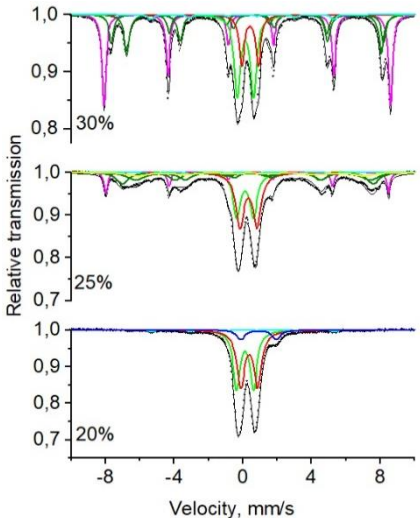
Acknowledgements: The authors thank Bulgarian National Science Fund for financial support through project No. КП-06-Дунав/4 ‘Self-heating magnetic nanoconstructs for theranostic applications (Acronym: SeNaTa)’, part of ‘Multilateral scientific and technological cooperation in the Danube region’.

# sP38. Combined EPR and Mössbauer investigation of soda-lime silicate glass-crystalline materials of high iron oxide concentration

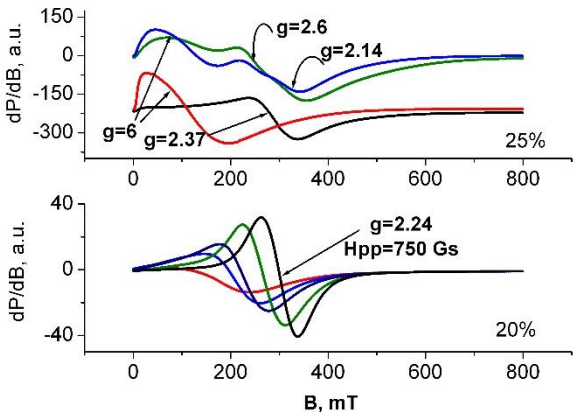
I. Mihailova[1]*, R. Harizanova[1], D. Paneva[2], Z. Cherkezova-Zheleva[2], R. Kukeva[3], R. Stoyanova[3], G. Avdeev[4], C. Rüssel[5]

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Preparation of glass-crystalline materials in the system $Na_2O/CaO/SiO_2/Fe_2O_3$ with high $Fe_2O_3$ concentration (20, 25, and 30 mol%) via the melt-quenching technique is reported. The obtained melts spontaneously crystallised during pouring to form magnetite ($Fe_3O_4$), hematite ($\alpha$-$Fe_2O_3$), and $\varepsilon$-$Fe_2O_3$ as identified by X-ray diffraction (XRD). Microstructure and elemental composition of the prepared materials were further investigated by scanning electron microscopy (SEM) and two different morphological types of Fe-containing crystals, needle-like and dendrite-shaped, were detected. Mössbauer spectroscopy showed presence of $Fe^{3+}$ and $Fe^{2+}$ as well as the existence of iron ions in both tetrahedral and octahedral coordination, and the precipitation of hematite, $\varepsilon$-$Fe_2O_3$, and magnetite. Electron paramagnetic resonance (EPR) spectroscopy of the glass-crystalline materials revealed the registration of three signals. Those were a weak signal at g≈4.2 attributed to isolated $Fe^{3+}$ ions in low-symmetry coordination, a broad signal at g≈2.0 corresponding to exchange-coupled $Fe^{3+}$ ions, and a low-field asymmetric signal at g≈20 ascribed to the presence of magnetic phase containing $Fe^{3+}$ ions.




Mössbauer spectra of the glass-crystalline samples registered at room temperature.




EPR temperature-dependent spectra of the glass-crystalline samples with 20- and 25-mol% $Fe_2O_3$.

Acknowledgement: This work was carried out with the financial support of Bulgarian National Science Fund by contract KP-06-N48/4.

## sP39. Dielectric properties of $Ce_{1-x}Gd_xO_{2-x/2}$ ceramics

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Dopant-modified ceria is a well-known material in modern ceramics because of its high oxygen ion conductivity for the fabrication of electrochemical devices such as fuel cells and oxygen sensors. Trivalent rare-earth ions are doped into ceria to increase the concentration of oxygen vacancies which lead to increase in conductivity. In the trivalent rare-earth doped ceria, the highest conductivities are observed for $Ce_{1-x}Gd_xO_{2-x/2}$.

$Ce_{1-x}Gd_xO_{2-x/2}$ powders were synthesized by ionic gelation method, which involved mixing of initial solutions of sodium alginate as a gelling agent and metal nitrates as $Ce(NO_3)_3.6H_2O$ and $Gd(NO_3)_3.6H_2O$), followed by heat treatment of the resulting gel at a temperature of 500°C. Obtained powder samples were pressed into disks and sintered at 1400°C for 3 h to produce ceramics. Results of XRD analysis of $Ce_{1-x}Gd_xO_{2-x/2}$ showed substitution of the cerium atoms with gadolinium in the cerium oxide crystal lattice as evidenced by shift of the diffraction peaks. Structural and morphological studies were performed by infrared spectroscopy and scanning electron microscopy. Infrared spectra of Gd-doped ceria powders were characterized by well pronounced band in the range 250–640 $cm^{-1}$ that arises from Ce–O and Gd–O stretching vibrations. Presence of the two oxidation states of ceria (+3 and +4) was established by XPS with the proportion of $Ce^{3+}$ being higher and increasing with higher gadolinium content. Dielectric properties were studied by means of the impedance spectroscopy method. Impedance modulus and the phase angle were measured as a function of temperature (from ambient to 700°C) and frequency within 1 Hz – 1 MHz. Results of the electrical measurements indicated that all ceramic samples were with potential for application as fuel cell electrolytes at intermediate temperatures.

# sP40. Catalytic behaviour of materials prepared by reusing recycled spent automotive catalysts

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Platinum group metals (PGMs) have been classified as critical raw materials [1,2]. These metals are being used in many industrial processes and most notably as automobile exhaust catalysts. According to strict exhaust emissions standards that have been imposed by European Union there is a need for decreasing toxic gas emissions from vehicles. PGM demand is extremely increasing with a subsequent rise of market prices.

Carbon monoxide (CO) is released into the environment by incomplete combustion of carbonaceous materials. CO sources are plentiful and except carbon dioxide ($CO_2$), carbon monoxide is the most abundant pollutant in the lower environment. Huge amounts of carbon monoxide are emitted world-over, mainly from transport, industrial, and domestic activities. Carbon monoxide is also a precursor of ground-level ozone, which can trigger serious respiratory problems. The etiology of CO toxicity is due to its effect on oxygen binding to the haemoglobin molecule. CO binds to haemoglobin forming carboxyhaemoglobin (COHb) with a 220% higher affinity to haemoglobin than oxygen. This reduces oxygen-carrying capacity of haemoglobin and leads to cellular hypoxia. Long-term exposure should not exceed 25 ppm in 8 h or 50 ppm in 4 h.

This work is based on platinum reuse after recycling from spent automotive catalysts (SACs). A Cu-Pt based catalyst supported on a $CeO_2$-$ZrO_2$ mixed oxide was synthesized by the wet impregnation method. Pt was derived from recycled leachate solution from end-of-life commercial diesel oxidation catalysts (DOC) using Monolithos single-step hydrometallurgical method for platinum group metals [3]. The prepared catalyst was pretreated via two different modes: calcination (sample A) and $H_2$ reduction followed by calcination in air (sample B).

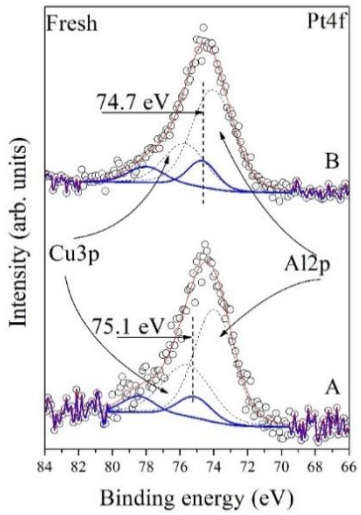



Fig. 1. XPS spectra of the Pt4f region.

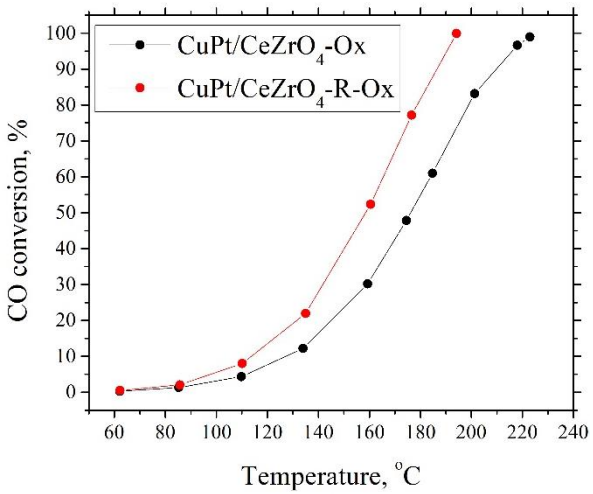



Fig. 2. Temperature dependence of CO conversion.

Obtained materials were characterized by numerous methods, such as XRD, XPS, and FTIR as well as TPR. Catalytic behaviour of the samples was tested in CO oxidation.

Chemical state of Pt, Ce, Zr, Cu and percentage of the different oxidation states of these elements at the catalyst surface were studied by X-ray photoelectron spectroscopy. The Pt 4f spectrum could be deconvoluted into two doublets ascribed to $Pt^{4+}$ presence at 74.6–74.9 eV (4f7/2) and 78.1–78.2 eV (4f5/2) [4]. The doublet was shifted toward higher binding energy values in the case of pretreated sample only by calcination and this could be explained by interaction of the Pt species with the support. From the TPR results, it was established that the sample was also reduced at a higher temperature relative to the sample reduced with subsequent calcination.

Prepared samples were investigated concerning their catalytic activity properties in the reaction of CO oxidation.

Prereduced sample revealed improved catalytic properties most probably because of better reducibility.

Acknowledgement: The authors gratefully acknowledge financial support by the project H2020-MSCA-RISE-2020 101007669: Chemistry of Platinum Group Metals, CHemPGM.

References

1. IPA fact sheets, 2023.
2. Johnson Matthey PGM Market Report, 2022.
3. I. Yakoumis, A. Moschovi, M. Panou, D. Panias, Single-step hydrometallurgical method for the platinum group metals leaching from commercial spent automotive catalysts, J. Sustain. Met., 6 (2020) 259–268.
4. H. Aguiar, J. Serra, P. Gonzalez, B. Leon, J. Non-Cryst. Solids, 355 (2009) 475–480.

# sP41. Characterisation of catalytic materials prepared by reuse of recycled platinum from spent automotive catalysts

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Catalysts play a crucial role for environmental protection and reducing harmful gas emissions from different exhaust systems [1]. While bulk properties of these catalysts, such as thermal stability and mechanical strength are important, surface properties are paramount for their catalytic performance [2]. Surface is where catalytic reactions occur, making it essential to understand its composition and structure [3]. This study focuses on the application of X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, and Fourier-transform infrared spectroscopy (FTIR) to investigate the properties of catalytic materials prepared by reuse of recycled Pt from spent automotive catalysts (SACs). Catalyst efficiency is considerably dependent on catalyst surface characteristics. Surface area, pore structure, and chemical composition have influence on how the catalyst could convert exhaust gases into less harmful substances. Presence of specific functional groups and oxidation state of the surface elements might affect adsorption and reaction of gases such as CO, NOx, and hydrocarbons [4].

XRD offers insight into the crystalline structure and phase composition of the catalyst. This technique measures diffraction patterns of the X-rays interacting with the crystal lattice providing information about the size, shape, and distribution of crystalline phases. XRD is particularly useful for detecting changes in the catalyst's structure after various treatments or catalytic tests under different operating conditions.

BET is a multipoint measurement of specific surface area through gas adsorption analysis, where an inert gas such as nitrogen is continuously flowing over a solid sample, or the solid sample is suspended in a defined gaseous volume.

FTIR spectroscopy provides detailed information about molecular bonds and functional groups present on the catalyst surface. By analysing the infrared absorption spectra, one may identify specific chemical compounds and understand their interaction with adsorbed species. FTIR analysis has revealed the presence of active functional groups that play a crucial role in catalytic reactions.

XRD measurements were performed using an Empyrean system manufactured by PANalytical, Almelo, The Netherlands. The diffractometer was configured with a Cu Kα tube, a parallel-beam mirror, and a PIXcel 3D detector (PANalytical, Almelo, The Netherlands). Obtained diffraction data were processed using the HighScore Plus 4.5 software and the ICSD database (Inorganic Crystal Structure Database).

Specific surface area, pore volume, and pore size distribution of the supported catalyst samples were determined by low-temperature (77.4 K) nitrogen adsorption using a Quantachrome Nova 1200e apparatus. The specific surface area was determined according to the BET method. The pore size distribution was made by the Barrett-Joyner-Halenda (BJH)

method, using the desorption branch of the isotherm. Total pore volume (Vt) and average pore diameter were calculated according to the Gurvich rule at a relative pressure close to 0.99.

Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) in transmission mode. The method of dilution of the studied sample in KBr disks at a concentration of 0.5% was used. The spectra were taken in the 400–4000 $cm^{-1}$ mid-infrared region at a resolution of 4 $cm^{-1}$ (data spacing 1.928 $cm^{-1}$) and 100 scans.

Mixed oxide $CeO_2$-$ZrO_2$-supported Cu-Pt based catalysts were synthesized through the wet impregnation method. Platinum was derived from a recycled leachate solution from end-of-life commercial diesel oxidation catalysts (DOC) using Monolithos' single-step hydrometallurgical method for platinum group metals [5]. The prepared catalyst was pretreated via two different modes: calcination or $H_2$ reduction followed by calcination in air. The obtained materials were examined by numerous methods, such as XRD, BET, FTIR, thermal analysis, and TPR. Sample catalytic behaviour was tested in the CO oxidation reaction.

Detailed analysis provided by FTIR, BET, and XRD was crucial to understand and optimize registered catalytic properties of the studied materials. Applied techniques offered valuable insights for further improvement of catalyst preparation methods. This was essential to enhance catalytic performance by contributing to better emission control and environmental sustainability.

Acknowledgement: The authors gratefully acknowledge financial support by the project H2020-MSCA-RISE-2020 101007669: Chemistry of Platinum Group Metals CHemPGM.

References

1. M. L. Grilli, A. E. Slobozeanu, C. Larosa, D. Paneva, I. Yakoumis, Z. Cherkezova-Zheleva, Platinum group metals: green recovery from spent autocatalysts and reuse in new catalysts. A review, Crystals. 13 (4), (2023) 550, https://doi.org/10.3390/cryst13040550.
2. A. L. Brown, D. C. Green, Importance of surface properties in catalysts, Catal. Rev., 63 (2), (2021) 231–255.
3. Y. Liu, H. Zhang, Surface characterization of automotive catalysts using XPS, Appl. Surf. Sci., 475 (2019) 739–748.
4. K. J. Smith, M. T. Jones, Advances in FTIR analysis of catalysts, J. Catal., 385 (2020) 112–121.
5. I. Yakoumis, A.-M. Moschovi, M. Panou, D. Panias, Single-step hydrometallurgical method for the platinum group metals leaching from commercial spent automotive catalysts, J. Sustain. Met., 6 (2020) 259–268.

# sP42. Application of mechanochemistry in recycling platinum group metals from spent automotive catalysts

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Mechanochemistry involves the use of mechanical energy to induce chemical reactions, typically through grinding, milling, or other mechanical processes. Due to environmental and economic benefits, this innovative approach has emerged as a viable method for recycling of platinum group metals (PGMs). By utilizing mechanical energy, mechanochemical processes facilitate recovery of valuable metals from various waste matrices without necessity for high temperatures or harsh chemical reagents. Application of mechanochemistry in PGMs recycling offers distinct advantages including reduced energy consumption, decreased emissions, and capability to process diverse feedstocks, such as electronic waste and spent automotive catalysts [1,2].

In this study, we employed different mechanochemical treatment conditions to optimize PGMs recovery from spent automotive catalysts. We used different characterization methods as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), and Fourier-transform infrared spectroscopy (FTIR) to analyse treated materials. Recent advance in mechanochemical methodologies have demonstrated significant improvement in efficiency and sustainability of metal recovery processes. Mechanochemical integration with green chemistry principles has promoted the development of innovative protocols that minimize the use of hazardous reagents and diminish environmental footprint of metal recycling operations [3,4]. Additionally, research into mechanochemical process scalability suggests feasibility for industrial-scale applications addressing increasing demand for PGMs in various high-tech and industrial sectors [5,6].

Registered powder diffractograms reveal predominantly the presence of crystal structure characteristic of catalyst ceramic monolith, namely cordierite structure. FTIR analysis is in line with XRD results (Fig. 1, left). Detected spectra in the 400–1600 $cm^{-1}$ region together with analysis of the main IR bands are displayed in figure 1 (right).

Results obtained from detailed XPS and SEM/EDS analyses demonstrate that optimal conditions for mechanochemical treatment were identified. Under these conditions, a higher PGMs concentration was observed on the surface of treated samples. This indicates that mechanochemical processing could effectively enhance metal accessibility from waste materials by creating new fresh surfaces. Thus, higher PGMs availability would bring about more accessible material for chemical reaction, e.g., by future extraction or catalysis. This investigation underscores mechanochemistry's pivotal role in advancing sustainable, green, and efficient recycling practices for precious metals manifesting certain potential for industrial-scale implementation.

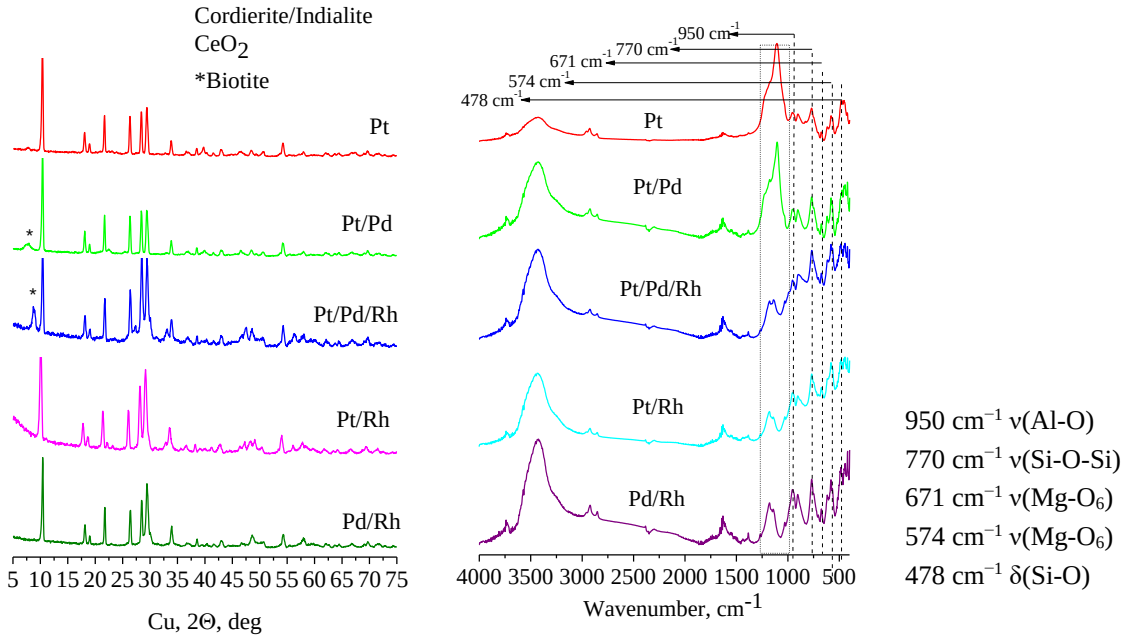



Fig. 1. Powder X-ray diffractograms (left) and FTIR spectra of initial materials (right).

Acknowledgement: The authors gratefully acknowledge financial support by project H2020-MSCA-RISE-2020 101007669: Chemistry of Platinum Group Metals, CHemPGM.

References

1. P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutková, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, Hallmarks of mechanochemistry: from nanoparticles to technology, Chem. Soc. Rev., 42(18), (2013) 7571–7637.
2. C. Zhang, Z. Xu, F. Wu, Mechanochemical processing of electronic waste for resource recovery, Environ. Sci. Technol., 54(10), (2020) 6062–6077.
3. V. V. Boldyrev, Mechanochemistry and mechanical activation of solids, Rus. Chem. Rev., 75(3), (2006) 177–189.
4. X. Ao, D. Li, Z. Fang, A review on mechanochemistry applications in waste management, J. Hazard. Mater., 369 (2019) 486–499.
5. J. Wang, W. Q. Han, C. Fan, Mechanochemistry: an efficient and versatile toolbox for synthesis, transformation, and functionalization of nanomaterials, Chem. Rev., 118(23), (2018) 10638–10690.
6. R. Schwarcz, R. Schach, Mechanochemical processes for the recycling of platinum group metals from spent automotive catalysts, Metall. Mater. Trans. B, 49(1), (2018) 197–206.

# sP43. Recycling of spent automotive catalysts and their reuse in CO oxidation reaction

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Recycling of spent automotive catalysts has garnered significant interest due to presence of platinum group metals (PGMs) such as platinum, palladium, and rhodium, which are crucial for catalysing various chemical reactions. Even though PGMs content in individual car catalyst is in the ppm range. Annual PGM consumption for fuel-car catalyst production is around 70%. Over time, these catalysts become deactivated because of diminished effectiveness in reducing harmful emissions from vehicle exhaust. Primary focus of catalyst recycling is on recovering valuable PGMs, while recycling the remaining part of the catalytic converters, mainly cordierite, but also rare earth elements, transition metals, etc., is also very important. Recycling spent automotive catalysts offers significant economic benefits by reducing production costs and conserving natural resources, and minimizes environmental impact by reducing waste.

Instead of discarding spent catalysts can be recycled providing significant advantages. PGM recycling is not limited to areas with natural deposits; it can occur wherever the products are used and where recycling technologies are available. Recycling spent catalysts reduces expenses associated with buying new products; especially as PGM demand and stocks are projected to rise, making PGM scrap increasingly accessible for recycling. PGM recycling enhances environmental sustainability by reducing the need for mining raw materials and lowering waste production, as the emission intensity from recycling PGMs is significantly lower than from primary production. PGM concentrations in recycled materials are often much higher than in natural ore deposits. Recycling conserves valuable and rare metals, such as PGMs and rare earth elements (REEs), which are crucial components of many catalysts.

Recycling methods are regeneration, direct recycling, and non-direct recycling. In regeneration, spent catalysts are restored to original performance levels. This process involves removing contaminants and reactivating the catalyst surface to regain its catalytic properties. Direct recycling is aimed at reusing spent catalysts without refining the metals. These catalysts are employed directly in reactions, such as CO oxidation, leveraging remaining activity. Non-direct recycling comprises recovering of valuable metals from spent catalysts. This involves mechanical, chemical, or thermal processes to extract and purify the metals for reuse.

Carbon monoxide (CO) oxidation is a key reaction in reducing vehicle emissions. A harmful gas (CO) converts into carbon dioxide ($CO_2$), which is less harmful. This reaction is essential in automotive catalytic converters that help clean exhaust gases.

Various catalysts are used to speed up CO oxidation. PGMs like platinum, palladium, and rhodium are particularly effective. These metals are often supported on oxide materials, which help improve catalyst performance.

This study explores efficient method for reuse of spent automotive catalysts without refining the valuable metals. Spent automotive catalyst material was treated toward direct application as a catalyst in environmental remediation reactions, particularly in carbon monoxide oxidation. We tested as-prepared catalysts and those subjected to additional mechano-

chemical activation in a planetary ball mill (Fig.1). Mechanochemically treated catalysts showed significantly improved performance in CO oxidation. Additionally, catalysts containing a combination of Pt, Pd, and Rh were more effective than those with individual metals were.

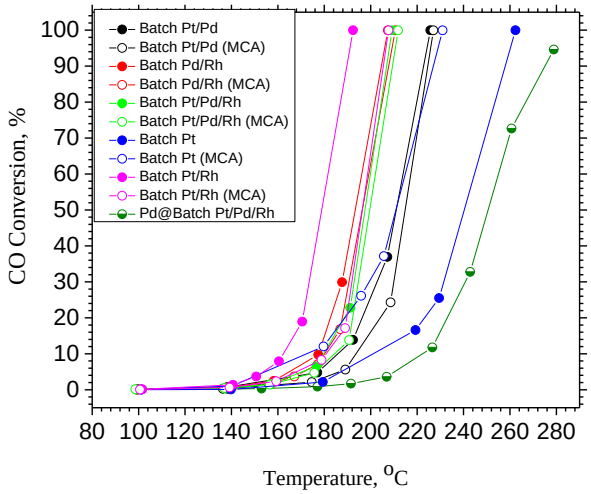



Fig. 1. CO conversion over investigated materials.

This demonstrates that the multimetallic synergy enhances catalytic efficiency, making these recycled materials especially valuable. Overall, recycling and treating spent catalysts can restore and even enhance functionality thus offering substantial environmental and economic benefits.

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# sP44. SEM investigation of spent automotive catalysts for further PGM reuse

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This SEM investigation describes morphology and dispersion state of prepared samples of automotive catalysts to extract platinum group metals (PGMs) obtained through mechano-chemical processing. PGM content on earth's upper continental crust is approximately 0.01 ppm and PGM ore mining takes place in limited geographical areas. Considering primary PGM production, the process is extremely expensive, complex, unhealthy, and challenging for the production countries. Secondary sources exploitation is preferable, since higher PGMs concentrations are involved, 70–100 times less energy is consumed, and higher recovery yields are achieved together with environmental footprint. Spent automotive catalysts (SAC) are the richest PGM secondary resource, being widely exploited for the PGMs recovery. Since 2011, PGMs have been included in the list of critical raw materials for the European Union. PGMs recovery from efficient recycling spent automotive catalysts minimizes also waste disposal. Platinum group metals, including platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir,) and ruthenium (Ru), are widely used due to the unique properties of high corrosion and oxidation resistance, high electrical conductivity and catalytic activity, heat resistance, high melting point, high mechanical strength, and good ductility and catalytic activity. Recycling of gold, platinum, iridium, and other precious metals has gained much attention in research industries as a possible plan to convert disposable material into a valuable renewable resource. During car catalyst performance, PGMs can agglomerate and are encapsulated into the inner layer of the monolith after long-term operation at high temperature. Thus, the catalysts become deactivated and have to be changed. However, spent automotive catalysts can be used as a secondary feedstock material. Spent catalytic monoliths containing PGMs should be characterized to define bulk composition, surface morphology, impurities, and any contamination that deteriorates the leaching procedure [1-3].

Scanning electron microscopy (SEM) is the key technique used for identification of the initial and treated SAC materials. This facility is used to characterize PGMs morphological features and dispersion state. SEM images demonstrate high non-uniformity of automotive catalysts and formation of a fresh surface that allows characterization and extraction of PGMs.

SEM-EDS analyses were performed on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350, High Wycombe, Buckinghamshire, UK) equipped with ultrahigh resolution scanning system (ASID-3D) at the following conditions: 20 kV accelerating voltage, I ~ 75 mA, vacuum medium in the range of 10−4 Pa, spot size 1 μm. Powder SAC samples underwent cross-section polishing and then were coated with gold for about 20 s. Gold of that thickness would have little or no effect on elemental analysis. Further, the gold-coated samples were used to determine chemical composition by EDS and examine morphology. Reported concentrations for each sample were

the average of ten performed measurements. Quantitative elemental determinations were conducted in different sample areas under × 1000 magnification conditions.

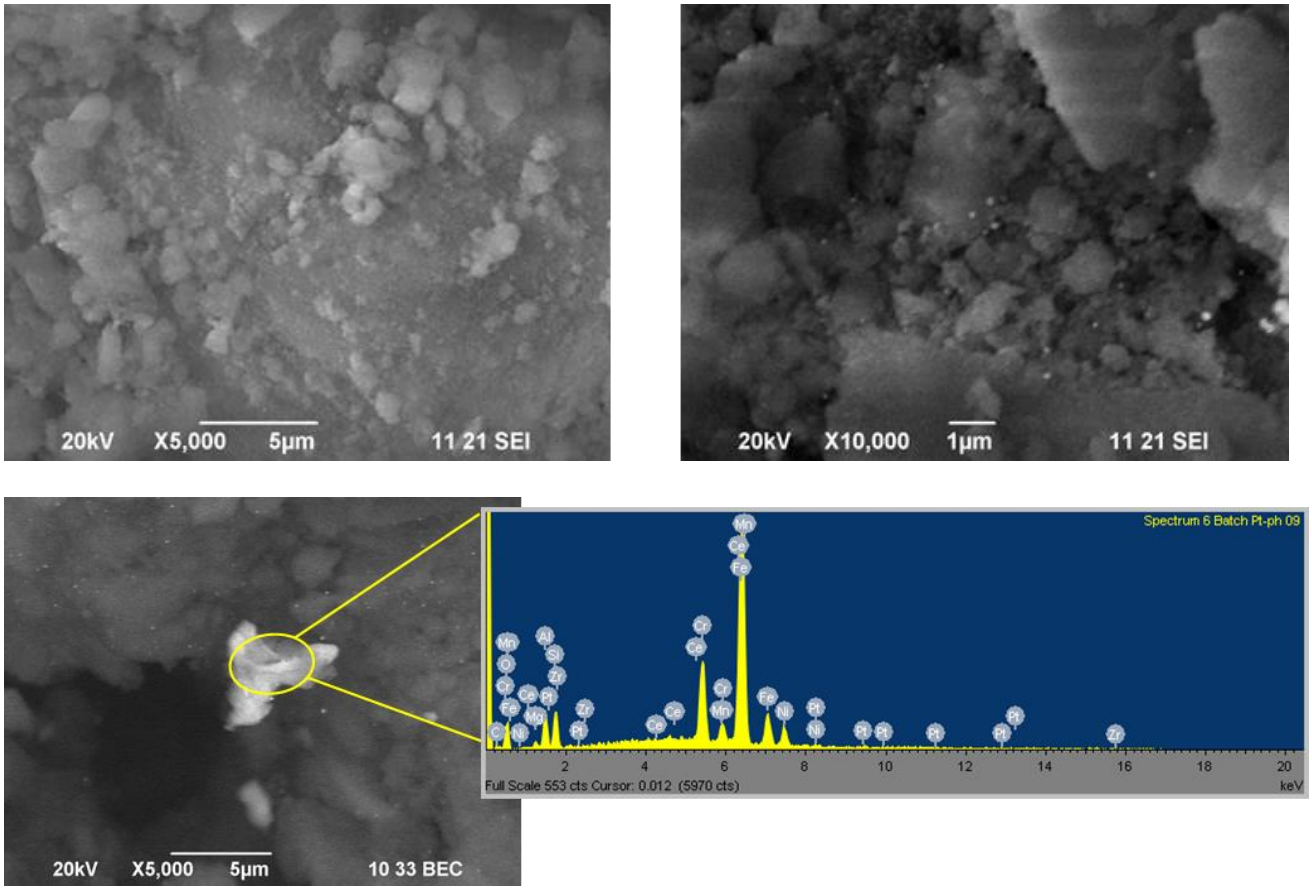



Fig. 1. SEM images of spent automotive catalyst samples.

According to energy dispersive X-ray spectroscopy analysis, both homogeneity and fine powder formation promoted leaching efficiency due to increased surface area. Usage of electron microscopy contributed to the characterization and visualization of the processes taking place in the recycling of automotive catalysts.

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References

1. D. J. de Aberasturi, R. Pinedo, I. R. de Larramendi, J. I. Larramendi, T. Rojo, Recovery by hydrometallurgical extraction of the platinum-group metals from car catalytic converters, Miner. Eng., 24(6), (2011) 505–513.
2. I. Yakoumis, A. Moschovi, M. Panou, D. Panias, Single-step hydrometallurgical method for the platinum group metals leaching from commercial spent automotive catalysts, J. Sustain. Met., 6(2), (2020) 259–268.
3. M.-L. Grilli, A.-E. Slobozeanu, C. Larosa, D. Paneva, I. Yakoumis, Z. Cherkezova-Zheleva, Platinum group metals: green recovery from spent auto-catalysts and reuse in new catalysts – A review, Crystals, 13(4), (2023) 550.

# sP45. Thermal analysis of spent catalysts: a TG/DTG-DSC-MS investigation of thermal behaviour in different gas atmosphere

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Thermal analysis is a methodology comprising several analytical techniques that are often implemented in studies investigating the chemical and physical properties of materials. This method allows studies of transformations occurring within the material, such as dehydration, decomposition, decarbonation, phase transitions, degradation, etc. In catalyst research, thermal analysis can be used to obtain information regarding composition, stability, activity, and catalyst life, in addition to investigating the transformations taking place in the bulk or at the catalyst surface during heating. Catalyst characterization is often a challenging task since the material may contain only small amount of active component(s) along with a certain amount of water. When coupled with mass spectroscopy (MS), this method could provide a much more detailed interpretation of the processes occurring in the catalysts, with the possibility of characterising different steps of catalyst preparation, solid-state reactions proceeding upon exposure of the precursors/catalysts to different atmosphere (oxidizing, reducing, inert), etc.

A TG/DTG-DSC-MS study of two spent catalyst samples, denoted as A and B, was performed where thermal behaviour of the latter was investigated in two different media: inert (argon) and oxidizing (air). Two main processes were registered in both samples and media: dehydration associated with release of water vapour in the low temperature region, and decarbonation related to $CO_2$ emission in the high temperature region. Appearance of phase transition at 300°C was registered with sample B. Under inert atmosphere, a mass increase varying within 4–10% was observed at temperatures up to 100°C and showing a gradual decrease in mass over 100°C. The results obtained provide information related to processing, stability, and reactivity of the investigated catalytic materials.

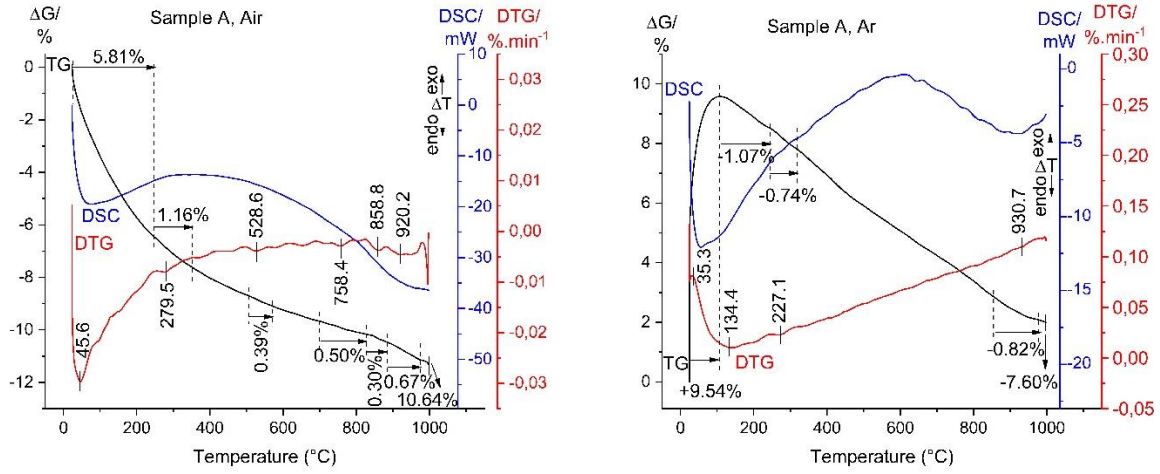



Fig. 1. TG/DTG-DSC analysis of sample A in oxidizing and inert atmosphere.

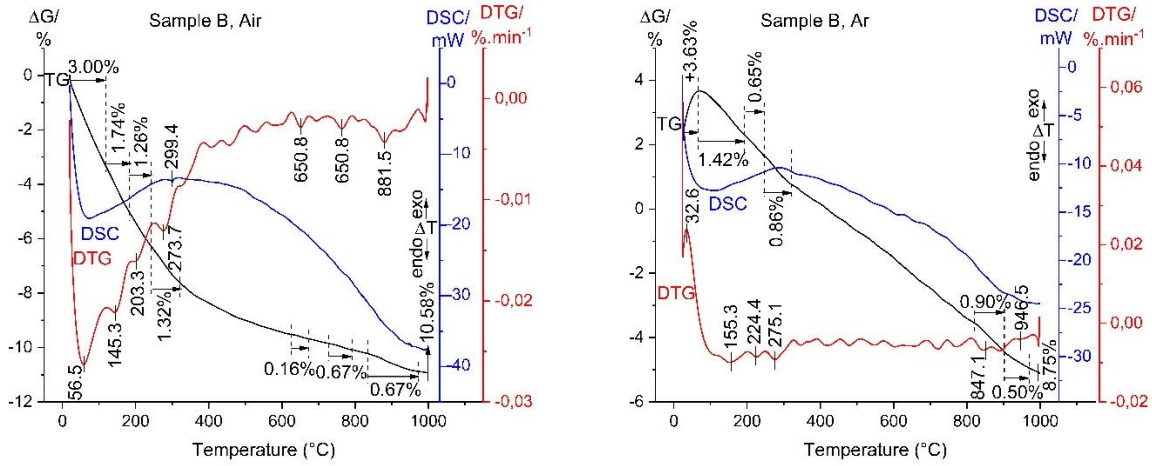



Fig. 2. TG/DTG-DSC analysis of sample B in oxidizing and inert atmosphere.

The samples were analysed using a Setsys Evolution 2400 thermal analyser (Setaram, France), combined with an OmniStar mass spectrometer, able to register volatiles $H_2O$ (18) and $CO_2$ (44) from room temperature to 1200°C at a heating rate of 10°C $min^{-1}$. Operational characteristics of the TG/DTG-DSC system were sample mass of 18.0±2.0 mg with mass resolution of 0.02 μg, alumina sample crucible of 100 μL volume, static air atmosphere, and 99% Ar at a flow rate of 20 mL $min^{-1}$.

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# sP46. Structure and morphology of high entropy oxides with spinel structure prepared via ball milling and their electrochemical properties

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High entropy oxides with spinel structure are facing scientific worldwide attention. In this study, we focused on synthesis and characterization of new types of inorganic spinel-structure materials including several elements. Apart from that, we reported a simple method to create oxygen defects, i.e., to prepare oxychloride or oxyfluoride derivatives in order to affect electrochemical properties of the prepared samples. It was shown that modification of the structure had a significant influence on the functional properties of synthesized spinels. This study presents a novel class of spinel-type high entropy oxides and derivatives. Samples of interest were prepared by a combination of ball milling and thermal treatment of the oxide precursors and LiF or LiCl as a lithium source for particular derivatives. Sample structure was investigated by XRD, HR-TEM, EDX, and XPS spectroscopy. It was found that lithium incorporation into the structure, together with anionic exchange, had a significant influence on crystallites short-range structural features, size, and morphology as well as oxidation and reduction processes within spinel structure. Charge capacity was tested by cyclic voltammetry. The results revealed that storage capacity and conductivity were affected by the formation of oxygen defects and lithium incorporation. In this context, the present results offer a potential easy way like a combination of mechanical milling and thermal treatment to prepare novel spinel-based materials with improved electrochemical properties.

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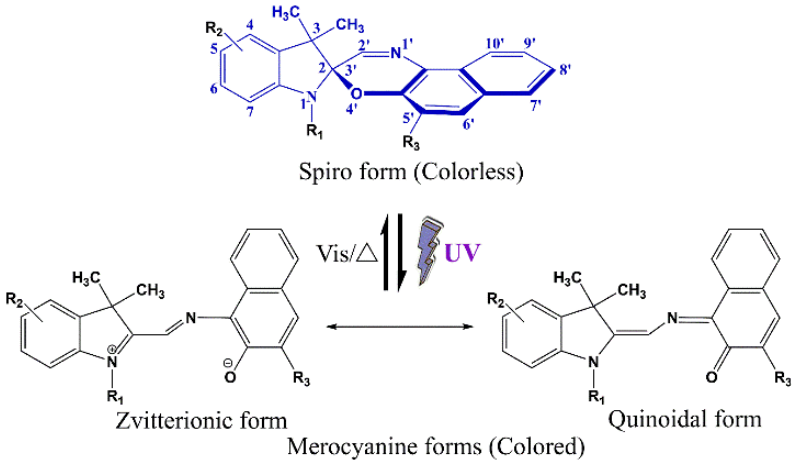
# sP47. Development of photochromic spironaphthoxazine molecular systems as photocontrollable 'smart' detectors for metal ions

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Modern practical goals impose stringent requirements on optical properties, temperature control, and operational stability of advanced photochromic materials as well as molecular switches and analytical devices based on such molecular systems. These criteria lead to an increase in the needs to develop new chemical structures and strategies to meet the requirements related to their applications.

We synthesized novel spironaphthoxazine (SO) molecular systems bearing various substituents in the naphthoxazine and indoline ring molecular moieties (Scheme 1). SO molecular structure and physicochemical properties were investigated by quantum chemical modelling.




$R_1 = CH_3, C_4H_9, C_4H_8SO_3H$, $R_2$ = OH, 2-benzothyazolyl, $R_3=CH_2=CH_2=CH_2=CH_2$

Scheme 1. Photochromism of substituted spiroindolinonaphtoxaxines.

We studied the effects of both the molecular structure of synthesized SOs and their solvation in various organic and inorganic solvents on the absorption properties and SO molecule complexation with some metal ions including harmful heavy metal ions. The effect of both solvent and designed molecular structure on thermal bleaching kinetics of the photomerocyanine (MC) form of the synthesized SOs were also investigated by means of optical absorption spectroscopy. Photomerocyanines of these SO compounds showed positive solvatochromism indicating that their excited state is more polar than the ground state. Thermal equilibrium between ground state populations of the colourless and coloured forms was influenced by solvent polarity as well as by substituent nature.

SOs complexation with selected metal ions in suitable solvents, including also water, was experimentally studied. Possibility to stabilize coloured MC form was analysed. SOs containing –OH substituents could readily form complexes with Al(III), Fe(II), or Cu(II). On the other hand, SOs with a benzothiazolyl substituent formed complexes with Ni(II), Co(II), Cd(II), or Zn(II).

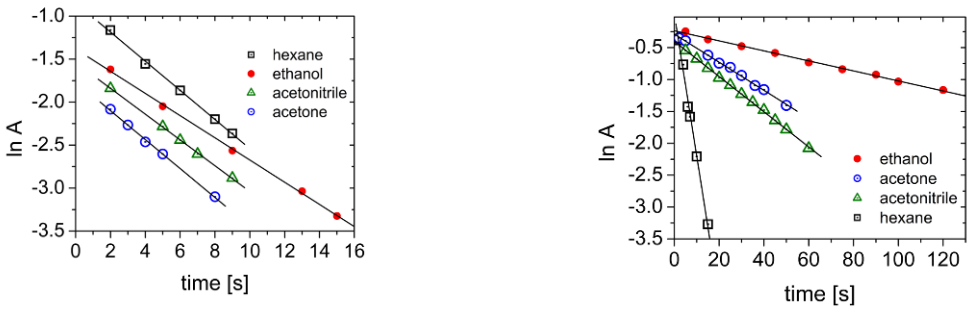



Fig. 1. Kinetic runs at 600 nm after irradiation of $1\times10^{-5}$ M solutions of SO designed with –OH group and benzothiazolyl substituents in solvents of different polarity.

SOs having a sulphobutyl substituent on the indoline fragment of the molecule could interact with Cd (II), Ca(II), Mg(II), Zn(II), or Pb(II) to bring about formation of coloured complexes of metal ions with merocyanine form of the synthesized SOs. Complex formation by SOs could be readily detected due to a change of both the intensity and shape of the MC absorption band in the visible spectral range around 630 nm (Fig. 2).

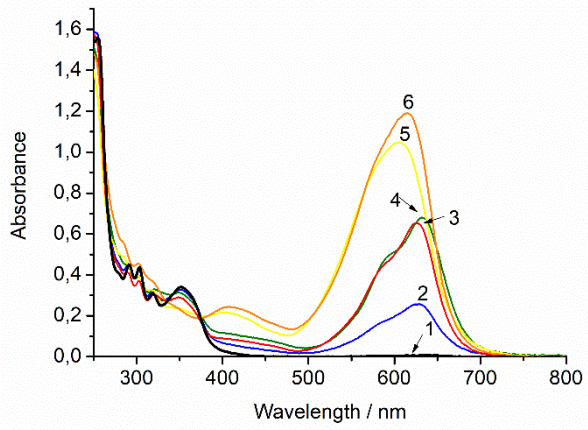



Fig. 2. Absorption spectra of MeCN solutions ($5\times10^{-5}$ M) of SO having sulphobutyl substituent on the indoline fragment of the molecule in the presence of 1 equiv. of Cd(II) (2), Mg(II) (3), Ca(II) (4), Zn(II) (5), Pb(II)(6).

The results of photo-physical characteristics, photo-transformations, and synthesized SOs complexation might be useful and could be applied in the highly sensitive and selective analytical techniques for metal ion sensing, detection of chemical compounds of environmental interest as well as for development of photo-switchable molecular devices.

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References

1. S. Minkovska, G. B. Hadjichristov, A. Neacsu, V. Chihaia, Y. V. Fedorov, Photoswitchable photochromic chelating spironaphthoxazines: synthesis, photophysical properties, quantum-chemical calculations, and complexation ability, ACS Omega, 9(4), (2024) 4144–4161.

# sP48. Spirooxazine derivative DFT simulations and spectroscopic properties of solid powder and solvent solutions

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Target compound in this work is a merocyanine form (MC) of a spirooxazine derivative with matching IUPAC name 4-[(2E)-1,1-dimethyl-2-({[(1Z)-2-oxo-1,2-dihydronaphthalen-1-ylidene]amino} methylidene)-1H,2H,3H-benzo[e]indol-3-yl]butane-1-sulphonic acid. The physicochemical properties of MC solid powder and its interactions with solvent solutions were investigated. MC powders obtained by desolvation from water, methanol, ethanol, and acetonitrile were physicochemically analysed using Fourier transform infrared spectroscopy. By using DFT calculations, the optimized molecular structure and the energy of individual molecular orbitals were predicted. Electronic properties such as ionization potential, electron affinity, and electronic excitation energies were calculated. In addition, based on DFT calculations crystalline structures were established by MC molecules packing. MC molecule showed solvatochromism when dissolved in water, glycerol, ethylene glycol, methanol, and ethanol. UV-Vis spectroscopy was used to determine the binding constants of the interaction between MC and considered solvents. UV-Vis data indicated that the magnitude of the shift depended on the strength of the interaction between the solvent and the molecules, which is determined by solvent polarity. MC changed colour from blue in a less polar solvent to red as the polarity of the solvent increased. The results showed that the strength of interactions between MC and solvent decreased on decreasing solvent polarity.

## sP49. The effect of ion exchange of clinoptilolite as a soil on radish physiological response

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Colonization of planets other than the Earth is not simple and there are many obstacles to overcome. One of the major issues is food availability. There is continuously increasing interest in 'soil-based' space agriculture. Spectral analysis suggested that components of the Martian regolith are more likely zeolites, and clinoptilolite is considered one of the most widespread zeolites on Mars planet.

The aim of this work is to investigate the effect of clinoptilolite particle size and ion exchange on radish growth, development, and physiological and biochemical characteristics. The following scenarios were used: clinoptilolite of granulous size 0.9–2.5 mm and 2.5–5.0 mm and modified clinoptilolite with ammonium and potassium ions. Our findings contribute to the development of formulations that meet specific chemical, biological, and agronomic requirements.

Germinability was investigated in three consecutive plantings. It was higher for $C_{NH4}$-2.5 compared to C-2.5 and $C_K$-2.5 during the first run. It is interesting to note that the weakest germination showed seeds on $C_K$-2.5. Dramatic reduction in seed germination was established only in $C_{NH4}$-5.0, while the germination was similar to $C_{NH4}$-2.5 during the second and third run. $C_K$-2.5 had positive effect on seed germination with experiment timing, being higher during third run.

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# sP50. Hydrogen production over nickel-based catalysts

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Several catalytic methods for decreasing greenhouse gas (GHG) emissions have been developed, such as steam reforming of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$), dry reforming of methane (DRM, $CH_4 + CO_2 \rightarrow CO + 2H_2$), partial oxidation of methane ($CH_4 + 1/2O_2 \rightarrow CO + 2H_2$), and autothermal reforming of methane. Climate change caused by continuously increasing emissions of greenhouse gases like carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) is one of the biggest challenges nowadays. It is well known that carbon dioxide and methane emissions cause more than half of the total greenhouse effect and have the greatest impact on the increase of average global air temperature. Methane dry reforming allows simultaneous conversion of both greenhouse gases carbon dioxide and methane into a syngas ($H_2$/CO) or hydrogen-rich synthesis gas, a valuable material for chemical industry.

It should be noted that DRM process has not yet been commercialized due to high endothermicity of the reaction and the lack of cheap, active, and stable catalysts. So, during the last decades great efforts were dedicated to find a suitable catalyst system for DRM exhibiting both high activity and high stability.

The nature of the active species of hydrotalcite-derived catalysts in catalytic DRM process is still a subject of extensive investigation by researchers. On the other hand, there is scarce information about formation of carbon species and their effect on DRM behaviour of Ni-based hydrotalcite like catalysts. In this connection, the present work is concentrated on the preparation method of hydrotalcite-derived Ni-based catalysts and their activity and stability in DRM. Significance of the metal particle size and distribution on the catalytic behaviour of nickel-based catalysts was related to applied preparation method and addition of a small amount of noble metal as palladium. The influence of different types of carbon species on catalyst behaviour was also evaluated.

Ni-based catalysts for dry reforming of methane were prepared by adopting a ‘memory effect’ from Mg-Al hydrotalcite (HT) as catalyst precursor. Physicochemical properties of hydrotalcite-derived catalysts in their oxide and reduced state as well as after the reaction of dry reforming of methane were studied by using different techniques, such as $N_2$ adsorption-desorption isotherm, thermogravimetric (TG) analysis, X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), Fourier-transform infrared (FTIR) and Raman spectroscopies, temperature-programmed reduction (TPR), and high-resolution transmission electron micro-scopy (TEM). It was shown that on heating the samples at a temperature of 600°C a periclase-like structure, Mg(NiAlO), was formed. Despite the formation of different types of carbon species as graphitic and disordered entities during the reaction, all catalysts exhibited high $CH_4$ and $CO_2$ conversions as well as a high stability in dry reforming of methane. Nickel supported on Mg-Al hydrotalcite was the most active in DRM reaction due to high accessibility of the reactant molecules to the active metal nickel particles owing to formation of eggshell type structure.

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