

Editorial

Transition-Metal-Containing Bifunctional Catalysts: Design and Catalytic Applications

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Chemical processes catalyzed by transition metals are widely applied and well established in modern industry. Nevertheless, the scientific background and new approaches to a catalyst's synthesis are constantly developing. Research efforts are mainly directed towards an improvement in catalytic activity and decrease in by-products and pollutants. For heterogeneous catalysts, there are a lot of opportunities for their rational design in terms of morphology and creation of different active centers in the same catalyst [1]. The multifunctionality of catalytic systems became a research trend in recent decades. Bifunctional catalytic systems are a particular case of multifunctional catalysis and are a promising area of research [2–4], providing broad opportunities for carrying out simultaneously few catalytic processes in a single apparatus. In this way, modern principles of “green” chemistry and sustainable development of chemical production can be implemented.

Bifunctional catalysis is a broad concept represented by several types of systems:

- Bimetallic catalysts containing two different active metals or their oxides;
- Catalysts consisting of an active metal in combination with the Brønsted and/or Lewis acid sites;
- Biocatalytic systems that include metal nanoparticles (NPs) and/or acid sites.

The combination of different functions in a single catalyst reduces the duration of the multi-stage process and usually increases the overall yield of the target product. At the same time, the implementation of cascade or tandem processes in the same apparatus using multifunctional catalysts is associated with several difficulties. For example, optimal conditions for each simultaneously proceeding reaction may differ; intermediate products occurring at different active centers can affect each other; and finally, the diffusion of reagents between active centers should be considered.

Due to the importance and complexity of catalysis using bifunctional systems, this Special Issue, titled “Transition-Metal-Containing Bifunctional Catalysts: Design and Catalytic Applications”, was organized. It consists of 11 contributions, including 2 reviews and 9 research papers. The aim of this Special Issue was to present and summarize recent advances in the development of bifunctional catalytic systems based on transition metals for different applications.

In the review by Nikoshvili and Matveeva (contribution 1), a variety of Pd-catalyzed tandem processes are described, which include not only truly tandem catalysis but also cascade and orthogonal catalytic reactions. The problem of defining tandem and related processes is discussed while emphasizing the role of distinct catalytic mechanisms and active species. Among the large number of homogeneous Pd-catalyzed tandem reactions presented, there are truly tandem processes, but also the related (one-pot, orthogonal, or domino) reactions. They were clearly distinguished, since in the referred scientific papers a double attribution was applied, being sometimes misleading. It is concluded by the authors that in the field of homogeneous tandem catalysis, a variety of conditions, possible



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additives, and reaction routes can be applied to provide the highest yields of desired products with the lowest environmental impact. In contrast, in the case of heterogeneous catalysis, the main direction of processes' development is an improvement in support properties, i.e., the use of supports bearing acid-base centers of Brønsted and Lewis. Such Pd-containing catalytic systems are usually based on oxidic supports and metal-organic frameworks and are often applied for the transformation of "platform chemicals" derived from plant biomass. Another approach used for obtaining bifunctional catalysts that is highlighted in the review is the combination of homogeneous and heterogeneous catalysis, e.g., immobilized metal complexes or enzymes. The combination of metal catalysis and biocatalysis is a promising alternative to traditional chemical routes of the synthesis of chiral compounds with high enantioselectivity. Thus, the review covers all areas of development regarding palladium-catalyzed tandem processes.

Another review (contribution 2) included in this Special Issue is the work of Stepacheva et al., which is devoted to the application of plant-biomass-derived materials as catalytic supports. Plant biomass is a renewable source used not only to produce fuels and "platform chemicals" but also for cheap and effective sorbents and catalytic supports. The authors of the review describe the current methods of biochar obtained from a variety of starting materials in detail. It is shown that acid-functionalized biochars produced by pyrolysis can be successfully used as catalysts for biodiesel production and for the transformation of carbohydrates into furfural, 5-hydroxymethylfurfural (5-HMF), and other valuable chemicals. Base-functionalized biochars are less used in biodiesel production due to their high saponification activity and sensitivity to water. Despite such disadvantages, it is noticed that base-functionalized biochars can provide high rates of transesterification under mild conditions. Moreover, authors show that biochars and biocarbons can be effective supports for a wide variety of transition metals (Mo, Co, Cu, Ni, Fe, Au, Ru, Pd) and be applied in heterogeneously catalyzed organic reactions and in electrocatalytic processes. This review can serve as a concise guide for the development of functionalized biocarbon-based material for catalytic applications.

The topic of carbon-supported transition metal catalysts is continued in contributions 3 and 4 of this Special Issue.

In the contribution 3 by Taran et al., the synthesis of Ru-containing catalysts supported on Sibunit[®] (commercial mesoporous carbon materials) and their application for reductive catalytic fractionation (RCF) of spruce wood is described. Sibunit[®] was functionalized with different oxygen-containing species, which allowed the researchers to prevent the sintering of ruthenium particles under high temperatures, being responsible for acidic properties. Thus, the series of bifunctional Ru/C catalysts was developed by varying the support acidity, catalyst grain size, content, and dispersion of Ru. The yield and composition of solid, liquid, and gaseous products of spruce wood RCF were carefully studied with various catalyst types, reaction times, and temperatures. Moreover, solid products were characterized with IR spectroscopy and XRD. Under optimal conditions (225 °C, 3 h) using the most acidic Ru/C, the liquid products enriched with phenolic compounds were synthesized, and the optimal trade-off between phenols (30.0 wt.%), polyols (18.6 wt.%), and solid products containing 84.4 wt.% of cellulose was achieved.

Kustov and Kalenchuk (contribution 4) reported a series of mono- and bimetallic Ni-Cr/C catalysts synthesized using Sibunit[®] as a support for the reaction of bicyclohexyl dehydrogenation applied in hydrogen storage systems. The catalysts' composition and morphology were characterized by the XPS, XRD, TPR, HRTEM, and electron diffraction methods. In contrast to the work of Taran et al. (contribution 3), the authors of contribution 4 highlighted the interactions between two active metals rather than the influence of the support. Despite the formation of a Cr-Ni solution and the change of nickel crystal lattice parameters, no obvious advantages for bimetallic Ni-Cr/C compared to monometallic systems were found, though the authors observed strong positive effect for the trimetallic Pt-Ni-Cr/C catalyst in an earlier study [5].

Among carbonaceous supports, polymers can serve as a promising alternative to chars. There is a big variety of functionalized polymeric materials for sorbents and catalytic supports [6]. Hypercrosslinked aromatic polymers are of special interest [7] due to their high porosity, chemical, and thermal stability.

Dutra et al. (contribution 5) developed bimetallic (Ru-Ni, Ru-Co, Ru-Cu) catalysts containing 3wt.% of Ru and 0.1 wt.% of the second metal supported on commercial hypercrosslinked polystyrene (HPS), which were tested in the reactions of transformation (hydrogenation, hydroformylation, oxidative cleavage, and deoxygenation) of canola fatty acid methyl esters (FAMEs). High values of FAME conversion (up to 99%) were attained, showing the prospect of HPS-based catalytic systems.

Though there are numerous carbonaceous materials available as supports, the synthesis of multifunctional catalytic systems is commonly based on different oxides and their mixtures. The series of contributions within this Special Issue were devoted to oxide catalysts (contributions 6–8) and to transition metals supported on oxides (contributions 9 and 10).

The group of scientists from Brazil in contribution 6 reported the synthesis of cerium oxide, molybdenum oxide, and mixed material $\text{Ce}_2(\text{MoO}_4)_3$ for the conversion of fructose to 5-HMF. It is well known that the main issue of this reaction is the formation of humins, which can be controlled by balancing acidity [8]. $\text{Ce}_2(\text{MoO}_4)_3$ revealed lower acidity compared to pure molybdenum oxide (see the data presented in contribution 6) that inhibited the formation humins to some extent (selectivity to 5-HMF increased from 14.5% up to 27.5% at a high fructose conversion). Among other byproducts, different acids (levulinic, acetic, formic, lactic), aldehydes (glyceraldehyde and pyruvaldehyde), and dihydroxyacetone were found. The highest selectivity to 5-HMF was found in the case of pure cerium oxide (70.2%); however, the conversion of fructose was about 50% (150 °C, 6 h). The stability and reuse of $\text{Ce}_2(\text{MoO}_4)_3$ was studied in four repeated runs and revealed a negligible variation in conversion and selectivity. Similarly, in contribution 7, the conversion of fructose was tested using tin, niobium, and tin-niobium oxides obtained with three different methods: coprecipitation (PPT), hydrothermal treatment using cetyltrimethylammonium bromide (CTAB), and Pechini treatment using glycerol (GLY). Independently of the synthesis method, mixed SnNb oxides were more active compared to the corresponding pure oxides, and they were highly selective due to having an appropriate balance between the Lewis and Brønsted acid sites. Among SnNb (GLY), SnNb (CTAB), and SnNb (PPT) materials, the highest fructose conversion (76.9% for 2 h and >90% for 6 h at 150 °C) and selectivity to 5-HMF (about 80%) were found for SnNb (CTAB), which makes SnNb oxides promising catalysts for the processes of biomass valorization.

Interesting work (contribution 8) devoted to oxide catalysts was presented by Mukhtarova et al., who studied the hydrodeoxygenation (HDO) of guaiacol (lignin-derived compound) to aromatics in the presence of MoO_x and WO_x generated in situ from corresponding carbonyls. The detailed characterization of the catalysts was carried out with XRD, XPS, HRTEM EDX, SEM, DRIFTS, and Raman spectroscopy methods. The influence of reaction conditions (temperature and H_2 pressure) on the conversion and selectivity of guaiacol to different products was studied, and the HDO pathways were proposed. Under the chosen reaction conditions (380 °C, 5 MPa of H_2 , 6 h, solvent—dodecane), the benzene-toluene-xylenes fraction was obtained with high yield (96%) over WO_x catalyst.

Shivtsov et al. in contribution 9 prepared a series of magnesium-aluminum oxides (Mg-Al-O_x) with different Mg/Al molar ratios (4:1, 2:1, 1:1, 1:2, and 1:4) with the aerogel method, which served as supports for Pd NPs. Chosen method of oxide synthesis allowed them to obtain materials with high specific surface areas (up to 600 m^2/g) for the development of bifunctional catalysts (1 wt.% of Pd) of tetradecahydrophenazine dehydrogenation with a high hydrogen evolution rate (252 $\text{mmol}\cdot\text{g}_{\text{Met}}^{-1}\cdot\text{min}^{-1}$). The authors of contribution 9 revealed that the most promising mixed oxides were characterized by significant concentrations of basic electron-donor sites responsible for the efficient stabilization of palladium NPs and alteration of the dehydrogenation mechanism.

Philippov et al. (contribution 10) reported transfer hydrogenation of biomass-like phenolic compounds such as guaiacol and dimethoxybenzenes (DMB) over novel Ni-SiO₂ and NiCu-SiO₂ catalysts under supercritical conditions at 250 °C using 2-PrOH as the only hydrogen donor. The role of copper in bimetallic catalytic systems was highlighted. Detailed kinetic analysis was carried out, showing the negative effect of Cu addition on the rate of guaiacol and 1,4-DMB conversion. However, in the case of 1,2-DMB and 1,3-DMB, Cu promoted their transformation to corresponding dimethoxycyclohexanes. Moreover, the addition of copper influenced the selectivity of the reaction products, which is an interesting result deserving further study.

The most exciting multifunctional catalytic systems are those that combine the features of transition metals, oxides, and carbonaceous materials. Thus, in contribution 11 presented by Sorokina et al., novel Cr-Zn/Ni composite materials based on an oxide support (SiO₂ or Al₂O₃) with embedded magnetic NPs and covered by a crosslinked pyridylphenylene polymer (PPP) layer were described. The developed nanocomposites were applied for CO₂ hydrogenation to methanol. The necessity of all the components was proven by the results of catalyst characterization and testing, as follows: PPP was found to prevent the aggregation of catalytically active species and enhanced the adsorption of CO₂ and H₂; magnetic NPs insured structural promotion, which was likely due to the formation of oxygen vacancies, and allowed for the fast and simple magnetic separation of the catalyst; the combination of the two metals (Cr-Zn and Cr-Ni) resulted in the creation of bimetallic interfaces. All these features allowed the authors of contribution 11 to obtain a highly active and stable catalytic system of methanol synthesis.

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List of Contributions:

1. Nikoshvili, L.Z.; Matveeva, V.G. Recent Progress in Pd-Catalyzed Tandem Processes. *Catalysts* **2023**, *13*, 1213. <https://doi.org/10.3390/catal13081213>.
2. Stepacheva, A.A.; Markova, M.E.; Lugovoy, Y.V.; Kosivtsov, Y.Y.; Matveeva, V.G.; Sulman, M.G. Plant-Biomass-Derived Carbon Materials as Catalyst Support, A Brief Review. *Catalysts* **2023**, *13*, 655. <https://doi.org/10.3390/catal13040655>.
3. Taran, O.P.; Miroshnikova, A.V.; Baryshnikov, S.V.; Kazachenko, A.S.; Skripnikov, A.M.; Sychev, V.V.; Malyar, Y.N.; Kuznetsov, B.N. Reductive Catalytic Fractionation of Spruce Wood over Ru/C Bifunctional Catalyst in the Medium of Ethanol and Molecular Hydrogen. *Catalysts* **2022**, *12*, 1384. <https://doi.org/10.3390/catal12111384>.
4. Kustov, L.M.; Kalenchuk, A.N. Effect of Cr on a Ni-Catalyst Supported on Sibunit in Bicyclohexyl Dehydrogenation in Hydrogen Storage Application. *Catalysts* **2022**, *12*, 1506. <https://doi.org/10.3390/catal12121506>.
5. Dutra, R.C.; Martins, T.V.S.; Rocha, D.d.G.; Meneghetti, M.R.; Meneghetti, S.M.P.; Sulman, M.G.; Matveeva, V.G.; Suarez, P.A.Z. Doped Ruthenium/Hypercrosslinked Polystyrene (HPS) Catalysts in the Modification of Fatty Acid Methyl Esters. *Catalysts* **2023**, *13*, 630. <https://doi.org/10.3390/catal13030630>.
6. Pryston, D.B.d.A.; Martins, T.V.d.S.; Vasconcelos Júnior, J.A.d.; Avelino, D.O.d.S.; Meneghetti, M.R.; Meneghetti, S.M.P. Investigation of CeO₂, MoO₃, and Ce₂(MoO₄)₃, Synthesized by the Pechini Method, as Catalysts for Fructose Conversion. *Catalysts* **2023**, *13*, 4. <https://doi.org/10.3390/catal13010004>.

7. Martins, T.V.d.S.; Pryston, D.B.d.A.; Meneghetti, S.M.P.; Meneghetti, M.R. Influence of Synthesis Methodology on the Properties and Catalytic Performance of Tin, Niobium, and Tin-Niobium Oxides in Fructose Conversion. *Catalysts* **2023**, *13*, 285. <https://doi.org/10.3390/catal13020285>.
8. Mukhtarova, M.; Golubeva, M.; Sadovnikov, A.; Maximov, A. Guaiacol to Aromatics: Efficient Transformation over In Situ-Generated Molybdenum and Tungsten Oxides. *Catalysts* **2023**, *13*, 263. <https://doi.org/10.3390/catal13020263>.
9. Shvitsov, D.M.; Koskin, A.P.; Stepanenko, S.A.; Ilyina, E.V.; Ayupov, A.B.; Bedilo, A.F.; Yakovlev, V.A. Hydrogen Production by N-Heterocycle Dehydrogenation over Pd Supported on Aerogel-Prepared Mg-Al Oxides. *Catalysts* **2023**, *13*, 334. <https://doi.org/10.3390/catal13020334>.
10. Philippov, A.; Nesterov, N.; Martyanov, O. Transfer Hydrogenation of Biomass-Like Phenolic Compounds and 2-PrOH over Ni-Based Catalysts Prepared Using Supercritical Antisolvent Coprecipitation. *Catalysts* **2022**, *12*, 1655. <https://doi.org/10.3390/catal12121655>.
11. Sorokina, S.A.; Kuchkina, N.V.; Grigoriev, M.E.; Bykov, A.V.; Ratnikov, A.K.; Doluda, V.Y.; Sulman, M.G.; Shifrina, Z.B. Cr-Zn/Ni-Containing Nanocomposites as Effective Magnetically Recoverable Catalysts for CO₂ Hydrogenation to Methanol: The Role of Metal Doping and Polymer Co-Support. *Catalysts* **2023**, *13*, 1. <https://doi.org/10.3390/catal13010001>.

References

1. Vojvodic, A.; Nørskov, J.K. New Design Paradigm for Heterogeneous Catalysts. *Nat. Sci. Rev.* **2015**, *2*, 140. [[CrossRef](#)]
2. Chakraborty, D.; Mullangi, D.; Chandran, C.; Vaidhyanathan, R. Nanopores of a Covalent Organic Framework: A Customizable Vessel for Organocatalysis. *ACS Omega* **2022**, *7*, 15275. [[CrossRef](#)] [[PubMed](#)]
3. Rudolph, M.A.; Isbrücker, P.; Schomäcker, R. Bifunctional Catalysts for the Conversion of CO₂ into Value-Added Products—Distance as a Design Parameter for New Catalysts. *Catal. Sci. Technol.* **2023**, *13*, 3469. [[CrossRef](#)]
4. Natarajan, S.; Manna, K. Bifunctional MOFs in Heterogeneous Catalysis. *ACS Org. Inorg. Au* **2024**, *4*, 59. [[CrossRef](#)] [[PubMed](#)]
5. Bogdan, V.I.; Kalenchuk, A.N.; Chernavsky, P.A.; Bogdan, T.V.; Mishanin, I.I.; Kustov, L.M. Synergistic Effect of Metal Components of the Low-loaded Pt-Ni-Cr/C Catalyst in the Bicyclohexyl Dehydrogenation Reaction. *Int. J. Hydrogen Energy* **2021**, *46*, 14532. [[CrossRef](#)]
6. Yuan, Y.; Yang, Y.; Zhu, G. Multifunctional Porous Aromatic Frameworks: State of the Art and Opportunities. *EnergyChem* **2020**, *2*, 100037. [[CrossRef](#)]
7. Huang, J.; Turner, S.R. Hypercrosslinked Polymers: A Review. *Polym. Rev.* **2017**, *58*, 1. [[CrossRef](#)]
8. Bounoukta, C.E.; Megías-Sayago, C.; Ivanova, S.; Ammari, F.; Centeno, M.A.; Odriozola, J.A. Pursuing Efficient Systems for Glucose Transformation to Levulinic acid: Homogeneous vs. Heterogeneous Catalysts and the Effect of Their Co-Action. *Fuel* **2022**, *318*, 123712. [[CrossRef](#)]

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