MDPI

Editorial

Advances in Hydrogen and Syngas Generation

Vladislav Sadykov [1,2]

1 Department of Heterogeneous Catalysis, Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia; sadykov@catalysis.ru; Tel.: +7-9139038312
2 Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russia

To solve problems related to global warming, environmental pollution, and green energy fields, a lot of research is now devoted to the catalysis of biofuels and biogas transformation into syngas and hydrogen. In this review, tasks and main trends in solving problems of designing efficient and stable coking active components of catalysts are carried out by tuning support nature, textural features, redox and acid/base properties, and preparation procedures the nature of supported metals/alloys (aimed at decreasing precious metals content or even using only Ni or Co), metal–support interaction, the addition of promoters as well as the design of structured catalysts, and modes of operation, reactor design (including integrated membrane reformers, sorption-enhanced water gas shift reactions, etc.) [1–4]. A summary of the content associated with selected papers devoted to these problems and published in *Energies* is presented below.

Abasaeed et al. [5] state that the role of La_2O_3 in addition to ZrO_2 and the Al_2O_3 support of Ni-based catalysts for the dry reformation of methane (DRM) was elucidated. La_2O_3 addition was shown to improve specific surface areas, dispersion, reducibility, metal–support interaction, and surface basic sites, which helps increase the hydrogen yield. However, carbon nanotubes were revealed in spent catalysts, which demonstrates that further efforts are needed to deal with this problem.

Mazhar et al. [6] studied co-loaded TiO_2 and $MgAl_2O_4$-supported catalysts in the DRM process. The basic nature of $MgAl_2O_4$ helped with the activation and dissociation of CO_2, while adding TiO_2 as a co-support provided strong metal–support interaction. This improved catalytic performance and provided stability. This agrees with results presented in the review paper by Sadykov et al. [1], where it was shown that the preparation of mesoporous supports comprised of $MgAl_2O_4$ or Mg-doped alumina with enhanced basicity allowed for the design of core-shell systems with a high working area of supported catalytic nanocomposite layers. This composition of complex oxides with high oxygen mobility and reactivity (perovskites, fluorites, and spinels) promoted by Ni + Ru increases their activity, thermal stability, and coking stability and decreases the content of rare earth elements.

Among oxide supports providing strong interaction with loaded metal nanoparticles and possessing the high oxygen mobility and reactivity required to suppress coking in fuel reforming reactions, the most popular are those based on doped ceria [7] or ceria-zirconia[1,8–10], . In the paper by Matus et al. [7], a series of mesoporous Ni-$M/Ce_{0.8}La_{0.2}O_{1.9}$ catalysts (M = Pt, Pd, Rh, and Re; molar ratio M/Ni = 0.003–0.012) were prepared and studied in the reaction of ethanol auto thermal reforming (ATR). The effect of the promoter on the functional properties of catalysts was studied, and the optimal composition of the catalyst 10Ni-0.4Re/$Ce_{0.8}La_{0.2}O_{1.9}$ was shown to provide a high hydrogen yield and stable performance in the ATR of C_2H_5OH.

In the series of papers [8–10], mixed ceria–zirconia oxides prepared in supercritical isopropanol streams were used as supports for Ni and tested in a methane dry reforming reaction. This method is considered very promising for the efficient production of nanomaterials. For mixed ceria–zirconia oxides, only the addition of complexing agents, such as acetylacetone into alcohol salts solution, allowed obtaining nanoparticles with the uniform

spatial distribution of Ce and Zr cations, thus providing high oxygen mobility required to prevent coking [1,8–10]. In the paper by Pavlova et al. [8], a series of 5%Ni-$Ce_xZr_{1-x}O_2$ (x = 0.3, 0.5, 0.7) catalysts have been prepared via one-pot solvothermal continuous synthesis in supercritical isopropanol and incipient wetness impregnation of $Ce_xZr_{1-x}O_2$ obtained by the same route. Despite a high dispersion of NiO and near-uniform distribution of Ni within Ce–Zr particles observed for the one-pot catalysts, they have shown a lower activity and stability in MDR as compared with impregnated ones. This is a result of a low Ni concentration in the surface layer due to the segregation of Ce and decoration of nickel nanoparticles with support species. This implies that a very strong metal–support interaction could result in hampering catalytic activity. On the other hand, in the paper by Bespalko et al. [9], for $Ni/Ce_{0.75}Ti_xZr_{0.25-x}O_{2-\delta}$ (x = 0.1, 0.2) catalysts prepared in supercritical isopropanol in CH_4 a dry reforming reaction, the highest conversion and maximum yield of products along with performance stability were achieved for the one-pot catalyst doped with titanium cations. Hence, such doping allows solving the problem of excessive decoration of Ni nanoparticles by oxidic fragments of support.

As mentioned in the paper by Fedorova et al. [10], for Ni-containing catalysts based on ceria–zirconia modified with Ti ($Ce_{0.75}Ti_xZr_{0.25-x}O_{2-\delta}$, x = 0.1, 0.2) or Nb + Ti ($Ce_{0.75}Ti_{0.05}Nb_{0.05}Zr_{0.15}O_2$) and prepared in supercritical conditions, their catalytic properties in methane dry reforming were studied in detail. It was shown that among impregnated samples, the most stable and active is the catalyst on support co-doped with Ti and Nb, while among the "one-pot" samples, the most active is the one on support doped with Ti. It has been shown that the turnover frequency (TOF) increases threefold upon the incorporation of titanium and niobium cations into mixed ceria–zirconia oxides. An inverse correlation between the values of the oxygen diffusion coefficients and the values of the specific catalytic activity was observed. This fact could be explained by the partial oxidation of metallic nickel particles and by the effects of nickel metal particle decoration with modified oxide support.

As an example of principally different type of catalytic support in the paper by Suboch and Podyacheva [11], bamboo-like nitrogen-doped carbon nanotubes (N-CNTs) were used to synthesize supported palladium catalysts (0.2–2 wt.%) for hydrogen production via gas phase formic acid decomposition. The beneficial role of nitrogen centers of N-CNTs in the formation of active isolated palladium ions and dispersed palladium nanoparticles was demonstrated. It was shown that although the surface layers of N-CNTs are enriched with graphitic nitrogen, palladium first interacts with accessible pyridinic centers of N-CNTs to form stable isolated palladium ions. The activity of Pd/N-CNTs catalysts is determined by the ionic capacity of N-CNTs and the dispersion of metallic nanoparticles stabilized on the nitrogen centers. The maximum activity was observed for the 0.2% Pd/N-CNTs catalyst consisting of isolated palladium ions. Similarly, high activity and stability were demonstrated in the formic acid decomposition by a single-atom Ni catalyst supported on N-doped porous carbon with active $Ni–N_4$ sites [2].

For the efficient transformation of fuels into syngas and hydrogen in industrial catalytic reactors, the processes of heat and mass transfer are to be optimized to prevent their limitations. This can be achieved by using structured heat-conducting substrates (honeycombs, stacks of microchannel planes, foams, gauzes, etc.) covered by thin layers of optimized active components [1,4]. In the processes of natural gas dry reforming, biofuels (ethyl acetate, glycerol, and turpentine oil) oxy-steam reforming in real concentrated feeds allows to provide their high conversions and syngas yield approaching equilibrium at short (~0.1 s) contact times with a temperature range of 700–800 °C [1]. This is impossible for reactors filled with granulated catalysts due to the pronounced effects of internal diffusion in granules, poor heat transfer from the reactor walls to the catalytic bed, and a high-pressure drop. In the water gas shift (WGS) reaction, the highest performance was obtained for the foam-structured catalyst since the tortuosity of the foam favored the axial and radial heat and mass transfer [4].

Another aspect of heat management in catalytic reactors is based on using heat exchangers to preheat the inlet feed by exit streams. This is especially efficient in the case of auto thermal reforming of biofuels on heat-conducting structured catalysts comprised of microchannel washes stacked into a cylinder, with the radial flow of the feed supplied into its central part and the heat-exchanger situated around the external reactor wall [1]. In the processes of the partial oxidation of a mixture of air with natural gas and liquid fuel (ethanol, ethyl acetate, and turpentine oil) into syngas at high flow rates (up to 40,000 h^{-1}) in this reactor, high syngas concentrations (50–60%) were obtained at optimized inlet feed compositions preheated only up to 50–100 °C.

To provide CO_2-free synthesis gas for jet fuel production, a sorption-enhanced water gas shift (WGS) process in cyclic breakthrough mode was studied in the isothermal packed bed microchannel reactor [12]. Here, a commercial $Cu/ZnO/Al_2O_3$ catalyst was combined with the potassium-promoted hydrotalcite-derived sorbent, and promising results were obtained for optimized parameters and reactor configuration, thus providing equilibrium CO conversion at 250 °C, even at contact times shorter than typical values.

For clear hydrogen production from ethanol, a promising approach is based on the integration of a catalytic reactor of EtOH steam reforming and H_2-permselective membrane [4]. This allows a shifting equilibrium of steam reforming reaction by removing hydrogen from the reaction zone as well as optimizing heat and mass transfer. Moreover, the analysis revealed that using a structured catalyst instead of the packed bed in the membrane reactor allowed the increase of both H_2 yield and recovery due to better catalytic activity as well as heat and mass transfer to the membrane.

Hence, tuning support texture, acid-base properties and its oxygen mobility/reactivity, transition metal–support interaction, heat and mass transfer in structured catalysts and reactors, and conjugating catalytic reactions with products separation provide the bases for achieving the highly efficient and inexpensive generation of hydrogen and syngas from biofuels required for solving the problems of the green energy field and global warming.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sadykov, V.; Simonov, M.; Eremeev, N.; Mezentseva, N. Modern Trends in Design of Catalysts for Transformation of Biofuels into Syngas and Hydrogen: From Fundamental Bases to Performance in Real Feeds. *Energies* **2021**, *14*, 6334. [CrossRef]
2. Bulushev, D.A. Advanced Catalysis in Hydrogen Production from Formic Acid and Methanol. *Energies* **2021**, *14*, 6810. [CrossRef]
3. Le, V.T.; Dragoi, E.-N.; Almomani, F.; Vasseghian, Y. Artificial Neural Networks for Predicting Hydrogen Production in Catalytic Dry Reforming: A Systematic Review. *Energies* **2021**, *14*, 2894. [CrossRef]
4. Meloni, E.; Martino, M.; Iervolino, G.; Ruocco, C.; Renda, S.; Festa, G.; Palma, V. The Route from Green H_2 Production through Bioethanol Reforming to CO_2 Catalytic Conversion: A Review. *Energies* **2022**, *15*, 2383. [CrossRef]
5. Abasaeed, A.; Kasim, S.; Khan, W.; Sofiu, M.; Ibrahim, A.; Fakeeha, A.; Al-Fatesh, A. Hydrogen Yield from CO_2 Reforming of Methane: Impact of La_2O_3 Doping on Supported Ni Catalysts. *Energies* **2021**, *14*, 2412. [CrossRef]
6. Mazhar, A.; Khoja, A.H.; Azad, A.K.; Mushtaq, F.; Naqvi, S.R.; Shakir, S.; Hassan, M.; Liaquat, R.; Anwar, M. Performance Analysis of TiO_2-Modified $Co/MgAl_2O_4$ Catalyst for Dry Reforming of Methane in a Fixed Bed Reactor for Syngas (H_2,CO) Production. *Energies* **2021**, *14*, 3347. [CrossRef]
7. Matus, E.; Sukhova, O.; Ismagilov, I.; Kerzhentsev, M.; Stonkus, O.; Ismagilov, Z. Hydrogen Production through Autothermal Reforming of Ethanol: Enhancement of Ni Catalyst Performance via Promotion. *Energies* **2021**, *14*, 5176. [CrossRef]
8. Pavlova, S.; Smirnova, M.; Bobin, A.; Cherepanova, S.; Kaichev, V.; Ishchenko, A.; Selivanova, A.; Rogov, V.; Roger, A.-C.; Sadykov, V. Structural, Textural, and Catalytic Properties of $Ni-Ce_xZr_{1-x}O_2$ Catalysts for Methane Dry Reforming Prepared by Continuous Synthesis in Supercritical Isopropanol. *Energies* **2020**, *13*, 3728. [CrossRef]
9. Bespalko, Y.; Smal, E.; Simonov, M.; Valeev, K.; Fedorova, V.; Krieger, T.; Cherepanova, S.; Ishchenko, A.; Rogov, V.; Sadykov, V. Novel $Ni/Ce(Ti)ZrO_2$ Catalysts for Methane Dry Reforming Prepared in Supercritical Alcohol Media. *Energies* **2020**, *13*, 3365. [CrossRef]
10. Fedorova, V.; Simonov, M.; Valeev, K.; Bespalko, Y.; Smal, E.; Eremeev, N.; Sadovskaya, E.; Krieger, T.; Ishchenko, A.; Sadykov, V. Kinetic Regularities of Methane Dry Reforming Reaction on Nickel-Containing Modified Ceria–Zirconia. *Energies* **2021**, *14*, 2973. [CrossRef]

11. Suboch, A.; Podyacheva, O. Pd catalysts supported on bamboo-like nitrogen-doped carbon nanotubes for hydrogen production. *Energies* **2021**, *14*, 1501. [CrossRef]
12. Stadler, T.J.; Barbig, P.; Kiehl, J.; Schulz, R.; Klovekorn, T.; Pfeifer, P. Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO: Investigation of Sorption Parameters and Reactor Configurations. *Energies* **2021**, *14*, 355. [CrossRef]