


## Editorial

# Applied Catalysis in Chemical Industry: Synthesis, Catalyst Design, and Evaluation

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Catalysis is a very important process with practical significance for sustainable development, energy production, environmental protection, food production, and water purification, among others, and catalytic processes produce almost 90% of the products in the chemical industry. Catalysis has great economic and strategic importance, making it a rapidly evolving field. In the face of significant contemporary challenges, it is essential to acquire fundamental knowledge about the structure and phenomena of catalytic surfaces and the relationships between a catalyst's composition, synthesis method, properties, and performance in industrial processes. Research is still needed to improve existing catalysts or to design new systems that can efficiently and selectively achieve a desired product through a given reaction. In this respect, surface science is necessary to gain deeper insight into the surface structure of catalysts, the chemical state of active sites and adsorbed species, the role of surface defects, and the mode of action of selected promoters. The combination of advanced ex situ experiments, the in situ characterisation of working catalysts, and theoretical studies leads to a better prediction of catalyst behaviour under specific process conditions and is required for the conscious design of catalysts with desirable properties.

This Special Issue contains 10 research articles devoted to designing and characterising heterogeneous catalytic systems for industrial chemical processes of high importance. The aim of this Special Issue is to collect the current state of knowledge, indicate areas that require further research, and demonstrate the direction of ongoing development work. Attention is focused on comprehensive experimental studies on the synthesis, characterisation, and performance evaluation of catalysts in various industrial processes. The Special Issue covers recent advances in the following topics: ammonia synthesis, the selective catalytic reduction of nitrogen oxides, hydrogen production from ethanol, and photocatalysis. The scope also includes an investigation of catalysts under conditions similar to industrial conditions, a comparison of the studied catalytic systems and the currently operating commercial systems, and a demonstration of the validity of their application in a given chemical process.

Hydrogen technologies are currently attracting significant attention from researchers and industry as new and prospective forms of processing and storing energy. The development of new and safe hydrogen storage and distribution methods is a critical problem that requires a solution. The method with the greatest prospect is based on bonding hydrogen with nitrogen to form an  $\text{NH}_3$  molecule. To correspond well with a hydrogen-based economy, it is crucial to develop catalytic systems that enable more sustainable methods of ammonia production capable of being conducted under milder conditions. Research is currently focused on developing active catalytic systems based on metals other than iron. These studies mostly focus on cobalt, and obtaining a technologically interesting cobalt catalyst with satisfactory activity, proper mechanical strength, adequate stability, and a favourable price requires optimising the catalyst's composition in terms of its active phase content, type and content of promoters; and the type and properties of the support, among other factors. In this respect, Patkowski et al. [1] investigated the effect of metallic cobalt content (ranging from 10 to 50 wt.%) on the structural parameters, morphology, crystal



**Citation:** Zybert, M. Applied Catalysis in Chemical Industry: Synthesis, Catalyst Design, and Evaluation. *Catalysts* **2023**, *13*, 607. <https://doi.org/10.3390/catal13030607>

Received: 10 March 2023  
Accepted: 15 March 2023  
Published: 17 March 2023



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structure, surface state, composition and activity of neodymium-oxide-supported cobalt catalysts. The activity strongly depended on the active phase's content due to the average cobalt particle size changes. The productivity per catalyst mass increased with the increase in cobalt content, while the TOF maintained constant. The TOF was only below average for the catalyst with the lowest Co content when the average Co particle size was below 20 nm. In this case, the predominance of strong hydrogen binding sites on the surface, which led to hydrogen poisoning, was observed. This effect was also related to the structural sensitivity phenomenon of the  $\text{NH}_3$  synthesis reaction carried out on cobalt observed by Zybert et al. [2]. These studies revealed a correlation between the reactivity of the cobalt surface during ammonia synthesis and the particle size of the active phase, which was supported by activated carbon. In turn, this strongly depends on the amount of the active phase. Increasing the amount of cobalt in the range of 4.9–67.7 wt.% resulted in a significant increase in the 3–45 nm range of the Co particle size. There is an optimal cobalt particle size (20–30 nm) that ensures the highest activity of the cobalt catalyst in the ammonia synthesis reaction. The observed size effect was most likely attributed to changes in the Co crystalline structure, i.e., the appearance of the hcp Co phase (which is more active than the fcc Co phase) for particles with a diameter of 20–30 nm. The addition of selected promoters was also required to increase the catalytic activity of this metal. Tarka et al. [3] explored the influence of barium content on the physicochemical properties and activity of a cobalt catalyst doubly promoted with cerium and barium. The barium promoter's dual modes of action (structural and modifying) were revealed; however, it strictly depended on the barium-to-cerium molar ratio. For the best performance of the CoCeBa system, the Ba/Ce molar ratio should be greater than unity. This results in a structural promotion of barium and a modifying action associated with the in situ formation of the  $\text{BaCeO}_3$  phase, primarily reflected in the differentiation of weakly and strongly binding sites on the catalyst's surface and changes in the cobalt surface's activity. The influence of alkali metals on ammonia synthesis catalysts is an ongoing debate. Electron transfers from the alkali to the active centres and the change in the surface structure or the crystallite sizes are often considered. In [4], Adamski et al. addressed the thermal stability problem of K-promoted cobalt molybdenum nitride catalysts as a critical factor in the practical application of catalysts. Catalysts based on the mixture of  $\text{Co}_3\text{Mo}_3\text{N}$  and  $\text{Co}_2\text{Mo}_3\text{N}$  phases were highly active in the ammonia synthesis process. Potassium promoted the catalytic activity, and the promoter content affected the phase composition. The potassium-free catalyst remained unchanged after the thermostability test, whereas the K-promoted catalysts lost their activity due to a decrease in surface area. The maximum surface area and activity were observed for the catalysts containing 0.8–1.3 wt.% of potassium, in which the concentration of the  $\text{Co}_2\text{Mo}_3\text{N}$  phase was the greatest.

Ammonia, which is easily available in nitric acid plants, is also used as a reducing agent in the selective catalytic reduction process ( $\text{NH}_3$ -SCR), where the reduction of  $\text{NO}_x$  with  $\text{NH}_3$  to form  $\text{N}_2$  and  $\text{H}_2\text{O}$  occurs. Saramok et al. [5] demonstrated the catalytic potential of low-cost, easy-to-prepare, iron-modified clinoptilolite in this process, which occurs within the range of 250–450 °C under near-industrial conditions, i.e., using a real tail gas mixture, which usually enters SCR reactors in nitric acid plants. The results of this study indicated that the presence of various iron species, including natural, isolated  $\text{Fe}^{3+}$  and the introduced  $\text{Fe}_x\text{O}_y$  oligomers, contributed to efficient  $\text{NO}_x$  reduction, especially in the high-temperature range in which the  $\text{NO}_x$  conversion rate exceeded 90%. The concentration of  $\text{N}_2\text{O}$  also decreased by 20% when compared to its initial concentration.

Effective methods for producing hydrogen from renewable resources are also being intensively investigated. The steam reforming of ethanol is one such promising method. Ulejczyk et al. [6] reported the development of a cobalt catalyst that produced hydrogen from a mixture of ethanol and water. This work revealed that excess water is beneficial and increases the concentration of  $\text{H}_2$  and  $\text{CO}_2$ . The metal catalyst was resistant to sintering and active phase migration, enabling a high ethanol conversion and a high hydrogen production efficiency. As carbon deposition is the primary deactivation mechanism for

catalysts in the ethanol steam reforming process, Greluk et al. [7] investigated the role of a potassium promoter on the stability and resistance to carbon deposit formation of nickel-based catalysts supported on  $\text{MnO}_x$ . The studies revealed that by modifying  $\text{Ni}/\text{MnO}_x$  with potassium, the catalyst stability can be improved for different  $\text{H}_2\text{O}/\text{EtOH}$  molar ratios under SRE conditions. The promoter inhibits the accumulation of carbon on the catalyst's surface, an effect resulting from the presence of potassium on the Ni surface. This leads to a decrease in the number of active sites available for methane decomposition and an increase in the rate of formed carbon's steam gasification.

In [8,9], the importance of designing reactors and catalysts for photocatalytic processes, which are essential for treating urban and industrial wastewater, was emphasized. García-Prieto et al. [8] conducted a kinetic study and modelled the heterogeneous photocatalytic degradation of aqueous ammonium/ammonia solutions using  $\text{SiO}_2$ -supported  $\text{TiO}_2$  in a pilot UV-C photoreactor; they considered both photolytic and photocatalytic processes. This paper presents a sensitivity analysis of the main variables and mechanisms for ammonia removal. It was stated that  $\text{NH}_4^+/\text{NH}_3$  can be decomposed by both photolysis and photocatalysis routes. However, the UV-C photocatalytic process was more effective for degrading  $\text{NH}_4^+/\text{NH}_3$  than the photolytic process. Pal et al. [9] demonstrated a unique templating method to anchor the  $\text{TiO}_2$ - $\text{SiO}_2$ -triblock copolymer composite on a cellulose matrix and obtained a pure, inorganic  $\text{TiO}_2$ - $\text{SiO}_2$  mesoporous nanostructure after burning out the cellulose template and the copolymer. The triblock copolymer acted as a structure-directing and mesopore-generating agent, whereas the  $\text{SiO}_2$  counterpart fixed the thermal stability of the anatase phase and the mesostructure, and the cellulose templating enhanced the specific surface area and porosity. The  $\text{TiO}_2$ - $\text{SiO}_2$  nanocomposites showed excellent thermal stability in the anatase phase and a much higher photocatalytic efficiency than the  $\text{TiO}_2/\text{SiO}_2$  without the cellulose templating, as did the standard reference catalyst, P25  $\text{TiO}_2$ .

Lastly, Woroszył-Wojno et al. [10] studied the problem of efficiently removing tar from the gas obtained after biomass pyrolysis. They used plasma-catalysis systems with nickel catalysts deposited on  $\text{Al}_2\text{O}_3$  and  $\text{CaO-Al}_2\text{O}_3$ . For the  $\text{NiO}/(\text{CaO-Al}_2\text{O}_3)$  catalyst, high conversions of toluene (as a tar imitator) were observed—up to 85%—which exceeded the results obtained without the catalyst. The products of the toluene decomposition reactions were not adsorbed onto its surface. The calorific value of the outlet gas was unchanged during the process and was higher than required for turbines and engines.

In summary, the articles published in this Special Issue are an excellent representation of the advances and current development directions in industrial catalysis. They emphasize the importance of progress in designing new catalysts and reactors for the advanced chemical industry. I would like to express my gratitude to the authors for their valuable contributions and to the reviewers for their time and many constructive comments, which helped improve the quality of the published papers. Special thanks to the Editorial Office of *Catalysts* for allowing me to serve as a Guest Editor. I hope that this Special Issue will greatly interest a broad group of readers, especially those involved in topics related to the synthesis and characterisation of catalytic systems for industrial chemical processes, heterogeneous catalysis, and surface science.

**Conflicts of Interest:** The author declares no conflict of interest.

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