

Recent Advances in Zeolites and Porous Materials Applications in Catalysis and Adsorption Processes

Maja Milojević-Rakić *  and Danica Bajuk-Bogdanović * 

Faculty of Physical Chemistry, University of Belgrade, 11000 Belgrade, Serbia

* Correspondence: maja@ffh.bg.ac.rs (M.M.-R.); danabb@ffh.bg.ac.rs (D.B.-B.)

Zeolites and porous materials are some of the most promising materials for various applications. Zeolites with highly ordered pore systems, high specific surface area and negatively charged framework enable the introduction of different functionalizing phases that can boost their performance. In addition, excellent adsorption and catalytic properties are often witnessed, with further research increasingly being transferred to the domain of biological applications.

The Special Issue “Zeolites and Porous Materials: Insight into Catalysis and Adsorption Processes” gives recent advances in developing zeolite-based and porous materials generally employed in adsorption and catalytic systems within ten research articles and three review contributions.

Zeolites and different porous materials are employed as perspective heterogeneous catalysts in several critical industrial and environmental processes. To contribute to a better understanding of factors affecting catalysis, Xian et al. studied Y zeolites with different textural properties as porous catalysts for the production of benzene, toluene, ethyl-benzene and xylene (BTEX) [1]. The hydrocracking of tetralin was investigated in a fixed-bed microreactor operated under high pressure. The main features affecting catalytic performance depended on aluminum content and the ratio between micro/mesoporosity in zeolite samples. A great extent of microporosity is beneficial for BTEX molecules synthesis, while the cracking was determined by thermodynamics and zeolites’ strong acidity, affecting equilibrium temperature [1].

Hierarchical zeolites may be synthesized to achieve mesoporosity development in addition to microporosity. Hierarchical structures are proposed for essential processes of fine chemicals production, methanol conversions, carbonization and biomass transformation. Different degrees of porosity may be induced through a consecutive fluorine/alkaline treatment of ZSM-5 zeolite, as presented by Guo et al. [2]. A specific delay in mesopore formation is associated with the fluorination procedure altering spontaneous porosity formation in an alkaline solution, enabling the prolonged formation of mesopores. Favorable electronic and steric conditions near aluminum sites play a dominant role in porosity development [2].

Textural properties are often addressed when hierarchical zeolites govern adsorption and catalysis. However, a hydrothermal synthesis procedure produces zeolites in powdered form. This drawback emerges due to pressure lowering in fixed-bed reactors operating in industrial processes. Different methods may be used to address this issue. Zeolites may be prepared in various geometries and particle sizes through the extrusion process and clay and oxides addition as binders. The development of hierarchical structures allows facilitated diffusion and mass transfer inside pores. A review by Asgar Pour et al. enabled insight into the extrusion procedure with binder as a new and emerging approach in shaping hierarchical zeolites conducted without binder [3]. This field requires novel investigations and refinements that would enable the preservation of initial zeolite structure and procedure scale-up to assist industry requirements [3].



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Post-synthetic procedures, such as desilication, dealumination and sequential treatments, may be applied to further increase zeolites' applicability. This is especially important for their performance in various industrial applications and petroleum processing. This specific tailoring of textural properties and active site evolution is assessed for different zeotypes, including MFI, FAU and SAPO frameworks. The modification of SSZ-32 zeolites by desilication and sequential desilication/dealumination steps treatments is proposed by Yang et al. [4]. The developed surface and acidity of modified zeolite supported on Pt were utilized for the catalytic hydroisomerization of long-chain n-alkanes. This study offers valuable insights into the fabrication of high-performance bifunctional catalysts by understanding the significance of the catalyst support in the hydroisomerization of long-chain n-alkanes. Moreover, it suggests an alternate approach for augmenting the low-temperature performance of diesel/lubricating oils in petroleum processing [4].

Petroleum processing extensively uses catalysts of large porosity, which are afterward disposed of without extensive recycling. This brings the necessity of dealing with spent ZSM-5 catalysts for methanol conversion to hydrocarbons. A route proposed by Yong et al. involves partial acid-induced dealumination of spent zeolite combined with alkali treatment to increase the specific surface of the resulting material [5]. Although treated spent adsorbent maintains the MFI framework, the dealumination procedure depends on acid use. Oxalic acid may be selected as it removes both framework and non-framework aluminum, increasing porosity and surface area. Furthermore, alkali treatment changes spent catalysts' morphological features, giving rise to its proposed adsorption performance for p-xylene and n-hexane removal. These findings support the idea of subsequent environmental application of spent catalysts/adsorbents, a novel perspective in sustainable solutions [5].

The production of pyridine is an example of a process that requires specific physicochemical characteristics and porosity of the catalysts. Pala-Rosas et al. investigated the catalyzed reaction of acrolein/ammonia amino-cyclization using a group of FAU zeolites with different Si/Al [6]. The catalytic activity showed that acrolein conversion favors higher Al content in Y zeolite in line with an acidity increase. Catalysts with substantial surface areas and developed porosity produced pyridines yield inversely dependent on total acidity. The high selectivity for 3-picoline was associated with an equal number of Brønsted and Lewis sites. On the other hand, a greater extent of Lewis acidity yields predominantly pyridine products. A detailed deactivation study supports the premise of the crucial role of zeolite large pore volume and BET surface affecting deactivation rate. These textural properties enable polyaromatics deposition on the catalyst, which lowers activity [6].

Catalyst deactivation due to coke deposition poses a significant problem in industrial processes. To investigate coke formation, ethanol dehydration was investigated as a model process by Verdeş et al. [7]. The 12-tungstophosphoric acid (HPW) and its Cs salt supported on SBA-15 support were employed as catalysts, and the additional effect of Pb doping was analyzed. Porous catalyst support enables higher conversion and selectivity and lowers coke formation. Pb doping has different effects; conversely, it supports coke formation for HPW catalysts while disabling coke formation when Cs is present. Thus, a co-doping procedure for catalysts and their dispersion over support may benefit industrial dehydration processes [7].

Porous materials are efficiently implemented in environmentally significant reactions, such as eliminating nitrogen oxides. For this purpose, a selective catalytic reduction (SCR) of nitrogen oxides with ammonia is recognized as a highly efficient method. Zhao et al. investigated the role of copper sites in the nitrogen oxide SCR with ammonia [8]. Several porous materials were tested to support copper catalytic sites: SSZ-13, ZSM-5 and Beta zeolites, with a targeted Si/Al ratio of 14 and Cu/Al set at 0.4. The amount of isolated Cu^{2+} ions in the catalysts determines Lewis acidity and is related to nitrate ions as intermediates in SCR at low temperatures. On the other hand, Cu^+ , along with Brønsted acid sites, is

associated with SCR performance at high temperatures. Cu-containing SSZ-13 zeolite performed optimally in the ammonia SCR process [8].

Another aspect of zeolites' application to atmospheric processes may be seen through vapor extraction with a perspective of clean water production. Such a specific design may be seen in a composite setup consisting of a 13X zeolite and graphene binder proposed by Gildernew et al. [9]. Tailoring of substrate structure to suit efficient sorption performance was accomplished by polymer guarding pore network during binder infiltration. Obtained composites with sustained channeling displayed a specific heat flux of around 7700 W/kg, with substantial improvement in mass transport [9].

Expensive and tedious procedures for synthesizing porous materials can fail to produce materials with substantial adsorption capacity and/or catalytic efficiency. Thus, the researcher's focus is shifted to utilizing or modifying readily available and affordable natural materials.

The porosity of catalysts is essential for the aforementioned acid/base catalysis and the redox processes sensitive to catalysts' textural properties. The oxygen reduction reaction is of utmost importance for fuel cell design. Bio-based carbons are at the forefront of this investigation due to their environmental soundness, conductivity, ease of doping and textural features, as summarized by Rupar et al. [10]. Biopolymers are selected as readily available precursors for carbon-designed ORR electrode materials. The preparation procedure for these functional carbons governs porosity development and influences their performance to a large extent [10].

Adsorption on zeolites and other porous materials is successfully applied both for pollutants removal from the environment and as support of pharmaceuticals. Organic dyes are often used as model compounds to test the availability of active sites on designated adsorbents. Different pristine silicate samples containing bentonite, kaolin, clinoptilolite and diatomite were applied for methylene blue removal [11]. Extensive dye removal was accomplished with the bentonite sample reaching a capacity of nearly 240 mg/g. To make a sustainable circle of contaminants removal from water, saturated adsorbents were carbonized in an inert atmosphere. This procedure provided a nitrogen-doped carbonaceous surface layer at the bentonite surface, producing a carbon/silicate composite. This novel composite sample was used as electroactive material for oxygen reduction under alkaline conditions. As the reduction pathway was assessed as a two-electron reaction, the main species were hydroperoxyl radicals, which can degrade methylene blue. After 60 min of reduction in the electrochemical reactor, only 30% of the dye remained. The proposed process of adsorption, carbonization of saturated adsorbent and production of electrode material for oxidative degradation of pollutants reported by Popadić et al. is a perspective route for sustainable environmental solutions focusing on porous materials [11].

Natural aluminosilicates are often functionalized as their synthetic counterparts to suit different pharmaceutical applications. Modified phillipsite samples can be treated to attain monolayer and bilayer coverage with surfactants—octadecyldimethylbenzylammonium chloride and dodecylamine as proposed by Smiljanić et al. [12]. Composites obtained in such procedures are used as supports for the non-steroid anti-inflammatory drug diclofenac sodium. A homogeneous adsorption site distribution is accomplished as adsorption isotherms follow the Langmuir model, with substantial drug loading of nearly 40 mg/g. Phillipsite samples functionalized with benzyl or pyridine groups are promising materials for pharmaceutical delivery systems [12].

To further highlight the diversity of zeolite features and applicability, a critical review by Mijailović et al. gives an overview of zeolite adsorption performance for pharmaceuticals [13]. This feature is addressed in two aspects—zeolites employed as efficient environmental adsorbents for pharmaceutical waste and, at the same time, promising drug delivery systems due to their favorable adsorption capacities and drugs' sustained release. Zeolites' aforementioned applications indicate the necessity of thermodynamic and kinetic investigation following the adsorption process. Detailed study of intermolecular interactions supported

by computation methods may guide future investigations of adsorption-aided solutions to environmental and pharmaceutical issues [13].

To conclude, the research and review papers published in the “Zeolites and Porous Materials: Insight into Catalysis and Adsorption Processes” issue address novel trends in industrial and environmental processes enabled by adsorption and/or catalysis involving porous materials. All contributions are valuable in the growing zeolite and porous materials studies field and will hopefully inspire new advanced solutions. As guest editors, we would like to thank all authors for their contributions and the Editorial team for their support during the realization of this issue.

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