



## Editorial Synthesis and Application of Zeolite Catalysts

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Zeolites play a central role in many industrial and chemical engineering processes involving solid catalysts, which have attracted a great deal of attention from chemists, chemical engineers, and materials scientists due to their fascinating features. Benefitting from the development of synthetic technologies, various engineered zeolites have been newly designed and synthesized. Zeolites with rationally designed size, shape, and connectivity of micropores have been synthesized with the aid of new organic structure-directing agent, which can change the framework structures and, thereby, the physicochemical properties. Zeolites simultaneously having different scales of porosity have also been synthesized, and the resultant hierarchically nanoporous structure paved a new express way to the diffusion-limited applications. The innovation of synthetic technologies also enables a synthesis of zeolites with chiral structures in recent years.

A great deal of research regarding the synthesis of zeolites, with better functions, as well as their catalytic applications, has been performed so far, and broad knowledge has been accumulated over the decades, which guided the current industrial society to a brighter and greener world. In this respect, the present Special Issue is aimed to report the latest research advances in the synthesis and characterization of zeolites and their catalytic applications. In total, 24 articles with experimental and theoretical approaches including two review articles were contributed on this issue.

Zeolites can be used as the solid catalysts or supporting materials for incorporation of metal nanoparticles. The H<sup>+</sup>-exchanged zeolite exhibited superb catalytic performance for catalytic copyrolysis of cork oak with waste polymer, in which HBeta zeolite showed fast pyrolysis activity due to the strong acidity and the appropriate pore diameter [1]. It was also confirmed that the formation of hierarchically nanoporous structure in HBeta zeolite by desilication is useful for giving high catalytic activity in the hydrocracking of large aromatic hydrocarbons, which can be attributed to the good dispersion of Ni<sub>2</sub>P catalysts and efficient accessible acid sites [2]. The acidic zeolite with MFI framework having a hierarchically nanoporous membrane structure exhibited high surface area and good diffusivity, resulting in the high catalytic performance in n-dodecane cracking [3]. Although the conventional MFI zeolite has a solely microporous structure, the acidic MFI zeolite exhibited a very prolonged catalytic lifetime in the dehydration of small alcohol (e.g., ethanol) to produce ethylene in the bench scale reaction [4]. In the same catalytic reaction, the nanosheet MFI zeolite with hierarchical mesoporosity can support high loading of  $WO_x$  nanoparticles with a very homogeneous distribution, which exhibited high and stable catalytic activity during the ethanol dehydration to ethylene [5]. The strong acidity of MFI zeolite was also useful for the methanol to propylene reaction, but the catalytic lifetimes were not sufficiently long due to too strong acidity [6]. Propylene was also produced from the propane dehydrogenation using Pt nanoparticles-supported nanosheet silicalite-1 zeolite, in which the propylene selectivity can be achieved more than 95% due to the suppression of side catalytic cracking by strong acid sites [7].

Additional metal-incorporated zeolites have been investigated in various catalytic processes. Cu-Fe exchanged SAPO-34 was investigated in selective catalytic reduction in NO<sub>x</sub> with NH<sub>3</sub>, in which the bimetal-exchanged SAPO-34 exhibited superior catalytic activity to the single metal-exchanged SAPO-34 [8]. Cu-exchanged MFI zeolite was theoretically investigated in the N<sub>2</sub>O decomposition reaction, and the DFT study proposed



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**Copyright:** © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the formation of NO is energetically favorable route for constructing a plausible reaction mechanism [9]. Various noble metal ions such as Ru, Rh, and Pd can also be incorporated to the MOR zeolite, which were used for the catalytic transfer hydrogenolysis of glycerol to produce 2-isopropoxy-propan-1-ol as a single product [10]. Similarly, Pt-incorporated USY zeolite exhibited bifunctional catalytic activity in the selective hydrocracking of decalin for upgrading low-quality real distillate feeds [11]. The acidity in Pt-loaded MRE zeolite was controlled by the addition of pseudoboehmite, by which the Pt-loaded hybrid catalyst showed very high catalytic activity in ring enlargement reaction of methylcyclopentane to produce benzene with high selectivity [12]. The acidity of MFI zeolite was also controlled by the impregnation of ZnO or ZnS, by which the yield of liquid hydrocarbons could be controlled during the conversion of low molecular-weight alkanes containing propane and butane [13]. Titanium-incorporated silicalite-1 (TS-1) was synthesized into a hierarchically nanoporous structure by carbon xerogel method, and the resultant hierarchical zeolite exhibited outstanding catalytic performance in oxidative desulfurization of bulky sulfur compounds, such as dibenzothiophene and 4,6-dimethyldibenzothiophene, due to the presence of mesoporous structures [14]. Natural zeolite was used for impregnation of Mn, by which the resultant zeolite exhibited high efficiency in economic removal of volatile organic compounds, such as acetaldehyde and ozone under non-thermal plasma reactor [15]. Ag-encapsulated MFI zeolite is known as a useful adsorbent for Xe separation from Xe/Kr mixture, but the contamination by chloride compounds deactivates the adsorption sites of Ag nanoparticles. The role of chloride compounds on the deactivation of Ag-MFI zeolite and the possibility for regeneration by temperature swing adsorption were investigated [16].

Synthesis research on the MFI zeolite was also considered in this Special Issue, in which the effect of ethanol on the morphology and textural properties was deeply investigated [17]. A method to obtain naturally occurring  $TiO_2$  on zeolite composite from green tuff was developed, which could be used as a natural photocatalyst [18]. In addition, two review articles focusing special attention on the synthesis of hierarchical zeolites and catalytic advances were reported [19,20]. Particular focus was laid on the green synthesis of hierarchical zeolites [19], and the catalytic applications of hierarchical zeolite nanosheets on the production of light olefin were comprehensively reviewed [20].

Not only the zeolite catalysts, but also other nanoporous catalysts were investigated in this Special Issue.  $Co_3O_4$  nanoparticle-functionalized mesoporous silica was synthesized via a spontaneous route, which exhibited excellence removal performance and degradation ability for methylene blue due to the large mesoporosity and, thus, high dispersion of  $Co_3O_4$  nanoparticles [21]. Nanoporous  $Al_2O_3$  was used as the catalyst as well as the support for other metal nanoparticles. MgO impregnated  $Al_2O_3$  was investigated in the catalytic decomposition of hydrofluorocarbon, which confirmed that the weak Lewis acid site of  $Al_2O_3$  and basic sites of Mg were advantageous for the high activity and catalyst lifetime [22]. NiO was also supported on  $SiO_2-Al_2O_3$  support via metal oxide-support interaction, in which the medium interaction strength preserving the active nickel oxides and acid sites was important for achieving optimal catalytic activity in ethylene oligomerization [23]. Pt metal nanoparticle embedded Co-based metal organic framework was pyrolyzed to porous carbon Pt@Co/C composite, which could be used as the Fischer-Tropsch catalyst achieving 35% CO conversion with various hydrocarbons at low pressure [24].

The diversity and broadness of all contributions in this Special Issue proved the prominence of nanoporous materials in many chemical applications including heterogeneous catalysis and environmental solution. Particular emphasis was laid on the zeolite-based catalysis in many chemical conversions. The contributed catalytic conversions have been investigated for several decades, but the importance can be continued in the future as the research on these themes is still actively and enthusiastically in progress.

Finally, we sincerely thank all contributors for their valuable works, as well as the editorial teams of *Catalysts*. We hope that this Special Issue inspires many worldwide

researchers in the catalysis of nanoporous materials including zeolites, nanoporous metal oxides, and metal organic frameworks.

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## References

- 1. Park, Y.; Lee, B.; Watanabe, A.; Lee, H.; Lee, J.; Kim, S.; Han, T.; Kim, Y. Catalytic Copyrolysis of Cork Oak and Waste Plastic Films over HBeta. *Catalysts* **2018**, *8*, 318. [CrossRef]
- Kim, Y.; Cho, K.; Lee, Y. Structure and Activity of Ni<sub>2</sub>P/Desilicated Zeolite β Catalysts for Hydrocracking of Pyrolysis Fuel Oil into Benzene, Toluene, and Xylene. *Catalysts* 2020, 10, 47. [CrossRef]
- 3. Diao, Z.; Cheng, L.; Hou, X.; Rong, D.; Lu, Y.; Yue, W.; Sun, D. Fabrication of the Hierarchical HZSM-5 Membrane with Tunable Mesoporosity for Catalytic Cracking of n-Dodecane. *Catalysts* **2019**, *9*, 155. [CrossRef]
- Moon, S.; Chae, H.; Park, M. Dehydration of Bioethanol to Ethylene over H-ZSM-5 Catalysts: A Scale-Up Study. Catalysts 2019, 9, 186. [CrossRef]
- Kim, H.; Numan, M.; Jo, C. Catalytic Dehydration of Ethanol over WO<sub>x</sub> Nanoparticles Supported on MFI (Mobile Five) Zeolite Nanosheets. *Catalysts* 2019, 9, 670. [CrossRef]
- 6. Feng, R.; Chen, K.; Yan, X.; Hu, X.; Zhang, Y.; Wu, J. Synthesis of ZSM-5 Zeolite Using Coal Fly Ash as an Additive for the Methanol to Propylene (MTP) Reaction. *Catalysts* **2019**, *9*, 786. [CrossRef]
- Wannapakdee, W.; Yutthalekha, T.; Dugkhuntod, P.; Rodponthukwaji, K.; Thivasasith, A.; Nokbin, S.; Witoon, T.; Pengpanich, S.; Wattanakit, C. Dehydrogenation of Propane to Propylene Using Promoter-Free Hierarchical Pt/Silicalite-1 Nanosheets. *Catalysts* 2019, 9, 174. [CrossRef]
- Doan, T.; Dam, P.; Nguyen, K.; Vuong, T.; Le, M.; Pham, T. Copper-Iron Bimetal Ion-Exchanged SAPO-34 for NH<sub>3</sub>-SCR of NO<sub>x</sub>. *Catalysts* 2020, *10*, 321. [CrossRef]
- Gao, C.; Li, J.; Zhang, J.; Sun, X. DFT Study on Mechanisms of the N<sub>2</sub>O Direct Catalytic Decomposition over Cu-ZSM-5: The Detailed Investigation on NO Formation Mechanism. *Catalysts* 2020, 10, 646. [CrossRef]
- Singh, B.; Kim, Y.; Kwon, S.; Na, K. Selective Catalytic Transfer Hydrogenolysis of Glycerol to 2-Isopropoxy-Propan-1-Ol over Noble Metal Ion-Exchanged Mordenite Zeolite. *Catalysts* 2019, *9*, 885. [CrossRef]
- 11. Oliveira Soares, L.; Castellã Pergher, S. Influence of the Brønsted Acidity on the Ring Opening of Decalin for Pt-USY Catalysts. *Catalysts* **2019**, *9*, 786. [CrossRef]
- 12. Park, Y.; Kim, Y.; Kim, J.; Park, Y.; Choi, Y.; Kim, J.; Jeon, J. Ring Enlargement of Methylcyclopentane over Pt/(HZSM-48+pseudoboehmite) Catalysts. *Catalysts* **2019**, *9*, 531. [CrossRef]
- Erofeev, V.; Khasanov, V.; Dzhalilova, S.; Reschetilowski, W.; Syskina, A.; Bogdankova, L. Acidic and Catalytic Properties of Zeolites Modified by Zinc in the Conversion Process of Lower C<sub>3</sub>–C<sub>4</sub> Alkanes. *Catalysts* 2019, *9*, 421. [CrossRef]
- 14. Pei, X.; Liu, X.; Liu, X.; Shan, J.; Fu, H.; Xie, Y.; Yan, X.; Meng, X.; Zheng, Y.; Li, G.; et al. Synthesis of Hierarchical Titanium Silicalite-1 Using a Carbon-Silica-Titania Composite from Xerogel Mild Carbonization. *Catalysts* **2019**, *9*, 672. [CrossRef]
- 15. Song, M.; Ryu, H.; Jung, S.; Song, J.; Kim, B.; Park, Y. A Hybrid Reactor System Comprised of Non-Thermal Plasma and Mn/Natural Zeolite for the Removal of Acetaldehyde from Food Waste. *Catalysts* **2018**, *8*, 389. [CrossRef]
- Monpezat, A.; Couchaux, G.; Thomas, V.; Artheix, A.; Deliere, L.; Gréau, C.; Topin, S.; Coasne, B.; Roiban, L.; Cardenas, L.; et al. Effect of Chlorine-Containing VOCs on Silver Migration and Sintering in ZSM-5 Used in a TSA Process. *Catalysts* 2019, 9, 686. [CrossRef]
- 17. Liu, X.; Sun, Y. Effect of Ethanol on the Morphology and Textual Properties of ZSM-5 Zeolite. Catalysts 2020, 10, 198. [CrossRef]
- Fujita, T.; Ponou, J.; Dodbiba, G.; Anh, J.; Lu, S.; Hamza, M.; Wei, Y. Removal of Banana Tree Fungi Using Green Tuff Rock Powder Waste Containing Zeolite. *Catalysts* 2019, *9*, 1049. [CrossRef]
- 19. Pan, T.; Wu, Z.; Yip, A. Advances in the Green Synthesis of Microporous and Hierarchical Zeolites: A Short Review. *Catalysts* **2019**, *9*, 274. [CrossRef]
- 20. Dugkhuntod, P.; Wattanakit, C. A Comprehensive Review of the Applications of Hierarchical Zeolite Nanosheets and Nanoparticle Assemblies in Light Olefin Production. *Catalysts* **2020**, *10*, 245. [CrossRef]
- 21. Zha, Z.; Zhu, W.; Chen, F.; Qian, J.; Liu, X.; Sun, L.; Wu, Z.; Chen, Z. Facile Synthesis of Co<sub>3</sub>O<sub>4</sub> Nanoparticle-Functionalized Mesoporous SiO<sub>2</sub> for Catalytic Degradation of Methylene Blue from Aqueous Solutions. *Catalysts* **2019**, *9*, 809. [CrossRef]
- 22. Andrew, C.M.A.; Sheraz, M.; Anus, A.; Jeong, S.; Park, Y.; Kim, Y.; Kim, S. Effect of Mg/Al<sub>2</sub>O<sub>3</sub> and Calcination Temperature on the Catalytic Decomposition of HFC-134a. *Catalysts* **2019**, *9*, 270. [CrossRef]
- Yoon, J.; Park, M.; Kim, Y.; Hwang, D.; Chae, H. Effect of Metal Oxide–Support Interactions on Ethylene Oligomerization over Nickel Oxide/Silica–Alumina Catalysts. *Catalysts* 2019, 9, 933. [CrossRef]
- 24. Panda, A.; Kim, E.; Choi, Y.; Lee, J.; Venkateswarlu, S.; Yoon, M. Phase Controlled Synthesis of Pt Doped Co Nanoparticle Composites Using a Metal-Organic Framework for Fischer–Tropsch Catalysis. *Catalysts* **2019**, *9*, 156. [CrossRef]