

Editorial

# Catalysis on Zeolites and Zeolite-like Materials

Wladimir Reschetilowski

Fakultät Chemie und Lebensmittelchemie, Technische Universität Dresden, Helmholtzstraße 14,  
01069 Dresden, Germany; wladimir.reschetilowski@tu-dresden.de

When the Swedish mineralogist Axel F. Cronstedt (1722–1765) described the previously unknown mineral group of hydrous framework silicates for the first time in 1756 [1,2], he could not have imagined the exemplary development that this mineral class, which he called “Zeolite”, would undergo over the following centuries. After the synthesis of zeolites on a technical scale became possible in the middle of the 20th century, based on systematic investigations by Richard M. Barrer (1910–1996) [3], the actual triumphant march of zeolites began. Today, they are used extremely widely as effective ion exchangers, adsorbents and catalysts in numerous branches of industry [4]. The first use of zeolite catalysts occurred 65 years ago, when researchers from Union Carbide Corp. tested zeolite Y as an isomerization catalyst. Over the past decades, progress in zeolite synthesis has enabled the discovery of new zeolite types, allowing for the development of new catalytic processes in petrochemical industries [5]. Moreover, new tools for zeolite modification have allowed for additional applications of zeolite-based catalysts in the field of environmental catalysis [6,7]. The development of new mesoporous and micro-/mesoporous or zeolite-like materials, such as metal–organic frameworks or intergrowth zeolites, as well as progress in computational chemistry and solid-state characterization techniques, have shown that the potential of ordered pore materials is still far from exhausted [8–10]. This is demonstrated by the papers in this Special Issue, “Catalysis on Zeolites and Zeolite-like Materials”, in which the latest developments and recent advances in the synthesis, characterization and application of zeolites or zeolite-like materials as catalysts are presented by renowned scientists. A total of eleven contributions have been published in this Special Issue, which are listed below under contribution 1 to contribution 10 and presented here in summary.

In their study, Zhang et al. (contribution 1) described the preparation of the hydrocracking catalysts by kneading and extruding the mixture of 10 wt.-% of industrially modified Y zeolites with a hierarchical structure, commercial alumina, nickel nitrate, and molybdenum oxide. The obtained bifunctional catalysts were characterized using XRD, N<sub>2</sub> adsorption–desorption, SEM, TEM, <sup>27</sup>Al-/<sup>29</sup>Si-NMR, in situ pyridine-FTIR, and NH<sub>3</sub>-TPD techniques. Finally, the catalysts were further investigated during the hydrocracking of the light diesel oil under different temperatures. It was found that even a small amount of specifically modified Y zeolite in the hydrocracking catalyst plays a key role, resulting in the selective hydrogenation of naphthalene and further ring-opening activity. The mesoporous structure of the zeolites provided an effective interface and improved the accessibility of acid sites to bulky reactants.

Li et al. (contribution 2) investigated the hierarchical high-silica USY zeolites with different micro-/mesoporous structures and Si/Al ratios in the catalytic cracking of methylcyclohexane to reveal the synergistic effects of acid sites and porous structures (“active region”). Indeed, as the catalytic results showed, the USY zeolites used had increased numbers of accessibly strong Brønsted acid sites and greatly enhanced diffusion ability due to the hierarchical pore structure, resulting in mainly monomolecular, protolytic ring-opening cracking and less bimolecular hydrogen transfer. In addition, zeolite acidity has been shown to influence the selectivity of cracking products: the increased acid strength can enhance the reactivity of heptane and heptene from the primary ring-opening, as well



**Citation:** Reschetilowski, W. Catalysis on Zeolites and Zeolite-like Materials. *Catalysts* **2024**, *14*, 128. <https://doi.org/10.3390/catal14020128>

Received: 7 January 2024

Revised: 2 February 2024

Accepted: 2 February 2024

Published: 7 February 2024



**Copyright:** © 2024 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/>).

as the  $\beta$ -scission from the C–H bond cleavage, resulting in fewer C7 products and more i-C4 and C3 products.

Chapellière et al. (contribution 3) synthesized a series of HY zeolites with increasing mesopore volume, characterized by various physical–chemical methods, and tested them for n-hexane cracking. The generation of mesoporosity influenced several other important parameters, such as the surface acidity and the formation of extra-framework aluminum. The catalytic cracking of n-hexane at different temperatures, coupled with kinetic analysis, proved to be a valuable tool to study the acidity of zeolites. The fact that n-hexane cracking proceeds through protolytic cracking over a wide range of operating conditions allows the use of the analytical form of the first-order rate equation. The rate equation contains three catalytic descriptors: the change in acid strength (deprotonation energy), the number of Brønsted acid sites, and the porosity through the effectiveness factor  $\eta$ .

Jaroszewska et al. (contribution 4) reported on the hydroisomerization of n-heptane using bifunctional Pt(Pd) catalysts supported on hierarchical Al-SBA-15/zeolite composites (where zeolite is  $\beta$ , mordenite or ZSM-5). All the catalysts were prepared by the extrusion of the mixture of powdered AlSBA-15/zeolite material with a binder (i.e., 20 wt.-% of boehmite), followed by impregnation with metal components (0.5 wt.-%). The composites showed higher activity in isomerization compared to Pt/AlSBA-15. The enhanced isomerization efficiency was explained by the appropriate metallic and acidic functions, as well as suitable transport properties. Combining Pt and Pd led to a notable synergetic effect, which exceeded that of the additive contribution of Pt and Pd in the metallic phase. Over bimetallic Pt-Pd/AlSBA-15- $\beta$ , the high yields of isomers (68 wt.-%) were observed, compared to 50 wt.-% for a control catalyst.

The conversion of different biogenic feedstocks to hydrocarbons is a major challenge when ensuring hydrocarbon and fuel supply despite the heterogeneity of this feed. In their study, Gille et al. (contribution 5) used different oxygenate model feeds, such as alcohols, aldehydes, carboxylic acids and esters, which were converted at 500 °C and 5 barg H<sub>2</sub> using H-ZSM-5 zeolite catalysts with various Si/Al ratios to identify the relationship between the feed structure and the final product distribution. In conclusion, for all oxygenates, after deoxygenation, an initial olefin distribution forms, which is typical for the respective carbon chain length and type of the functional group. This olefinic backbone is converted in a subsequent reaction network, as described in the hydrocarbon pool concept for alcohol conversion. The particular novelty of the findings is the systematic extension of the concept to other feedstocks with oxygen-containing functional groups in biomass conversion.

Nadolny et al. (contribution 6) investigated the influence of remaining acid sites in Ni-containing aluminosilicates on the formation of highly octene isomers in the heterogeneously catalyzed oligomerization of n-butene. In this study, it was shown that some octene isomers are exclusively formed via an acid-catalyzed mechanism as a result of methyl group migration at the surface of a mesoporous catalyst. Specifically, the isomers 4,4-dimethylhexene (4,4-DMH) and 3-ethyl-2-methylpentene (3E-2MP) exhibit a systematic correlation compared to the amount of 3,4-dimethylhexene (3,4-DMH) formed at acid sites. By using this aluminosilicate for oligomerization after impregnation with a nickel precursor, the amount of 4,4-DMH and/or 3E-2MP indicates the extent of acid site coverage by nickel ions. As a result, predictions can be made about the further catalyst activity in industrial operation.

The following study by Han et al. (contribution 7) concerns Cu-exchanged mordenite zeolites for the selective oxidation of methane to methanol. The focus is on investigating the effects of Al distribution on methane oxidation over these zeolite catalysts, which provide an effective way to detect the difference in activity between mononuclear and polynuclear Cu-oxo species. It was shown that the Cu-oxo clusters derived from the Al pair sites were more reactive than the CuOH species grafted onto the isolated Al sites, which is consistent with on-site spectroscopic characterization in the ultraviolet and visible ranges and density functional theory calculations. Further theoretical analysis of the first C–H bond cleavage

in methane on these Cu-oxo species revealed that the stabilization of the methyl group formed was the predominant factor in determining the reactivity of methane oxidation.

Kohler et al. (contribution 8) investigated the catalytic effectiveness of Sn-Beta zeolite in the conversion of lignocellulosic biomass-derived glucose and xylose into lactic and levulinic acid. The reactions were carried out in a batch reactor using water as the solvent. When biomass-derived sugar solutions were tested, the yields of lactic acid were significantly higher than those from the optimized model solution experiments. These biomass-derived sugar solutions contained residual levels of CaSO<sub>4</sub> from the neutralization step of the hydrolysis process. Through further investigations, it was found that the sulfate ions increased the Brønsted basicity and the calcium increased the Lewis acidity of the reaction solution, and that the combination of both effects increased the conversion of the original sugars into lactic acid. These effects were verified by testing other organic bases to isolate the Brønsted acid neutralization effect and the Lewis acid enhancement effect.

Knoevenagel condensation is a special case of aldol condensation and one of the most established carbon coupling reactions for the synthesis of fine chemicals and biologically active substances [11]. Grass et al. (contribution 9) conducted a comparative study of the catalytic activity of layer-like zeolite X from three different synthesis routes in a liquid-phase Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl trans- $\alpha$ -cyanocinnamic acid. It was shown that the charge-balancing cations (Na<sup>+</sup> and K<sup>+</sup>) and the morphological properties had a strong influence on the apparent reaction rate and degree of conversion. The highest initial reaction rate could be found for the layer-like zeolite X synthesized by the additive-free route in the potassium form. In most cases, the potassium-exchanged zeolites enabled higher maximum conversions and higher reaction rates compared to the zeolite X catalysts in sodium form.

SAPO-34 molecular sieves have excellent form selection and controllability in the chemical industry, as well as being one of the best industrial catalysts for converting methanol to olefin [12]. Han et al. (contribution 10) described a new route to the ionothermal synthesis of triclinic SAPO-34. The results show that the formation mechanism of the hierarchical pores is in accordance with Ostwald ripening theory, and the accumulation of grains constitutes the existence of mesopores and macropores. The crystallization temperature, ionic liquid type, and organic amines can effectively change the morphology and crystallinity of the SAPO-34 molecular sieve. A lower crystallization temperature is beneficial for the formation of flaky crystals, while a higher crystallization temperature is beneficial for the generation of large-size cubic crystals. In addition, it can be proven through NMR and TG analyses that ionic liquids and organic amines can be used together as structure-directing agents.

**Acknowledgments:** As Guest Editor of the Special Issue “Catalysis on Zeolites and Zeolite-like Materials”, I am thankful to all the authors for submitting their high-quality research to this Special Issue and to the anonymous reviewers for their time and effort in reviewing the manuscripts.

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

#### List of Contributions

1. Zhang, M.; Qin, B.; Zhang, W.; Zheng, J.; Ma, J.; Du, Y.; Li, R. Hydrocracking of Light Diesel Oil over Catalysts with Industrially Modified Y Zeolites. *Catalysts* **2020**, *10*, 815.
2. Li, Y.; Qin, B.; Hao, W.; Du, Y.; Ma, J.; Li, R. Protolytic Ring-Opening Cracking of Methylcyclohexane over Hierarchical High-Silica USY Zeolite: A Haag-Dessau Cracking. *Catalysts* **2022**, *12*, 697.
3. Chapellière, Y.; Daniel, C.; Tuel, A.; Farrusseng, D.; Schuurman, Y. Kinetics of n-Hexane Cracking over Mesoporous HY Zeolites Based on Catalyst Descriptors. *Catalysts* **2021**, *11*, 652.
4. Jaroszevska, K.; Fedyna, M.; Masalska, A.; Łużny, R.; Trawczyński, J. Promotional Effect of Pd Addition on the Catalytic Activity of Composite Pt-Pd/AlSBA-15- $\beta$  Catalyst for Enhanced n-Heptane Hydroisomerization. *Catalysts* **2021**, *11*, 377.

5. Gille, T.; Seifert, M.; Marschall, M.S.; Bredow, S.; Schneider, T.; Busse, O.; Reschetilowski, W.; Weigand, J.J. Conversion of Oxygenates on H-ZSM-5 Zeolites—Effects of Feed Structure and Si/Al Ratio on the Product Quality. *Catalysts* **2021**, *11*, 432.
6. Nadolny, F.; Alscher, F.; Peitz, S.; Borovinskaya, E.; Franke, R.; Reschetilowski, W. Influence of Remaining Acid Sites of an Amorphous Aluminosilicate on the Oligomerization of n-Butenes after Impregnation with Nickel Ions. *Catalysts* **2020**, *10*, 1487.
7. Han, P.; Zhang, Z.; Chen, Z.; Lin, J.; Wan, S.; Wang, Y.; Wang, S. Critical Role of Al Pair Sites in Methane Oxidation to Methanol on Cu-Exchanged Mordenite Zeolites. *Catalysts* **2021**, *11*, 751.
8. Kohler, A.; Seames, W.; Foerster, I.; Kadrmas, C. Catalytic Formation of Lactic and Levulinic Acids from Biomass Derived Monosaccharides through Sn-Beta Formed by Impregnation. *Catalysts* **2020**, *10*, 1219.
9. Grass, J.-P.; Klühspies, K.; Reprich, B.; Schwieger, W.; Inayat, A. Layer-Like Zeolite X as Catalyst in a Knoevenagel Condensation: The Effect of Different Preparation Pathways and Cation Exchange. *Catalysts* **2021**, *11*, 474.
10. Han, L.; Yan, X.; Guo, L.; Duan, Y.; Wang, Z.; Lu, T.; Xu, J.; Zhan, Y.; Wang, J. Ionothermal Synthesis of Triclinic SAPO-34 Zeolites. *Catalysts* **2021**, *11*, 616.

## References

1. Cronstedt, A.F. Rön Och Beskrifning om en Obekant Bärgr Art, som Kallas Zeolites. *Acad. Handl. Stockholm* **1756**, *18*, 120–130.
2. Colella, C.; Gualtieri, A.F. Cronstedt's zeolite. *Microporous Mesoporous Mater.* **2007**, *105*, 213–221. [[CrossRef](#)]
3. Barrer, R.M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, UK, 1978.
4. Flanigen, E.M. Molecular Sieve Zeolite Technology—The First Twenty-Five Years. *Pure Appl. Chem.* **1980**, *52*, 2191–2211. [[CrossRef](#)]
5. Weckhuysen, B.M.; Yu, J. Recent advances in zeolite chemistry and catalysis. *Chem. Soc. Rev.* **2015**, *44*, 7022–7024. [[CrossRef](#)] [[PubMed](#)]
6. Iwamoto, M. Zeolites in Environmental Catalysis. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1395–1410.
7. Yilmaz, B.; Müller, U. Catalytic Applications of Zeolites in Chemical Industry. *Top. Catal.* **2009**, *52*, 888–895. [[CrossRef](#)]
8. Zhou, H.-C.; Kitagawa, S. Metal-Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418. [[CrossRef](#)] [[PubMed](#)]
9. Dusselier, M.; Davis, M.E. Small-Pore Zeolites and Catalysis. *Chem. Rev.* **2018**, *118*, 5265–5329. [[CrossRef](#)] [[PubMed](#)]
10. Wang, Y.; Tong, C.; Liu, Q.; Han, R.; Liu, C. Intergrowth Zeolites, Synthesis, Characterization and Catalysis. *Chem. Rev.* **2023**, *123*, 11664–11721. [[CrossRef](#)] [[PubMed](#)]
11. Opanasenko, M.; Dhakshinamoorthy, A.; Shamzhy, M.; Nachtigall, P.; Horáček, M.; Garcia, H.; Čejka, J. Comparison of the catalytic activity of MOFs and zeolites in Knoevenagel condensation. *Catal. Sci. Technol.* **2013**, *3*, 500–507. [[CrossRef](#)]
12. Yu, W.; Wu, X.; Cheng, B.; Tao, T.; Min, X.; Mi, R.; Huang, Z.; Fang, M.; Liu, Y. Synthesis and Applications of SAPO-34 Molecular Sieves. *Chem. Eur. J.* **2022**, *28*, e202102787. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.