



Recent advances in zeolite chemistry and catalysis

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Zeolites are crystalline microporous aluminosilicates, which are built up from corner-sharing SiO_4 - and AlO_4 -tetrahedra. These porous materials are formed in nature in association with volcanic activity, but can also be synthesized in the

laboratory. Currently, there are 229 different zeolite structures known, not necessarily composed of SiO_4 - and AlO_4 -tetrahedra as many elements from the periodic table can now be an integral part of zeolite framework structures. Interestingly, theory has predicted that millions of other zeolite structures can be constructed from the primary building blocks of zeolites, illustrating the enormous potential of this research area for designing new functional porous materials.

The Swedish chemist Axel Cronstedt was the first to describe zeolites in 1756. He noted that the mineral stilbite appeared

to boil when heated. Cronstedt therefore named these materials zeolites or “boiling stones” (from Greek ζέω – to boil and λίθος – stone). Zeolites are used in large quantities in a variety of commercial processes. The largest zeolite application is certainly detergency. Zeolites can be used as ion-exchange reagents to remove Ca^{2+} and Mg^{2+} ions from “hard” water. The second largest application is catalysis, with Fluid Catalytic Cracking (FCC) and Hydro-Cracking (HC) as the leading commercial processes in the oil refinery industry. Other uses include adsorbents, as well as various uses of natural zeolites,

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including soil conditioners, nutrient release agents in horticulture, odor control agents in pet litter, and selective removers of radio-active isotopes (e.g. ^{137}Cs and ^{90}Sr) from polluted water streams.

As mentioned above, the largest applications of zeolites as catalyst materials are found in FCC and HC. However, there are other applications of zeolites in oil refinery, such as alkylation, isomerization, dewaxing and reforming. In petrochemical complexes, the production of cumene and ethylbenzene, as well as the isomerization of xylenes are key examples of zeolite-based catalytic technologies. More recently, methanol-to-hydrocarbons (MTH) technology has been commercialized for the production of gasoline, aromatics and olefins, including propylene. Zeolites are core to MTH catalysts, while zeolite-based catalysts have also found applications in the treatment of car exhaust gases (i.e., NO_x removal). Zeolites are also explored for their use in biomass catalysis and in the low temperature activation of methane to form oxygenates, such as methanol. For each of these applications the overall stability of the zeolite towards water and impurities (e.g. P and S compounds) is an important issue.

These developments and related successes have only been possible by our increased knowledge and related technological advances in the tailoring of zeolite-based catalyst materials. More specifically, in the last decade we have seen an expanding scientific base, often obtained by a synergistic approach between experiment and theory, for the advanced synthesis and use of zeolites. Not only are we now able to prepare a more diverse slate of zeolite structures and compositions, it is now also possible to synthesize e.g. single layered zeolite nanosheets and complex multi-scale designed zeolite composites. Just as important is that zeolite characterization can be performed at both the single atom and single molecule level, sometimes even under truly operando reaction conditions, while non-invasive analysis of entire zeolite-based reactor beds and catalyst extrudates also became feasible. The aim of this themed issue of *Chemical Society Reviews* is to sample recent progress in zeolite chemistry and catalysis in these important scientific directions.

During the last decade, as discussed in the review article by Yu, Corma *et al.* (DOI: 10.1039/c5cs00023h), three synthetic strategies have led to the discovery of new zeolite materials with novel structural features. These approaches involve the use of (a) pre-designed organic structure directing agents (SDAs), including quaternary and diquaternary SDAs, P-containing SDAs, proton sponges, imidazolium derivatives, and metal complexes; (b) heteroatom substitutions in aluminophosphates, silicates, and germanates; and (c) topotactic transformations of 2D–3D, 3D–2D–3D, and 3D–3D structures.

Another synthetic approach, which is coined the ADOR protocol, is reviewed by Morris, Cejka *et al.* (DOI: 10.1039/c5cs00045a), and involves the sequence of assembly, disassembly, organization and re-assembly processes to synthesize new zeolites. In this review article, the authors discuss the critical factors of germanosilicate-based zeolite materials required for application of the ADOR protocol and describe the mechanism of hydrolysis, organization and condensation to form new zeolites starting from the UTL framework structure.

Zeolite materials can be made and shaped in different sizes, forms and appearances. One of them is in the form of membranes. In their critical review paper (DOI: 10.1039/c5cs00292c), Caro, Tsapatsis and co-workers discuss the latest developments in the synthesis of zeolite membranes, with an emphasis on seed assembly and secondary growth methods. The article also reviews the current industrial applications of zeolite membranes, the feasibility of their use in membrane reactors and their hydrothermal stability. Finally, metal–organic framework (MOF) membranes are compared with zeolite membranes.

Another trend is to synthesize zeolite crystals in the nano-size range, and these crystals often have different properties to their bulk analogues. In their review article (DOI: 10.1039/c5cs00210a) Mintova, Valtchev and co-workers discuss the recent developments in the synthesis and unconventional applications of nano-sized microporous crystals, including framework (zeolites) and layered (clays) type materials. The article includes a comprehensive

analysis of the emerging applications of these materials in the fields of semiconductors, optical materials, chemical sensors, medicine, cosmetics, and the food industry.

Theoretical chemistry has clearly changed the way in which we approach zeolite science and technology. Computational methods can now be used routinely to model and, with increasing success, predict the reactivity as well as the molecular sorption and diffusion properties of a wide variety of zeolite structures. The extensive review by Van Speybroeck, Catlow and co-workers (DOI: 10.1039/c5cs00029g) elaborates on the advances in computational approaches and their applications within the field of zeolite chemistry. A review of the modeling efforts used to unravel zeolite formation processes is presented, including zeolite surface modeling and structural modeling to guide processes towards desired structures for a given application. Furthermore, with a wide variety of applications, including CO_2 capture and hydrocarbon conversion processes, the authors provide a flavor of what is currently possible with theoretical chemistry.

The accessibility of zeolite materials is of paramount importance for their application in catalysis. As a consequence, a lot of attention has been directed to the understanding and tailoring of zeolite micro-, meso- and macro-porosity, leading to the concept of hierarchical zeolites. De Jong and co-workers' review article (DOI: 10.1039/c5cs00155b) provides a general overview of the different synthetic methods for the introduction of additional porosity in zeolite materials, including a discussion of the advantages and limitations of the different synthetic approaches developed. Essential for such assessment is the development and application of 2D and 3D microscopy techniques, and the correlation of these microscopic results, based on the use of either optical light, X-rays or electrons, with bulk characterization data as well as catalytic performances.

One of the prime and widely used characterization techniques for investigating functional porous materials is vibrational spectroscopy. The most popular methods are infrared (IR) and Raman spectroscopies, and to a lesser extent

inelastic neutron scattering (INS) spectroscopy. In their paper (DOI: 10.1039/c5cs00396b), Lamberti, Bordiga, Thibault-Starzyk and co-workers review the fundamentals and applications of these three techniques in the field of zeolites and zeotype materials. Making use of these vibrational methods, it is possible to investigate in great detail the role of Brønsted and Lewis acid sites in surface reactivity and catalysis. A detailed analysis of the differences between probe molecules, and their role in assessing proton affinity and shape selectivity, is presented. Furthermore, more recent developments in the field of space and time resolved measurements are discussed. Very interestingly, the article also highlights the importance of linking experimental results with theoretical interpretations of the vibrational spectra measured.

Fluid catalytic cracking (FCC) is one of the major conversion processes in oil refinery and is responsible for the production of the majority of our gasoline. This technology also produces an important fraction of the propylene used in the polymer industry. In their review article (DOI: 10.1039/c5cs00376h), Vogt and Weckhuysen discuss the recent developments in FCC chemistry and technology. The paper starts with a general background on FCC, including some historical facts, the main reaction, process and reactor design aspects, as well as the internal structure and composition of FCC catalyst particles. This introduction is followed by a discussion of three main developments in the field. Firstly, noted improvements in FCC catalyst materials are discussed, with a

focus on the introduction of new zeolites, the quest to increase propylene selectivity and the control over hierarchical porosity. Secondly, the change in raw feedstocks, including the co-processing of biomass, and new applications of FCC catalyst materials are highlighted. Finally, the most recent developments in FCC catalyst characterization are reviewed, with an emphasis on single FCC catalyst particle analysis.

As mentioned above, the MTH catalytic process provides an efficient route for the conversion of methanol, indirectly obtained from natural gas, coal or biomass, into olefins, aromatics and gasoline. Although commercially implemented, improvements in product selectivity as well as catalyst stability are still needed. These ambitions require a more fundamental understanding of the formation, catalytic mechanism and degradation of the active centers. Olsbye, Fan and co-workers focus their critical review article (DOI: 10.1039/c5cs00304k) on the progress recently achieved by a combination of theoretical calculations, model studies, operando spectroscopy and catalytic testing on the formation of the initial hydrocarbon species, and the consecutive transformation of these hydrocarbons into deactivating coke species.

In their review paper, Beale, Szanyi and co-workers (DOI: 10.1039/c5cs00108k) summarize the results of recent studies on zeolite-based catalysts for the selective catalytic reduction (SCR) of NO_x using NH_3 as the reducing agent. After providing some historical background in addition to synthetic protocols for the development of zeolite-based SCR catalysts,

synthetic strategies for SCR-active zeolite materials with the **CHA** framework topology are discussed. This is followed by the proposal of possible structure–activity relationships to guide the design of more active and selective NO_x SCR catalysts.

Another emerging application of zeolite materials is in the conversion of biomass-derived oxygenates into fuels and chemicals. Zeolites possessing Lewis-acid metals, such as Al, Ga, Sn, Ti and Zr, hold a lot of promise in this direction. Pérez-Ramírez and co-workers (DOI: 10.1039/c5cs00028a) provide a comprehensive review paper on the versatility and scalability of bottom-up and top-down approaches to introduce Lewis-acid functionalities into zeolite materials.

In their review paper (DOI: 10.1039/c5cs00109a), van der Bij and Weckhuysen discuss the intricate, but complex chemistry between zeolite materials and phosphorus, the latter which can act as either a promoter or poison to the catalysis. For example, phosphatation is a well-known post-synthetic modification of zeolite ZSM-5 applied not only to alter its hydrothermal stability and acidity, but also to increase its selectivity towards *e.g.* propylene in FCC catalysis. Another illustrative example includes the problems noted by phosphorus poisoning of zeolite-based SCR catalysts. This review provides the reader with an extensive overview of the academic literature, from the first reports in the late 1970s until the most recent studies, in which advanced characterization techniques have been used to pinpoint the structural and physicochemical effects of phosphorus on zeolite-based materials.