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Recent advances in zeolite science based on advance characterization techniques

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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ABSTRACT

This short review summarizes recent research highlights that manifest the progress that is currently experienced in the field of zeolite synthesis, characterization and catalysis as reported in the period of January 2012 to June, 2013 and with emphasis in the application and development of advanced characterization techniques. The review is divided into three sections that focus on New Materials Synthesis, Advances in Characterization and Catalysis.

1. Introduction

A search using the keyword ‘zeolites’ on the Web of Science® for the years of 2012 and 2013, yields at the time of submission of this document a total of 4295 new publications. To put this in context, the number of publications in the Journal of the American Chemical Society in the same period is 4268. This number reveals the importance of zeolite materials across the chemical sciences and increasingly other areas such as biology and medicine, and the vitality of the field as a research subject. Since it is not possible to distill this large number of publications into a short review, we have chosen to describe the findings of a small number of reports that communicate what, to the authors, are significant advances in specific areas of zeolite science. The review is divided into three sections that focus on New Materials Synthesis, Advances in Characterization and Catalysis; we hope that this selection captures the dynamism and innovation that is being observed in the field. Our focus has been almost exclusively on experimental findings and not on theoretical developments, although this is also an area of current rapid growth and likely to become increasingly important in the future.

2. New materials synthesis

The Tsapatsis group [1] has used repetitive branching during crystal growth to prepare a new type of hierarchical zeolite material. They targeted an MFI-type structure, as it often presents 90° rotational intergrowths, and selected the organic structure-director tetrabutylphosphonium to attempt to control the rate of intergrowth formation. In a siliceous synthesis gel they identified synthesis conditions that maximize branching rates. The result is a material built of very thin MFI-type sheets or plates (1–5 unit cells thin) that yield a self-pillared structure, with the short plates perpendicular to each other. These ordered aggregates have dimensions of about 200 μm. Fig. 1 shows transmission electron microscopy and scanning electron microscopy images that reveal the presence of the flat pillars and the dimensions of the pillared aggregates observed at the end of the synthesis. Adsorption and catalytic studies reveal the presence of large pores within these particles and show that a large fraction of the acid sites are on the external surface of the pillars that form these interesting particles. Other materials where epitaxial growth is possible (EMT/FAU, CHA, CAN/SOD) could also yield pillared structures as well. Repetitive branching has been used in the synthesis of other crystals with complex structures but this is the first indication that it can be controlled during zeolite synthesis to a degree that materials with novel properties can be obtained. This novel hierarchical material overcomes the practical difficulties of dealing with suspensions of nanoparticles, and is less expensive and easier to scale-up than the synthesis of thin-plates of ZSM-5 crystals as reported by the Ryoo group [2].

A different example of nanosheet assemblies with intracrystalline mesoporosity was reported by Schwieger and co-workers [3] who synthesized Faujasite (FAU)-type zeolite X (Si/Al < 1.5). Using the organosilane surfactant 3-(trimethoxysilyl)propyl hexadecyl dimethyl ammonium chloride (TPHAC), a Faujasite structure free

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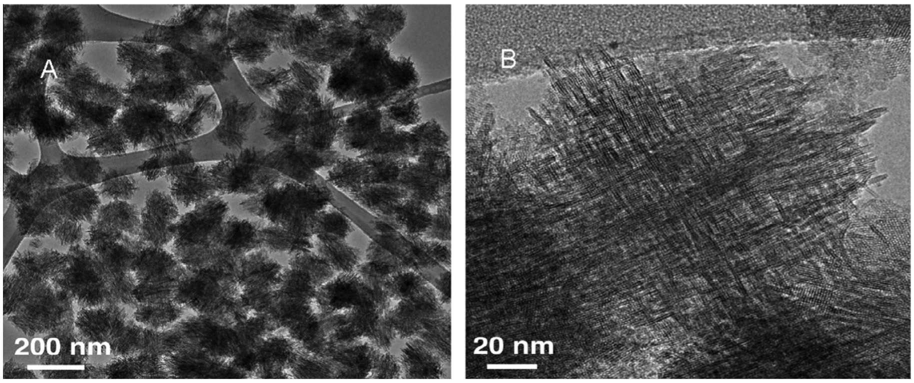

Figure 1. TEM images of the self-pillared zeolite nanosheet structures discovered by Zhang and co-workers. Image A shows the size of the clusters of nanosheets formed by this synthetic procedure. Image B shows a higher magnification image where the perpendicular stacking of the nanosheet structures can be identified more clearly. Adapted from [1]. Reprinted with permission from AAAS.

of competing crystalline phases and amorphous material was synthesized. SEM images revealed that the morphology of the synthesized material resembles ball-shaped house-of-cards-like nanosheet assemblies. The formation of zeolitic nanosheets induced by TPHAC has not been observed with any other zeolite type [4,5]. The reason for the structural effect of TPHAC may be the interplay between surface activity of the structure director and the charge balancing effects of the inorganic cation. N_2 adsorption experiments of the mesoporous zeolite X revealed a pronounced hysteresis and TEM revealed the mesoporous structure. The discovery of mesoporous FAU-type zeolite X and pillared ZSM-5 zeolite with similar mesoscopic structure suggests that introduced mesoporosity in zeolites may be a useful venue to minimize diffusion effects in zeolite catalysts.

By investigating the early stages of formation of organic-free FAU/EMT materials, the Mintova group at Caen [6] has identified low-temperature conditions (303 K) where ultra-small (6–15 nm) EMT hexagonal crystals can be formed. Higher temperatures led to phase transformations to FAU and SOD-type structures. To clarify the difference between the syntheses, the authors carried out high-resolution transmission electron microscopy (HRTEM) investigations of the synthesis gels revealing details about the structural evolution of the inorganic species (Fig. 2). The authors propose that the EMT particles are a kinetically metastable product observed in this crystallization field and that higher temperatures prompt the transformation of these crystals into the more stable phases. This is an important synthetic innovation because it allows for the inexpensive synthesis of an interesting catalyst and highlights the importance of molecular-level studies to identify new opportunities for the synthesis of materials with nanoscale control.

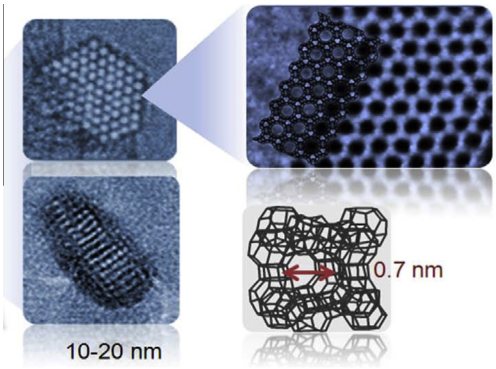

Figure 2. TEM image of EMT-type nanocrystals captured in the early stages of crystallization of FAU-type synthesis gels. The images shows views along the [001] and perpendicular to the [001] direction (left), and a comparison of an image and the structure of EMT-type zeolites. Adapted from [6]. Reprinted with permission from AAAS.

A very different type of mesoscopic porous structure has been created by Liu and co-workers [7]. They have prepared a new form of hierarchical porous material by generating b-aligned mesopores in single crystals of zeolite ZSM-5. Using a copolymer of polystyrene and 4-polyvinylpyridine methylated at the pyridine groups, they generated a cationic polymer that exhibits strong electrostatic interactions with the pores of a growing zeolite surface. Syntheses of materials with random mesopores in ZSM-5 zeolites have been previously reported [8–11], and zeolite particles grown inside ordered-mesoporous carbons have shown to be nearly single crystals; but this is the first time that surface interactions between the polymer and the growing zeolite crystal have led to predominantly b-aligned mesopores (see Fig. 3). The alignment of the mesopores was confirmed by SEM and TEM investigations. The sample showed excellent thermal stability and superior catalytic activity for the conversion of bulky organic molecules. Reactions such as the condensation of benzaldehyde with pentaerythritol were investigated revealing that the acid sites present on the surface of the mesopores are indeed active for catalytic transformations and their reactivity is not hampered by diffusion limitations. This novel approach to mesopore formation is a proof-of-concept for the idea of using self-assembly for the organization of micro and mesoscopic structure in a functional whole. It remains to be seen if this or similar approaches can be applied to different materials, but the possibilities are bright for further progress in this direction.

An interesting advance in the preparation of novel zeolite structures has been reported by the group of Martens and Kirschhock at Leuven [12]. They have taken advantage of the fact that double 4-rings (D4R) in germane-silicate zeolites are rich in germanium and can be hydrolyzed more easily than the rest of the zeolite structure. They have hydrolyzed the D4R in the IM-12 zeolite (UTL) which yields as the product a new zeolite structure denominated COK-14. Starting with the UTL structure (containing 14- and 12-ring pores) containing siliceous sheets connected by D4Rs, they have, in fact, 'sigma' (σ) contracted the structure of IM-12 to form a new structure with 12- and 10-ring pores. This new silicate has a new unique framework topology and displays interesting structural features. The degermanation method reported by this group should be applicable to a number of germanosilicate materials that contain silicate sheets separated by D4Rs and could yield a number of novel materials as there are numerous zeolites (ITQ-7, ITQ-13, etc.) that have D4R as structural units.

Roth and collaborators [13] have applied a different approach (termed 'ADOR: assembly-disassembly-organization-reassembly') to generate new zeolite structures. These authors also take