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n-Alkane hydroconversion on Zeogrid and colloidal ZSM-5 assembled from aluminosilicate nanoslabs of MFI framework type

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n-Alkane hydroisomerisation and hydrocracking experiments reveal that ZSM-5 materials synthesized by self-assembly of nanoslabs show different molecular shape selectivity than ZSM-5 synthesized by hydrothermal methods.

ZSM-5 zeolite and Silicalite-1 having a MFI topology are traditionally crystallised from a hydrogel under hydrothermal conditions.[1] Alternative syntheses involve the self-assembly of MFI type nanoslabs, obtained by reaction of tetraethylorthosilicate in concentrated tetrapropylammonium (TPA) hydroxide solution at room temperature.[2] Typical nanoslab dimensions are 1.3 × 4 × 4 nm^3. Heating causes the nanoslabs to fuse laterally to 1.3 × 8 × 8 nm^3 tablets, which aggregate further to colloidal zeolite.[3,4]

An interposed fusion of nanoslabs into a material denoted Zeogrid is obtained by precipitation of a nanoslab-cetyltrimethylammonium (CTMA) composite and subsequent calcination.[5] Zeogrids have dual porosity with ultramicropores inside the original nanoslabs and super-micropores between slabs, in contrast to colloidal Silicalite-1, having ultra-micropores only (Fig. 1).

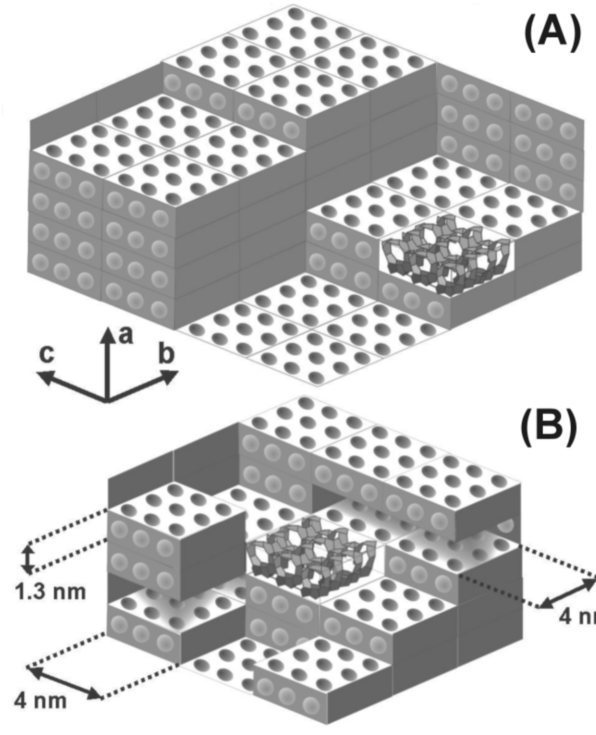

Fig. 1 Illustration of the surface of colloidal Silicalite-1/ZSM-5 (A) and Zeogrid (B) derived from nanoslabs. The framework of one nanoslab is shown in detail. Black dots represent large pockets at zigzag channel orifices.

We synthesized aluminium-doped Zeogrid (Si/Al = 100), labeled ZG, and colloidal ZSM-5 (Si/Al = 50) from aluminium doped nanoslabs, converted these materials into bifunctional catalysts by deposition of 0.5 wt.% Pt, evaluated their performance in decane hydroisomerisation and compared the shape selectivity with conventional ZSM-5 catalyst. A colloidal ZSM-5 sample (cZSM-5 (1d)) was obtained by heating nanoslab suspension at 120 °C for 1 day. The correspondence of the structure and porosity of these aluminium doped materials with previously obtained pure silicate versions was confirmed through XRD and nitrogen physisorption.

The decane hydroconversion has been shown to be a very suitable test reaction which is able to classify zeolites according to the architecture of their voids.[6] Provided acid and metal functions are balanced, the selectivity patterns within the isomer and cracked product fractions are imposed by the steric constraints of the pore system and are rather insensitive to differences in acidity.[7]

Decane hydroisomerisation experiments† were performed using a high-throughput reactor.[8] Commercial ZSM-5 (CBV5020, PQ Corp.) with a Si/Al ratio of 25, denoted further on with ZSM-5, served as reference. The turnover frequencies (TOF) in mole decane converted per mole aluminium per hour at 185 °C were 154 and 35 for ZSM-5 and cZSM-5 (1d) respectively. At 210 °C, the TOFs on cZSM-5 (1d) and ZG were 326 and 9, respectively. Decane was converted into monobranched and dibranched skeletal isomers, and cracked products. The total isomer yield and the yield of specific product fractions are presented in Fig. 2. On ZSM-5, cracking is the dominating reaction pathway. The isomers formed are mainly monobranched. On cZSM-5 (1d), the total isomerisation yield and the yield of dibranched isomers was surprisingly high, *viz.* 70% and 30% at the maximum, respectively. The ZG catalyst showed similar behaviour, though lower yields were obtained.

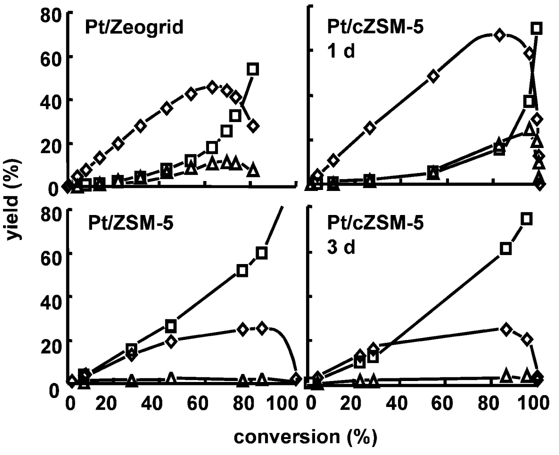

Fig. 2 Total isomer yield (◇), yield of dibranched isomers (△) and of cracked products (□) from decane.

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Among the methylnonane products, ZSM-5 favours 2-methylnonane over 3-, 4- and 5-methylnonane (Fig. 3) This behaviour is a general property of medium pore zeolites.[6] The preferential formation of 2-methylnonane has been ascribed to transition state shape selectivity,[9,10] product selectivity[11,12] or pore mouth catalysis.[13] Surprisingly, the 2-methylnonane isomer was not the preferred isomer on ZG and cZSM-5 (1d). At low conversion, its formation was even kinetically suppressed, which is typical for large pore zeolites such as zeolite Y.[7]

Large pore zeolites yield ethyloctanes in significant amounts, while medium pore zeolites yield little ethyloctane products.[6] The 4-ethyloctane content in the monobranched isomer fraction at 10% conversion was: ZG (6%) > cZSM-5 (1d) (1.3%) > ZSM-5 (0.5%). In particular the ZG catalyst behaved like a large pore zeolite. ZSM-5 strongly suppressed ethyloctane formation.

The content of branched isomers in the individual carbon number fractions of the cracked products was analysed. Zeogrid and cZSM-5 (1d) favoured strongly the formation of branched products. This is again a large pore rather than medium pore zeolite characteristic.[6]

In conclusion, Zeogrid and colloidal zeolite cZSM-5 (1d) derived from nanoslabs do not show the molecular shape selectivity encountered on conventional ZSM-5. They behave like large pore zeolites. In Zeogrid, it is tempting to ascribe the large pore behaviour to catalysis in the super-micropores, devoid of sterical constraints of MFI type ultra-micropores. However, a similar selectivity pattern for decane hydroconversion was observed on the colloidal zeolite (cZSM-5 (1d)), devoid of super-micropores. This shows the large pore behaviour is a property of the nanoslabs themselves. Inspection of the surfaces of colloidal ZSM-5 and Zeogrid (Fig. 1) reveals the abundant presence of (100) faces exposing openings of zigzag channels. These openings correspond to half-intersections and offer significantly more space for reacting molecules compared to channel sections. The absence of molecular shape selectivity could be due to catalysis in these wide pockets and to a special manifestation of the nest effect.[14,15]

When the synthesis time under hydrothermal conditions of the colloidal ZSM-5 was prolonged to 3 days (sample cZSM-5 (3d)), the selectivity of the catalyst became similar to that of commercial ZSM-5 (Figs. 2–3). The hydroisomerisation activity was poor (Fig. 2), 2-methylnonane was the preferred methylnonane isomer at low conversion levels (Fig. 3), and the cracked products were less branched. SEM analysis of the cZSM-5 (1d) and (3d) samples revealed a change in morphology. The original irregular morphology was caused by the packing of nanotablet staples. After three days at 120 °C, SEM revealed an onset of formation of larger crystal faces. The driving force for these changes is Ostwald ripening, driven by solubility differences depending on surface curvature. Ostwald ripening of self-assembled materials causes the molecular shape selectivity in decane hydroisomerisation and -cracking to appear. At this stage, it is unclear whether the changes are due to alterations in framework termination, or aluminium positions. Currently, we are trying to address this pertinent question.

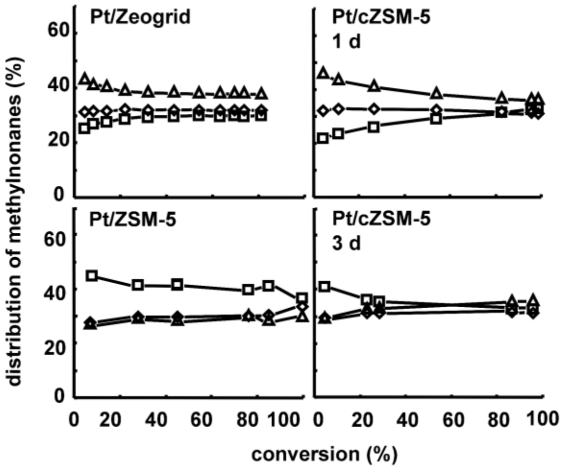

Fig. 3 Distribution of monomethylnonanes against conversion. 2-Methylnonane (□); 3-methylnonane (◇); 4- and 5-methylnonane (△).

In conclusion, nanoslabs provide a pathway to synthesize MFI type Zeogrid and colloidal ZSM-5 catalysts, which exhibit molecular shape selectivity atypical for conventionally prepared ZSM-5. The shape selectivity of colloidal ZSM-5 can be changed to conventional ZSM-5 selectivity by Ostwald ripening of the zeolite particles.

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Notes and references

† Decane hydroconversion was performed in a unit with 15 parallel reactor tubes, loaded with fixed beds of 35 mg catalyst. The H_2/decane molar ratio was 375. The contact time W/F_0 was 1656 kg.s.mol^{-1}.

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