

## Zoned MFI films by seeding

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The synthesis and characterization of zoned MFI films consisting of intergrown TPA-silicalite-1 and ZSM-5 crystals are described.

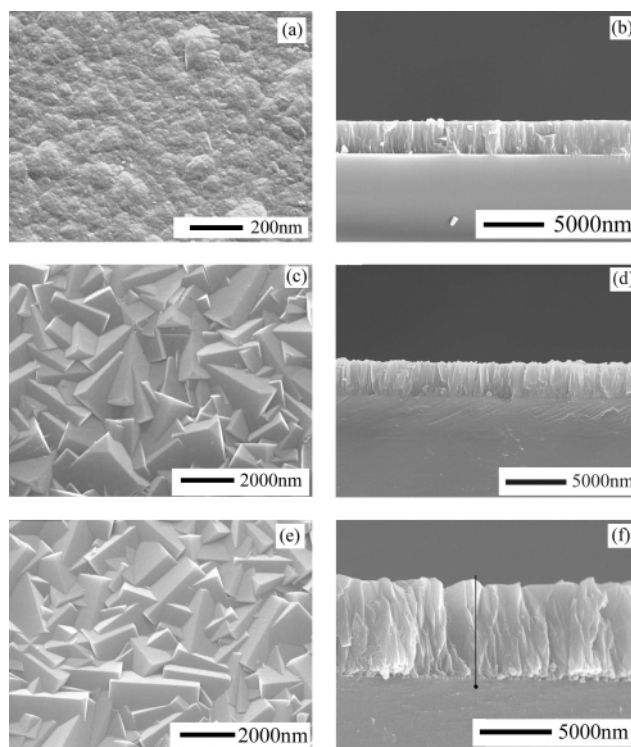
ZSM-5 is a zeolite which is used for shape selective acid catalysis. However, it is only the internal sites that are shape selective, the external sites are not. Various strategies have been used to improve the ratio of shape selective sites to non-selective sites. Large crystals have a higher ratio, but the increased diffusional length reduces activity, and deactivation can be more severe for larger crystals.<sup>1</sup> Chemical vapour deposition (CVD) of silica has been used to coat the external surface in order to eliminate the external sites.<sup>2–5</sup> However, the pore opening size and the activity may be reduced if this method is employed. A more elegant way to eliminate the external acid sites would be to prepare a compositionally zoned zeolite catalyst, *i.e.* to synthesize an inactive outer shell of aluminium free silicalite-1 on aluminium-containing ZSM-5 crystals. The pore openings would be unaffected if the channels propagate continuously from the interior of the ZSM-5 catalysts and through the external silicalite-1 shell. Materials that are claimed to be zoned have been evaluated previously by adsorption and catalytic testing.<sup>5–7</sup> It has been shown that at least some of the external acid sites of the materials were eliminated and shape selectivity increased. However, extensive characterization by means other than catalytic evaluation have not been carried out to determine whether such materials truly consist of a continuously propagating channel system through the compositionally zoned regions. The present communication describes the preparation and characterization of relatively thick zoned zeolite films consisting of TPA-silicalite-1 and ZSM-5 layers on quartz substrates. Such samples are well suited for characterization by techniques such as SEM, EDS and the preferred orientation of the crystals can be evaluated by XRD in order to elucidate the channel structure of the material. Additionally, these materials themselves possess a potential for various applications.<sup>7</sup>

A method employing seeding<sup>8</sup> was used for preparation of the zeolite films. TPA-silicalite-1 crystals with an average size of 60 nm were adsorbed on charge-reversed quartz substrates. The seeded substrates were further used to synthesize three different types of zeolite films (samples A, B, C). TPA-silicalite-1 films (A) were prepared by hydrothermal treatment of the seeded quartz substrate in a synthesis solution with a molar composition of 3 TPAOH : 25 SiO<sub>2</sub> : 1500 H<sub>2</sub>O : 100 EtOH at 100 °C for 3 days.<sup>8</sup> After the first synthesis step, the samples were rinsed with a 0.1 M ammonia solution and a fresh synthesis solution with the same composition was used for further hydrothermal treatment. This sequence was repeated four times in total to reach a crystallization time of 12 days. ZSM-5 films (B) were prepared by hydrothermal treatment of the seeded quartz substrate in a synthesis gel free from organic templates at 180 °C for 18 h.<sup>9</sup> The molar composition of the gel was 30 Na<sub>2</sub>O : 1 Al<sub>2</sub>O<sub>3</sub> : 103 SiO<sub>2</sub> : 4000 H<sub>2</sub>O. Zoned TPA-silicalite-1/ZSM-5 films (C) were prepared by a two-step crystallization procedure. In the first step, a TPA-silicalite-1 film was synthesized in the same way as for sample A. In the second step, the rinsed TPA-silicalite-1 film obtained from the first step was hydrothermally treated in the same way as for sample B. After

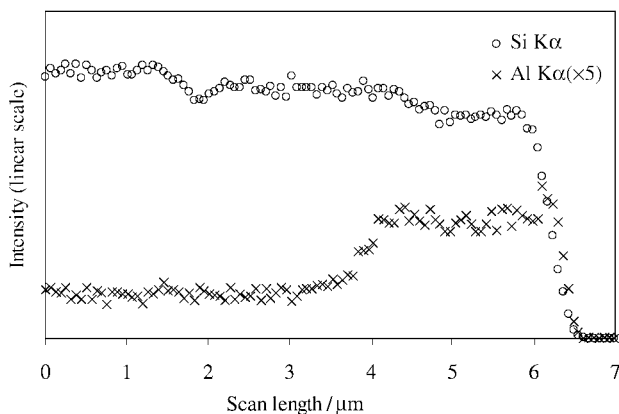
completion of the two-step procedure the samples were rinsed with a 0.1 M ammonia solution to remove sediments and unreacted gel adsorbed on the film as described for sample B.

Fig. 1 shows SEM micrographs of the three samples. Fig. 1(a) and (b) show the top- and side-view images of sample A. The film thickness is *ca.* 2.8 μm and the texture is columnar. The surface of the film is relatively smooth. Fig. 1(c) and (d) show the top- and side-view images of sample B. The film consists of well intergrown crystals of ZSM-5 with very well developed crystal faces. The thickness of this film is *ca.* 3.4 μm. Fig. 1(e) and (f) show the top- and side-view images of sample C. After the second step, the morphology of the film has changed completely. The surface of the film is no longer smooth as for sample A, but well defined crystal faces constitute the surface, as in sample B. The thickness of film is *ca.* 6.3 μm, which agrees well with the sum of the film thickness of samples A and B. No border can be seen between the two different layers of silicalite-1 and ZSM-5 and the texture is still columnar.

The marker in Fig. 1(f) indicates the position of the EDS line scan shown in Fig. 2 which shows the Al Kα and Si Kα signals. The start of the EDS line scan at 0 μm in Fig. 2 corresponds to the dot in Fig. 1(a) on the quartz substrate. The Si signal is approximately constant over the quartz support and the zeolite, indicating an equal amount of Si in the zeolite and quartz. The Al signal from the support and the silicalite-1 film, (×5) is not



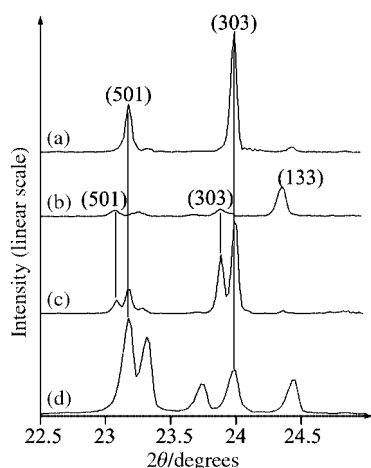
**Fig. 1** SEM micrographs of the films. Top-view image of sample A (a), side-view image of sample A (b), top-view image of sample B (c), side-view image of sample B (d), top-view image of sample C (e) and side-view image of sample C (f).



**Fig. 2** Si K $\alpha$  and Al K $\alpha$  signals of the EDS line scan indicated by the line in Fig. 1(f), the scan starts at the position of the dot. The Al K $\alpha$  signal was multiplied by 5.

zero owing to the continuous background signal (no Al atoms could be detected by EDS in sample A). The Al signal increases abruptly after *ca.* 3  $\mu\text{m}$  which agrees well with the silicalite-1 film thickness of sample A of *ca.* 2.8  $\mu\text{m}$ . From the EDS analysis the Si/Al ratio for the ZSM-5 layer was estimated to be *ca.* 10, which is a quite low value for ZSM-5 and identical to one reported previously.<sup>9</sup>

Fig. 3 shows X-ray diffraction patterns of samples A–C and a purified bulk product powder sample from TPA-silicalite-1 film synthesis. The powder sample [Fig. 3(d)] was used as a reference and considered to have a random orientation. It was reported previously that the (501) peak dominates in the pattern for TPA-silicalite-1 films with thickness of *ca.* 1.0  $\mu\text{m}$  on silicon wafers.<sup>8,10</sup> However, in the pattern for sample A [Fig. 3(a)], the (303) peak dominates. This suggests that with increasing crystallization time not only the film thickness increases, but also the preferred orientation of the crystals changes so that the (303) peak dominates in films with a thickness of 2.8  $\mu\text{m}$ . In the pattern for sample B [Fig. 3(b)], the (133) peak is dominant, which is in agreement with previous findings.<sup>8</sup> In the pattern for sample C [Fig. 3(c)], two (303) peaks, one from ZSM-5 and one from TPA-silicalite-1 dominate. Since the unit cell of ZSM-5 is larger than that of TPA-silicalite-1, the ZSM-5 peak occurs at lower  $2\theta$ .<sup>11</sup> The exact location of the (303) peaks was also determined by mixing silicon powder with TPA-silicalite-1 powder and ZSM-5



**Fig. 3** XRD patterns of sample A (a), sample B (b), sample C (c) and TPA-silicalite-1 powder (d).

powder prepared from the synthesis mixtures used for film growth. The position of the (303) peak for ZSM-5 and for TPA-silicalite-1 was 23.86 and 23.98°, respectively. The fact that the (303) peak and not the (133) peak dominate in the zoned film indicates that the orientation of the crystals in the ZSM-5 part of the zoned films is controlled by the orientation of the TPA-silicalite-1 crystals in the first film. In other words, according to the XRD data, the TPA-silicalite-1 crystals in the first film continue to grow to form the ZSM-5 film, resulting in a zoned MFI film with a continuous channel system. Because the ZSM-5 layer covers the TPA-silicalite-1, based on the thickness, diffraction angle and absorption coefficient of the ZSM-5 film, about 20% of the signal from the silicalite-1 film should be absorbed by the ZSM-5 film. Also, the crystal size in the ZSM-5 film should be larger due to the continued growth of the crystals in the silicalite-1 layer. Therefore, the (303) peak from the ZSM-5 part should be more intense than from the TPA-silicalite-1 part since the films have similar thickness. However, Fig. 3(c) shows the opposite, *i.e.* the (303) peak from the ZSM-5 part is weaker than from the TPA-silicalite-1 part. This could be due to somewhat lower crystallinity of the ZSM-5 layer in the zoned film, which was also indicated by XRD data from powders of ZSM-5 and TPA-silicalite-1 with similar crystal size.

In summary, this communication presents a method for preparation of zoned MFI type films containing TPA-silicalite-1 and ZSM-5 layers. The most significant finding is that such films are not only compositionally zoned but also appear to consist of a continuously propagating channel system through the zoned regions, according to SEM/EDS and XRD data. In order to further verify that the channel system propagates continuously, TEM studies of the interface of zoned films on carbon fibres will be carried out and the results presented elsewhere. The same general method can be used for the preparation of zoned films with the reversed positioning of the layers, *i.e.* silicalite-1 covering ZSM-5, which is of more practical interest for preparation of catalysts free of external sites as discussed in the introduction. Also, the preparation method has been modified to synthesize zoned films with a non-continuous channel system. Characterization results for these zoned films will be presented in a subsequent publication.

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