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Parallel Synthesis of ZSM-5 Zeolite Films from Clear Organic-Free Solutions**

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High-throughput synthesis and screening ("combinatorial") techniques have been recently introduced to the discovery and optimization of solid-state materials,[1–3] such as phosphors,[4] superconductors,[5] dielectrics,[6] and heterogeneous catalysts.[7–11] In this study parallel synthesis is applied to prepare supported ZSM-5 zeolite films. Identifying compositions that produce a microscopically continuous zeolite film usually constitutes the first step in zeolite membrane synthesis,[12, 13] an area that has attracted considerable attention in the last decade due to prospective gas separation applications.[13–17] Zeolite films are also of interest for sensor and nonlinear optical material applications.[18, 19] Zeolite film synthesis, in which film thickness, composition, and even crystallite orientation can be controlled,[19–22] offers an interesting approach to the preparation of catalytic libraries.

There are several reports on the parallel synthesis of zeolite powders.[23–25] Akporiaye and co-workers developed a convenient multiwell autoclave wherein one hundred or more distinct reaction mixtures could be treated hydrothermally. The solid products were washed in situ and transferred to individual sample holders for X-ray analysis.[23] Other groups employed post-synthetic treatment to attach the powder products to a silicon wafer or filter paper to eliminate the need for individual sample handling. X-ray microdiffraction was then used to identify individual sample members. Klein et al.[24] used a silicon wafer as the bottom of a multiwell autoclave and, after reaction, heated the precipitates to bond them to the wafer. They also applied this technique to produce zeolite libraries for catalytic investigation.[26] Bein and co-workers designed a centrifuge apparatus that allowed quantitative product recovery onto filter paper without manipulation of individual samples.[25]

Parallel film synthesis in the present study was carried out in a multiwell reactor similar to that used in reference [24]. The reactor, shown schematically in Figure 1, contains twenty-one wells of approximately 3 mm diameter and 5 mm depth drilled in a Teflon block. After the solutions had been introduced, the substrate alumina disk was placed on top of the wells and was covered by a cylindrical Teflon block. The sandwich was enclosed in a Parr reaction bomb, with the Teflon cap of the bomb applying the necessary pressure for sealing the wells. No additional water was added into the bomb. The diameter of the substrate disk was 2.5 cm, chosen to fit in the sample holder of the scanning electron microscope (SEM). The volume of solution in each well was 35 μL, a little less than the 40 μL volume of the wells. To ensure full contact of the substrate with the solution, the bomb was inverted and gently shaken several times with the substrate at the bottom of the solution and then placed in the oven either with the substrate placed horizontally at the bottom of the synthesis solution, or was rotated by 90° to fix the substrate in a vertical position. Upon opening the autoclave at the completion of the reaction no loss of liquid from the wells was observed and all zeolite films were found firmly attached to the substrate. The morphology of the films was examined by scanning electron

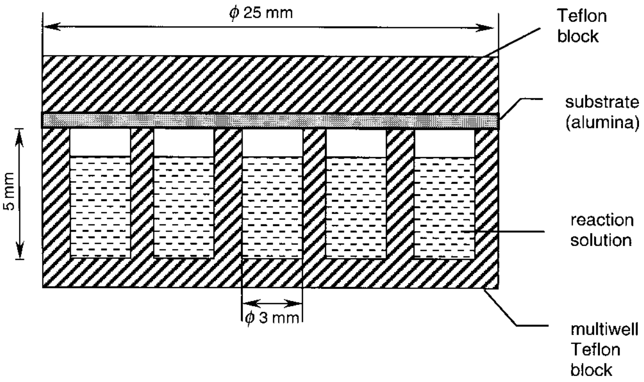

Figure 1. Cross-section of the multiwell reactor.

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microscopy (SEM). X-ray diffraction (XRD) analysis of the films ideally should be carried out by a microdiffractometer. Such an instrument was not available and, instead, a conventional powder XRD diffractometer was used, with a lead foil covering all but one film at a time.

Initial experiments were carried out to test the effectiveness of sealing and the effect of substrate orientation. Figure 2 displays a 21-member array of zeolite films prepared by using identical composition in all wells (SiO_2:0.15TPABr:0.7NaOH:98H_2O; TPA = tetrapropylammonium) with the substrate held in the vertical position. Figure 2B and C show one member of the array under higher magnification and indicate that the sealing was effective in confining the hydrothermal reaction inside each of the reaction wells. The film shown in Figure 2B is circular and of uniform appearance, suggesting that the substrate surface covered by the well was uniformly wetted despite the incomplete filling of the well (Figure 3). A simple experiment conducted at room temperature showed that the liquid assumes the configuration of Figure 3a in preference to the alternative shown in Figure 3b, evidently due to a lower surface energy more than balancing the slightly higher gravity potential at such a small volume-to-surface ratio.

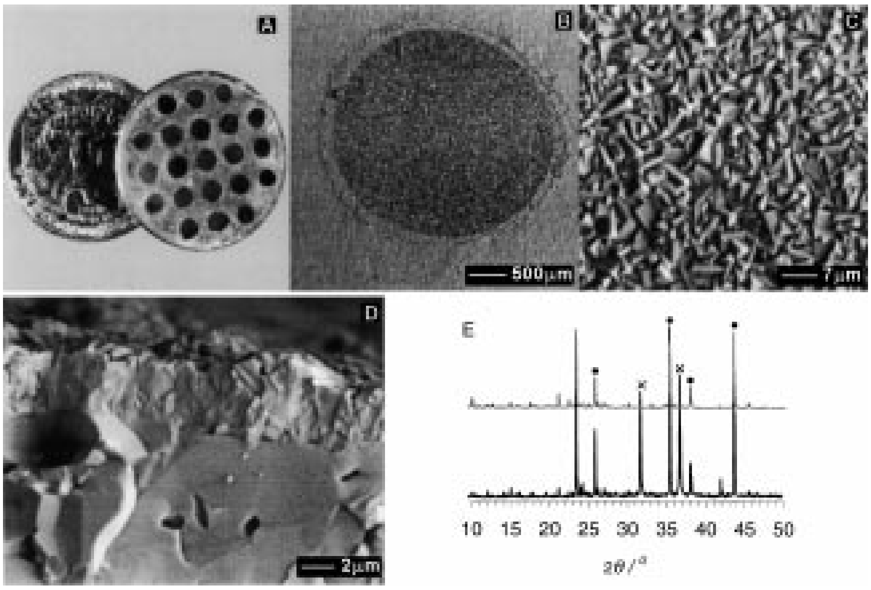

Figure 2. An array of ZSM-5 zeolite films grown on an alumina disk. The hydrothermal reaction was carried out on a seeded alumina disk for 16 h at 150 °C with the substrate held vertically during synthesis. A) The disk is displayed alongside a quarter coin in the background; B, C) one of the films under magnification; D) SEM image of a film cross-section; E) X-ray diffraction patterns of one of the array films (bottom) and a conventionally grown film (top). The dots mark peaks from the alumina substrate, and the crosses mark peaks from the lead mask.

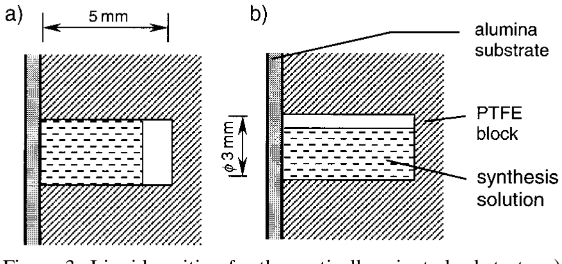

Figure 3. Liquid position for the vertically oriented substrate. a) Horizontal solution column formed following the adopted loading procedure. b) Position not realized.

Another issue of interest is how the film morphology compares with that produced at higher volume-to-surface ratios under conventional conditions. In the present experiments, the ratio of solution volume to substrate surface was about 0.5 cm, less than one-tenth of the ratio 5 – 20 cm used previously in our laboratory for zeolite film synthesis.[12, 13, 22] The zeolite films shown in Figure 2 were about 5 μm thick, and were well crystallized. They displayed morphology similar to that of films prepared conventionally from the same composition on porous or dense alumina but in larger autoclaves using 10 – 150 mL solution.[12] On the other hand, the X-ray diffraction pattern of the films prepared by parallel synthesis differs somewhat from the pattern of the conventionally grown films in relative peak intensities, indicating lesser orientation of crystallites in the films grown in the wells. Preferred orientation of seeded growth is known to result from competitive growth of the fastest growing crystallographic axis, usually the *c* axis,[20, 21] and depends on the extent of film growth. The lesser orientation of the films grown in the wells is then consistent with the lower volume-to-surface ratio of the wells.

Substrate orientation had an obvious effect on zeolite film morphology. Figure 4 shows a ZSM-5 film prepared by placing the substrate horizontally at the bottom of the solution during parallel synthesis under otherwise identical conditions to those of Figure 2. While the vertical synthesis geometry yielded a smooth and well-intergrown film, the horizontal geometry produced a continuous film with larger embedded particles, evidently as a result of precipitation of homogeneously grown crystals. At the larger volume-to-surface ratios used in standard autoclaves, precipitation of homogeneously grown species is more extensive when the substrate is placed at the bottom of the solution.[12]

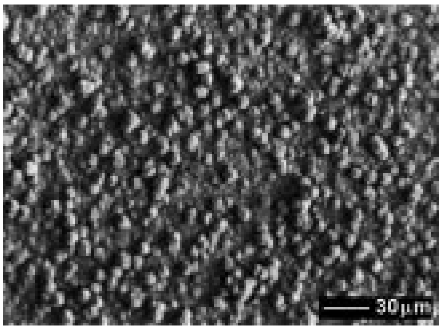

Figure 4. A ZSM-5 film prepared with the seeded alumina disk placed at the bottom of the solution.

After the preliminary experiments, parallel synthesis was further applied to explore zeolite ZSM-5 film preparation from clear, organic-free synthesis solutions. Compared to the standard ZSM-5 synthesis that involves organic tetrapropylammonium (TPA^+), the organic-free synthesis employs chemicals of lower cost and toxicity. More importantly from the standpoint of film or membrane synthesis, it renders unnecessary the calcination employed to remove the TPA^+ ions, during which lattice changes often produce microcracks in the films.[27–29] Organic-free synthesis of ZSM-5 in either powder[30–32] or film[33] form invariably employed hydrogel reaction mixtures, but clear solutions containing organic templates have been widely used in ZSM-5 membrane synthesis to minimize spatial inhomogeneity. They have also been quite popular in mechanism investigations of zeolite powder synthesis owing to the ease of product separation.

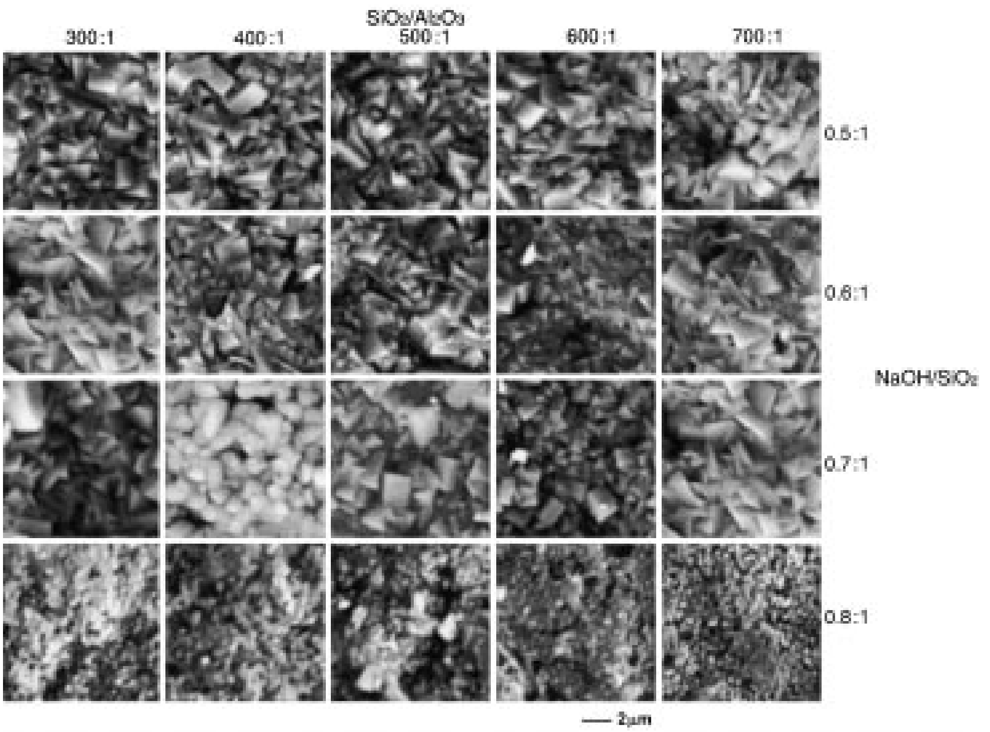

Figure 5. ZSM-5 films prepared from clear synthesis solutions of composition $SiO_2{:}x\,NaOH{:}y\,Al_2O_3{:}80\,H_2O$. The reaction was carried out at 180 °C for 16 h on a seeded alumina disk held vertically.

Exploration of clear, organic-free solutions for ZSM-5 film growth in the range $SiO_2{:}x\,NaOH{:}y\,Al_2O_3{:}80\,H_2O$ by parallel synthesis using 20 different compositions is summarized in Figure 5. As expected, alkalinity was the major factor in the formation of a clear solution, and for $NaOH/SiO_2 \geq 0.5{:}1$ the solutions were clear. Figure 5 indicates that NaOH was also the most important factor affecting film morphology and that a $NaOH/SiO_2$ ratio of $< 0.8{:}1$ was required to form a continuous film. Interestingly, within the composition space $0.5{:}1 \leq NaOH/SiO_2 \leq 0.7{:}1$ and $300{:}1 \leq SiO_2/Al_2O_3 \leq 700{:}1$ the film morphology appeared insensitive to solution composition. Energy dispersive spectroscopy (EDS) gave for all films the estimate Si/Al ~ 20:1 (atomic ratio), close to the lower bound allowed for ZSM-5. This ratio is much lower than the ratio Si/Al = 150–350:1 in the solution, indicating that aluminum-rich species are predominantly involved in the growth of the ZSM-5 crystals in the absence of TPA^+ templates. The Si/Al ratio of these films is comparable to the Si/Al ~ 15:1 ratio of ZSM-5 membranes prepared by using TPA^+-free hydrogels,[33] and much lower than the Si/Al ratio of 100–200:1 often measured for ZSM-5 films prepared by using TPA^+ templates.

ZSM-5 films were also prepared conventionally from 10 mL solution to compare with the films synthesized in parallel. Figure 6 shows a conventionally grown film that displays morphology similar to that obtained by parallel synthesis. Additional films were prepared conventionally varying SiO_2/Al_2O_3 ratios in the synthesis solution from 200:1 to 600:1. There was little effect of the SiO_2/Al_2O_3 ratio on morphology. The X-ray diffraction patterns of films grown in parallel and conventionally had some differences as noted previously.

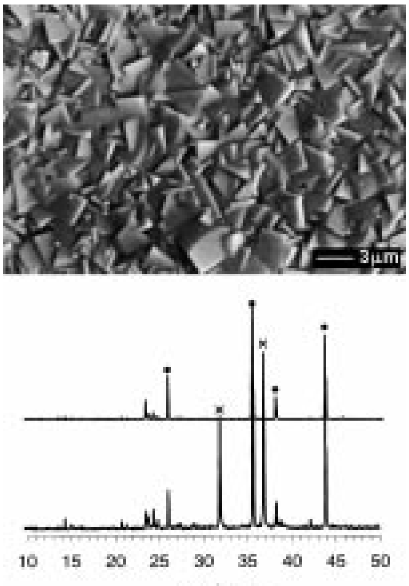

Figure 6. Top) SEM image of a ZSM-5 film prepared conventionally on a seeded alumina substrate placed in a 10 mL reactor. The reaction was carried out for 16 h at 180 °C in a clear solution of composition $SiO_2{:}0.5\,NaOH{:}1/300\,Al_2O_3{:}80\,H_2O$. Bottom) X-ray diffraction pattern of the film (top curve), compared with that of a film prepared by parallel synthesis (bottom curve). The peaks marked with a dot originate from the alumina substrate, and the peaks marked with a cross from the lead mask.

In summary, parallel synthesis of ZSM-5 zeolite films was demonstrated using a 21-well reactor. Holding the substrate vertically provided uniform wetting of the substrate in the well area and favored heterogeneous film growth. The films prepared by parallel synthesis were shown to have similar morphology to those synthesized under conventional conditions but their X-ray diffraction patterns indicate lesser orientation of crystallites. Parallel synthesis was used to screen the composition space of organic-free clear synthesis solution for ZSM-5 film growth. The composition SiO_2:(0.5–0.7) NaOH:(1/300–1/700) Al_2O_3:80 H_2O resulted in continuous ZSM-5 films of Si/Al ~ 20:1.

Experimental Section

Two types of silicon sources were used: sodium silicate solution (14% NaOH and 27% SiO_2), and tetraethylorthosilicate (TEOS). Sodium silicate was filtered by using a Buchner funnel with a coarse fritted disc immediately before use. When TEOS was used as the silicon source, it was first dissolved in tetrapropylammonium hydroxide (TPAOH) to form a clear solution of composition TEOS:0.15 TPAOH:0.7 NaOH:98 H_2O, which was then filtered before use with a PTFE filter (0.45 μm). Tetrapropylammonium bromide (TPABr) solution (25 wt%) was prepared and filtered with 0.45 μm cellulose acetate membranes.

The synthesis mixture was prepared by mixing a measured amount of chemicals in a transparent LDPE vial of volume 1 mL (Nalgene). When sodium silicate solution was used, H_2SO_4 (5 N, VWR) was added to adjust the alkalinity of the final solution. After thorough shaking, a clear synthesis solution was formed and aged for one day at room temperature without stirring before being introduced into the well for reaction. Occasionally, the synthesis mixtures turned turbid immediately after mixing, but the solution became clear after standing for several hours.

The substrates employed were nonporous α-alumina disks of diameter 2.5 cm. Prior to seeding the substrates were cleaned by a procedure described in reference [22]. Seeding of the entire substrate surface with a monolayer of silicalite particles was carried out using a previously developed protocol.[12, 33] The seeds about 0.4 μm in size were finer than the substrate roughness and did not cause problems in sealing under pressure against the Teflon surfaces.

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Bowl-Shaped Tris(2,6-diphenylbenzyl)tin Hydride: A Unique Reducing Agent for Radical and Ionic Chemistry**

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Trialkyltin hydrides (R_3SnH) are widely utilized in numerous radical reactions including reductive dehalogenations,[1, 2] desulfurizations,[3] and radical cyclizations.[4] Among several R_3SnH (R = Me, Bu, Ph), Bu_3SnH is the most popular reagent in radical chemistry. The Bu_3SnH-mediated radical reactions exhibit high regio- and stereoselectivity by changing radical initiators (azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), *hν*, Et_3B, etc.) and/or the reaction conditions.[5] Alternatively, such stereoselectivity is also achievable by replacing Bu_3SnH or Ph_3SnH[6] with the sterically more hindered $(Me_3Si)_3SiH$.[7] However, it is apparent that there

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