JOURNAL OF Materials CHEMISTRY

ZSM-5 films prepared from template free precursors

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Received 15th May 1998, Accepted 30th June 1998

Thin continuous films of zeolite ZSM-5 were synthesized on quartz substrates. The substrates were first surface modified and covered by a monolayer of colloidal silicalite-1 seed crystals. These crystals were grown into continuous films with thicknesses in the range 230–3500 nm by hydrothermal treatment in a synthesis gel free from organic templates. The preferential orientation of the crystals constituting the film was initially one with the *c*-axis close to parallel to the substrate surface. During the course of crystallization this orientation changed to one with most of the crystals having the *c*-axes directed approximately 35° from perpendicular to the substrate surface. A mechanism explaining this behavior is proposed. The final thickness of the film was controlled by the synthesis time but also by the addition of seed crystals to the synthesis gel. Films prepared according to this method may be of great value for the development of zeolite based membranes.

Introduction

Zeolites are currently attracting an increasing interest for the development of molecular sieve membranes and films as well as for use as host structures for oriented guest molecules.[1–4] This interest is mainly due to the unique porosity of zeolites accompanied by their thermal and chemical stability. These materials are expected to find practical applications in shape selective sensors, membranes for separation and catalytic purposes and a number of other novel devices.[5–10]

The preparation of zeolite films and membranes involves a number of additional constraints in comparison with the bulk synthesis of the corresponding zeolite powder products.[11–14] In order to form a film on a substrate, the surface of the substrate must be compatible with the zeolite, *i.e.* the chemical and structural properties of the surface must be such that zeolite crystallization preferentially occurs on the substrate. Some substrate types do not allow for direct crystallization of continuous zeolite films. Although this compatibility is mainly dependent upon the properties of the surface, it is also affected by the composition of the synthesis mixture and the conditions used for crystallization. To facilitate zeolite film formation on a substrate, a layer of colloidal zeolite seed crystals can be attached to the surface, *e.g.* by electrostatic adsorption. These seed crystals ensure the compatibility by serving as growth centers for further crystallization. This approach has proven very flexible and useful for a number of zeolite–substrate combinations, including surface modified noble metal substrates.[15–18] In most of the intended applications of zeolite films the possibility to prepare a film is not sufficient. For optimal utilization of the film, *e.g.* in a membrane or a size selective chemical sensor, it is also of major importance that the zeolite pores, and thus the zeolite crystals, in the film are oriented in the desired manner.

Most of the research work up to date concerning the preparation of zeolite films has dealt with MFI-type molecular sieves (*i.e.* silicalite-1 and ZSM-5).[5] This is partly due to the fact that MFI-type zeolites are prepared from chemically rather uncomplicated systems with a reasonable crystallization rate at modest temperatures and with a good reproducibility. The focus on MFI-type zeolites is, however, mainly explained by the great interest of these zeolites in several of the potential applications of molecular sieve films.

MFI-type zeolites are generally prepared in the presence of an organic template, tetrapropylammonium hydroxide, which is incorporated into the zeolite structure and has to be removed by calcination in order to open up the pore structure and render the zeolite useful. Owing to differences in thermal expansion of the zeolite film and the substrate material and/or due to the contraction of the zeolite lattice as the template molecules are removed, small cracks are formed in the film in the calcination step. As the potential usefulness of zeolite films for separation purposes is based on the fact that the pores of the zeolite can give a molecular sieving effect, cracks in the film are obviously detrimental.

An attempt to circumvent the crack formation due to calcination was recently reported.[19] Here it was shown that the preparation of a ZSM-5 film with a final thickness of about 500 nm and with an open pore structure can be accomplished by crystallization of the film in the absence of organic templates.

The present paper reports on a detailed investigation of parameters affecting the crystallization of ZSM-5 films on quartz substrates from synthesis gels free from organic templates with emphasis on the effects of synthesis time and addition of seeds to the synthesis mixture on the film growth rate, the final film thickness, and the orientation of the zeolite crystals constituting the films.

Experimental

Growth of ZSM-5 films

Quartz plates (10 × 10 mm, Marke Tech Int.) polished on both sides were used as substrates in all experiments. The quartz plates were cleaned and surface modified with a cationic polymer according to a previously described procedure.[20] A colloidal sol of monodisperse silicalite-1 crystals (diameter 90 nm) was prepared according to the procedure of Persson *et al.*[21] and washed repeatedly with distilled water. A monolayer of these crystals was adsorbed onto the substrate surface by immersion of the surface modified substrates into a sol with a solids content of 2.5 wt.% for 1 h. After adsorption, the substrates were dried at room temperature and calcined at 500 °C for 1 h.

A gel with the molar composition: $28Na_2O:1.5Al_2O_3:100SiO_2:4000H_2O$ was prepared by mixing (2 h homogenization) aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$, Riedel de Haën, p.a.], sodium silicate powder (63% SiO_2, 18% Na_2O, Riedel de Haën) and distilled water. Substrates with adsorbed seed crystals were placed horizontally at the bottom of PTFE-lined

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stainless steel autoclaves and contacted with the synthesis gel for 3–21 h at 180 °C in an oven to induce further growth and intergrowth of the seed crystals into continuous films of ZSM-5. In order to investigate the possible use of seed crystals to control the final film thickness, experiments were performed in which various amounts of calcined 90 nm silicalite-1 crystals were added to the synthesis gel prior to the homogenization. After the hydrothermal treatment, the autoclaves were taken out from the oven and rapidly cooled to room temperature. Prior to characterization the plates were washed in an ultrasonic bath using the washing sequence: distilled water–acetone–0.1 M ammonia. ZSM-5 crystals formed in the bulk phase concurrently with the growth of the adsorbed crystals were washed with distilled water and dried at 100 °C before being subjected to characterization.

Characterization of products

Crystallinity and orientation of the ZSM-5 crystals constituting the films were examined by X-ray diffractometry (XRD) using a Siemens D 5000 X-ray diffractometer equipped with a Göbels mirror, a 12 cm soller slit and a secondary LiF monochromator. The incidence angle was 1.0°. A highly crystalline powder sample of ZSM-5 prepared using the experimental conditions described above was used as a reference in the XRD measurements. A calculated powder pattern for TPA-ZSM-5[22] was used as a reference when indexing the recorded patterns.

The morphology of the ZSM-5 films was studied by scanning electron microscopy (SEM, Philips XL 30, equipped with a LaB_6 emission source). SEM side-view images were used for measurement of film thickness. Elemental analysis of zeolite films and of powder samples was performed using an EDS-system (Link Isis, accelerating voltage 20 kV) attached to the SEM.

Specific surface areas of powder samples were measured by nitrogen adsorption using a Micromeritics ASAP 2010 surface area/pore size analyzer. Samples were outgassed at 250 °C for 10 h prior to analysis.

Results and discussion

Film growth on seeded substrates

A series of experiments was performed using the synthesis conditions specified above (see Experimental section) in order to study the growth of zeolite ZSM-5 films on seeded quartz substrates in the absence of templating organic molecules. In order to avoid effects of sedimentation of crystals growing in the bulk phase onto the surface of the growing films and secondary nucleation starting from such crystals, analyses were restricted to the downward facing surface of the substrate. All films obtained in this series were continuous with a uniform surface. Extensive secondary nucleation most likely originating from seeds deposited onto the surface by sedimentation was observed for the upwards facing surface in the autoclave during the synthesis but only minor secondary nucleation was observed for the downward facing surface focused upon in this work.

As mentioned in the experimental section, all samples were subjected to ultrasonic treatment directly after the crystallization. In no instances could any signs of film detachment from the surface be detected as judged from SEM micrographs. The zeolite films obtained are thus very firmly attached to the quartz substrate surfaces.

The increase in film thickness with time, as measured from SEM micrographs, is shown in Fig. 1. The rate with which the thickness increases with synthesis time increases somewhat until the synthesis mixture is depleted of nutrient and crystallization discontinues. The average growth rate as estimated from the SEM micrographs is approximately 175 nm h^{-1}. In accordance with observations made in previous studies in our laboratory, where seeded substrates have been used for growth of zeolite films, the growth rate appears to be linear after a short induction time. The final film thickness obtained is approximately 3400 nm. SEM micrographs showing surface as well as side-view images of samples obtained after various crystallization times are shown in Fig. 2. The first micrograph [Fig. 2(a), 3 h of crystallization], shows a film consisting of a gel-like layer with embedded ZSM-5 crystals. However, XRD data on the same film indicate no amorphous material. This could be due to the small amount of such material. After 6 h of crystallization [Fig. 2(c), (d)], a continuous ZSM-5 film consisting of intergrown crystals and with a thickness of approximately 520 nm has formed. In this micrograph [Fig. 2(c)], crystals with a rather peculiar morphology are seen. One exposed crystal face is very even whereas the others are rough. After 10 h of hydrothermal treatment [Fig. 2(e), (f)], the film has grown to a thickness of approximately 1420 nm. Relatively well developed crystal faces with an edge length of about 500 nm are observed at this point. A rough surface morphology of certain crystal faces can be noted for this sample as well but the roughness is less pronounced than for the sample prepared using a synthesis time of 6 h. After 14 h of crystallization, the film thickness has increased to approximately 1800 nm. Smooth crystal faces are seen in the image of this sample [Fig. 2(g), (h)]. The pointed edges in the micrograph are probably due to crystals preferentially oriented with the *c*-axis directed upwards from the substrate surface. The *c*-axes seem, however, not to be aligned perpendicular to the substrate surface, but rather to deviate from this direction to some extent. In the final product obtained after 18.5 h of hydrothermal treatment [Fig. 2(i), (j)] the film consists of well intergrown crystals of ZSM-5 with very well developed crystal faces. The thickness of this film is approximately 3400 nm whereas the size of the crystals exposed at the surface is in the range 400–1000 nm. From the micrograph, the crystals appear to be preferentially oriented in the same manner as described for the sample crystallized for 14 h.

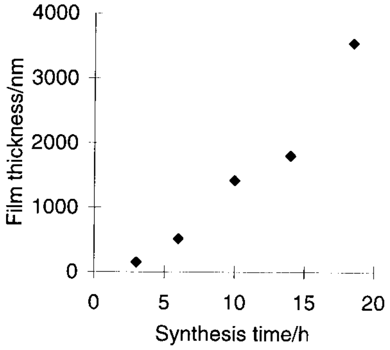

Fig. 1 Film thickness as a function of synthesis time. No seeds added to the synthesis gel.

In some experiments, samples were left in contact with the synthesis gel for periods extending beyond the point where growth of the film discontinued. In contrast to what we have observed for films prepared from clear solutions at 100 °C,[15] the films were affected by this further treatment. A decrease in film thickness was observed upon prolonged exposure indicating dissolution of the crystals. The reproducibility of the events taking place at this stage of the treatment was, however, relatively poor. X-ray diffractograms of samples obtained after various crystallization times are shown in Fig. 3. The diffractogram recorded for the reference powder sample is typical for the MFI structure with relative peak intensities close to those of the calculated pattern for ZSM-5[22] when taking into account that the XRD data were recorded with thin film accessories and with a constant incidence angle. In the diffractograms of the film samples, the relative intensities

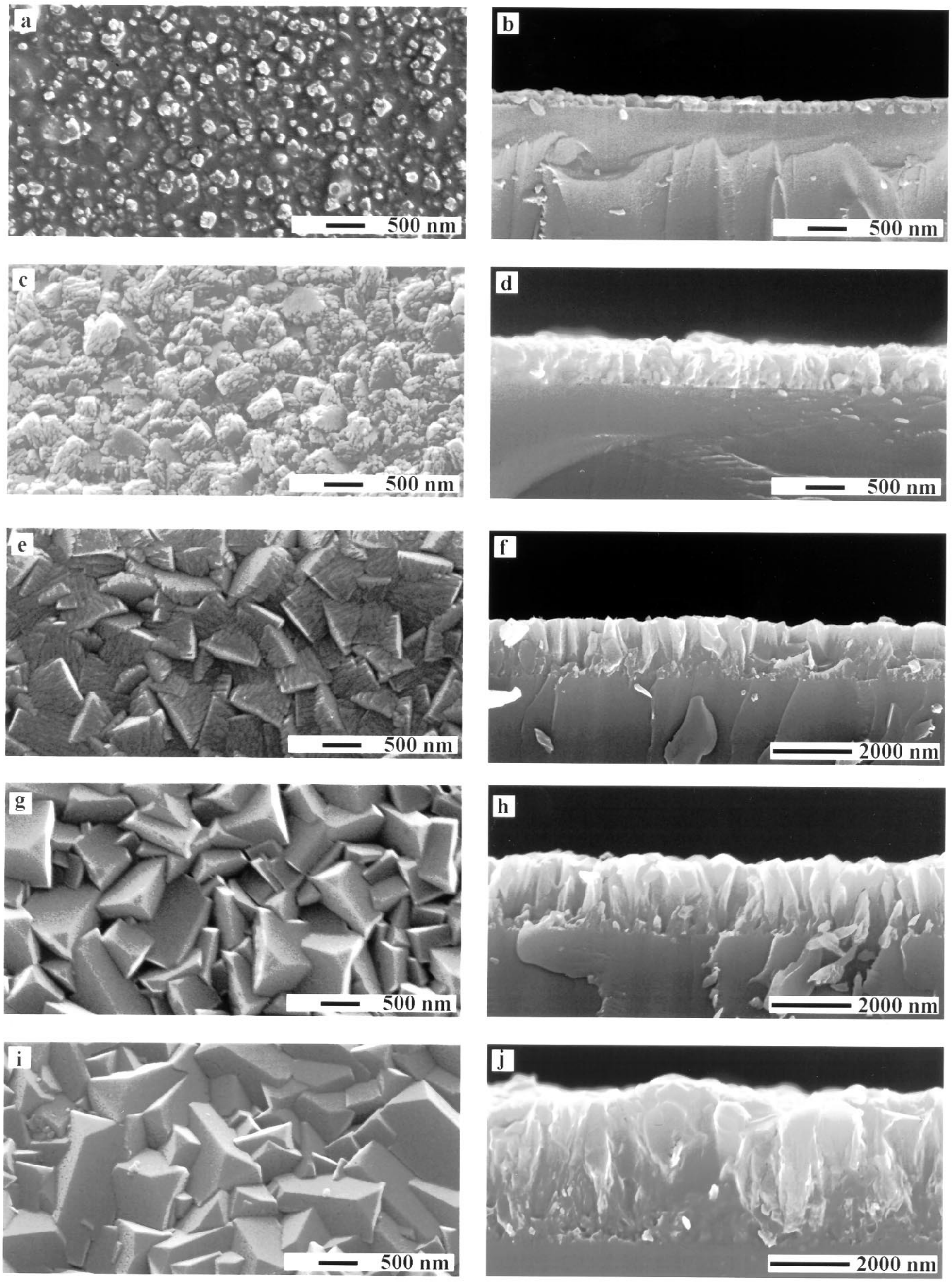

Fig. 2 Top (a) and side (b) view of the film formed after 3 h of crystallization. Top (c) and side (d) view of the film formed after 6 h of crystallization. Top (e) and side (f) view of the film formed after 10 h of crystallization. Top (g) and side (h) view of the film formed after 14 h of crystallization. Top (i) and side (j) view of the film formed after 18.5 h of crystallization.

of certain peaks are enhanced whereas those of others are suppressed in comparison with the reference, indicating a certain degree of orientation of the individual crystals making up the films. In order to assess the orientation of the film, crystallograpic preferred orientations (CPO) were calculated for various combinations of peaks. CPO(051/501) was defined in the following manner:[23]

$$\mathrm{CPO}(051)/(501)=\frac{I_{\mathrm{S}}^{(051)}/I_{\mathrm{S}}^{(501)}-I_{\mathrm{P}}^{(051)}/I_{\mathrm{P}}^{(501)}}{I_{\mathrm{S}}^{(051)}/I_{\mathrm{S}}^{(501)}}$$

where I=peak intensity and P and S refer to the powder reference and the film sample, respectively. CPO(051)/(501) describes the direction of the *b*-axes and *a*-axes of the crystals constituting the film. If CPO(051)/(501)=0, then the crystals constituting the film are randomly oriented in this respect, as is the case with the crystals in the powder sample. A value of 1 implies that the *a*-axes, see Fig. 4, of the majority of crystals constituting the film are parallel to the substrate surface and that the *b*-axes are oriented perpendicular to the substrate surface. If, on the other hand, all the crystals in the film are oriented with the *a*-axes perpendicular and the *b*-axes parallel to the substrate surface the CPO value will be equal to $-\infty$. Fig. 5 shows that CPO(051)/(501) is close to 0.6 and independent of film thickness. The *a*-axes of most of the crystals in all films are thus probably oriented more in a parallel direction to the substrate than in a perpendicular direction to the substrate.

Defining CPO(002)/{(200)+(020)} in analogy with CPO(051)/(501), this value will reflect the amount of crystalline material with the *c*-axis perpendicular to the substrate surface. This CPO has a value of about -1.3 for the film formed after 6 h of crystallization, indicating that the dominat-

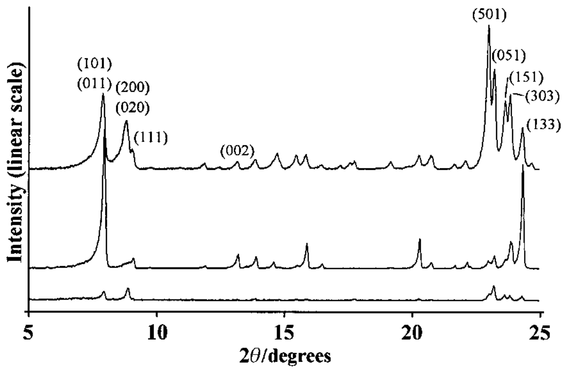

Fig. 3 XRD patterns of the powder reference sample (top), of the film formed after 19 h of crystallization (middle) and of the film formed after 6 h of crystallization (bottom). The background is subtracted from all patterns.

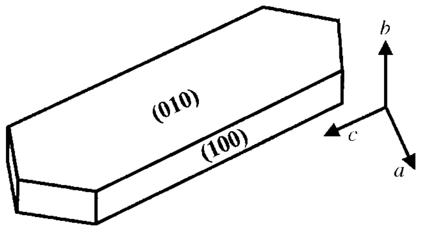

Fig. 4 Crystallographic faces and axes in a ZSM-5 crystal with the characteristic coffin morphology.

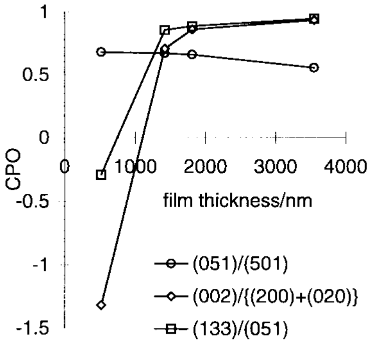

Fig. 5 Crystallographic preferred orientation (CPO) as a function of film thickness.

ing orientation of the *c*-axis is close to parallel to the substrate surface in this sample. The value of this parameter increases to values in the vicinity of 1 for thick films, indicating that most of the crystalline material is oriented with the *c*-axis close to perpendicular to the substrate surface and that the *a*- and *b*-axes are oriented almost parallel to the substrate surface.

If CPO(133)/(051) is defined as above, this value will correspond to the fraction of crystals which are tilted with the *c*-axes at an angle to the substrate surface. If CPO(133)/(051) = 1 the crystals are directed in such a way that the (133) planes are parallel to the substrate surface. The angle between the *c*-axis and the normal to this plane is 35°. Fig. 5 shows that CPO(133)/(051) increases from a value of about -0.3 to a value close to 1 when the film thickness increases. This shows that the amount of crystalline material oriented with the (133) plane parallel to the substrate surface increases or, in other words, that the amount of crystalline material oriented with the *c*-axes at an angle of 35° from the normal of the substrate surface increases as the film grows thicker.

A possible explanation for the trends shown in Fig. 5 may be as follows.[24] The seed crystals are adsorbed with the *b*-axes almost perpendicular to the substrate surface. This is indicated by SEM micrographs and is also reasonable since the (010) face is the largest face of the seed crystals. However, a few of the crystals are tilted, probably due to the fact that they are twinned. This situation corresponds to a value of CPO(051)/(501) close to 1 and a value of both CPO(002)/{(200)+(020)} and CPO(133)/(051) <0, which is in accordance with the observations made for very thin films (*i.e.* the initial growth phase). Upon hydrothermal treatment, the crystals grow in all possible directions until a dense film is formed. Due to steric hindrance, further growth is thereafter only possible in the direction perpendicular to the substrate surface, unless some crystals are sticking out from the surface. Since the growth rate is highest in the *c*-axis direction, this is, however, likely to be the case and the tilted crystals oriented with the *c*-axis deviating from the normal of the substrate surface will win the growth competition. The crystals oriented with their *c*-axis parallel to the substrate surface will thus be encapsulated and further growth will be hindered in all directions. This would explain why CPO(002)/{(200)+(020)} and CPO(133)/(051) approaches a value of 1 as the film thickness increases.

An alternative explanation to the changes in CPO observed could be a secondary nucleation on the film surface concurrently with the nucleation taking place in the bulk phase. If the secondary population grows with a different orientation than that of the adsorbed seeds a gradual change of the CPO (measured for the entire film) will occur. This explanation does, however, appear less likely.

Effects of seed addition to the synthesis gel

A series of experiments was performed in order to study the effects of addition of colloidal ZSM-5 seed particles to the synthesis gel on the growth of ZSM-5 films on seeded substrates. The objectives of the addition of seeds to the synthesis gel were to use the competitive crystal growth in the bulk phase to control the thickness of the ZSM-5 films and to investigate whether this mode of growth control would affect the orientation of the crystals in the films.

Table 1 shows the growth of ZSM-5 films as a function of time for preparations containing various amounts of ZSM-5 seed particles, added prior to the hydrothermal treatment. The final film thickness reached in experiments with addition of 0.15 and 0.30 wt.% seeds are 1000 and 350 nm, respectively, to be compared with 3400 nm obtained without addition of seeds. The orientation of the films obtained in this series was studied by XRD. The general trends observed for the samples prepared without seed addition to the synthesis gel, *i.e.* a change from an orientation with the *a*- and *c*-axis parallel to the substrate surface to an orientation with the *c*-axis directed upwards from the substrate surface with increasing film thickness, was observed for these samples as well. It appears that this change is occurring somewhat faster (at smaller thickness) when seed crystals are added. The quality of the diffractograms obtainable for the thinnest films of this series is, however, not sufficient to draw any definite conclusions about orientational changes during the crystallization process.

Table 1 Synthesis conditions and film thickness for experiments with seeds added to the synthesis gel

% Seeds in the gel	Synthesis time/h	Film thickness/nm
0.15	6	380
0.15	10	710
0.15	20.5	1000
0.3	3	75
0.3	6	230
0.3	10	390
0.3	19	350

Some of the powder samples crystallized in the bulk of the synthesis gel concurrently with the growth of the films were analyzed by nitrogen adsorption and surface areas were calculated using the BET equation. Measured surface areas were in the vicinity of 300 $m^2 g^{-1}$, *i.e.* somewhat lower than values usually obtained for MFI-type zeolites but clearly showing that the pore system of the ZSM-5 is accessible for the nitrogen molecules. The relatively low surface area of the bulk phase zeolite may be due to the presence of unreacted, amorphous zeolite precursor species in this sample. The chemical composition of ZSM-5 crystallized in the bulk as well as of the ZSM-5 films was analyzed by EDS. A Si/Al ratio of 12.6 was obtained for the bulk phase zeolite, whereas the corresponding value measured for a 3400 nm film was 11.5.

Conclusions

Thin continuous films of ZSM-5 with thicknesses in the range 230–3500 nm were grown on seeded quartz substrates from a synthesis mixture free from organic templates. The individual crystals of ZSM-5 are initially preferentially oriented with the *b*-axis perpendicular to the surface. During the crystallization the orientation changes gradually to one where the majority of the crystals are oriented with the *c*-axis directed at an angle of 35° from the normal to the substrate surface. This behavior can be explained in terms of competitive growth of different crystal surfaces and the steric limitations inherent in the growth of zeolite films. The thickness of the films can be controlled either by discontinuation of the crystallization at a desired time or by the addition of seed crystals to the synthesis gel which will grow concurrently with the ones attached to the surface and thereby accelerating the depletion of nutrient in the gel. The latter method appears to give additional possibilities for controlling the final orientation of the crystals in the film.

The method developed in this laboratory for the preparation of thin ZSM-5 films may be of great value for the use of zeolite films in membranes for separation applications. Since the films prepared by this method do not contain any organic template blocking the pore channels of the zeolite, a calcining step for removal of templates is not necessary. Such a step is often detrimental due to the formation of microcracks in the zeolite film. The use of the method for membrane preparation is currently being evaluated.

The authors gratefully acknowledge the financial support given to this work by the Swedish Council for Engineering Sciences (TFR). We are also grateful to the Wenner-Gren Foundation and the Lars Hierta Foundation (S. M. and V. V., respectively).

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Paper 8/03687J