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Preparation of ZSM-5 films from template free precursors

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Thin films of zeolite ZSM-5 on quartz substrates have been prepared in the absence of organic templates by growth of adsorbed seed crystals attached to a polymer-modified substrate surface.

Owing to their potential advantages in a number of advanced applications, the preparation of thin films or membranes of molecular sieves has attracted considerable interest in the past few years.[1–5] Films of molecular sieves in general and zeolites in particular are very promising in membranes, sensors, conductors, and non-linear optical materials, to name a few areas of interest.[6–9] Most of the work reported to date has concerned polycrystalline MFI (ZSM-5 or silicalite-1) films. ZSM-5 membranes have, for example, been prepared by *in situ* hydrothermal crystallization on porous α-Al_2O_3 in the presence of organic templates.[10] Other strategies for the preparation of MFI type films have been reported by Valtchev and Mintova[11] and by Hedlund *et al.*[12] The common factor in all work reported so far is that organic templates are used in the synthesis procedure. In order to render the pore system of the zeolite film accessible and thus to make it useful in the applications of interest, removal of the organic template by calcination is required. Unfortunately, the calcination procedure often results in the formation of micro-cracks which are detrimental if the film is intended to be used as a membrane. One possible way to circumvent the problems associated with the calcination would be to find conditions for zeolite film preparation in the absence of template molecules. ZSM-5 powder samples have been prepared in aluminosilicate systems free from organic templates.[13–15]

Here we report on the direct preparation of a continuous ZSM-5 film from precursors free from organic templates by the growth and intergrowth of seeds attached to a modified quartz substrate surface by means of electrostatic adsorption.

Quartz plates (10×10 mm, MarkeTech Int.) polished on both sides were cleaned for 10 min in acetone under ultrasonic action and then boiled in a mixture with the molar composition 278 H_2O : 9 H_2O_2 : 10 HCl for 10 min. The surface of the quartz plates was modified by adsorption of a cationic polymer according to the procedure described by Hedlund *et al.*[12] in order to achieve a positive surface charge. Colloidal ZSM-5 seed crystals with an average size of 90 nm, prepared by the method described by Persson *et al.*,[16] were then adsorbed in a monolayer onto the surface. The substrates with the adsorbed layer of seed crystals were calcined in air at 500 °C for 1 h, cooled to room temperature and immersed in an aluminosilicate synthesis gel containing no organic template. Continued crystallization of the seed crystals into a continuous film was performed in a 50 ml PTFE vessel contained in a stainless steel autoclave under autogeneous pressure at 180 °C for 6 h without agitation. After complete crystallization the autoclaves were rapidly cooled and the bulk product was separated by filtration, washed and dried at 100 °C. The quartz plates were washed repeatedly with distilled water, acetone and 0.10 M ammonia solution under ultrasonic action and dried at room temperature. The PTFE vessel was cleaned with hydrofluoric acid prior to each synthesis in order to avoid seeding effects. The molar composition of the synthesis gel was 28 Na_2O : Al_2O_3 : 100 SiO_2 : 4000 H_2O. The gel was prepared by addition of an aqueous solution of aluminium sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$, Riedel de Haen, p.a.] to a solution of sodium silicate (63% SiO_2, 18% Na_2O, Riedel de Haen) under stirring. The resulting gel was stirred for 1 h before use.

Scanning electron microscopy (SEM) was used for the characterization of both ZSM-5 films and crystals formed in the bulk of the synthesis gel. SEM micrographs were recorded with a Philips XL 30 microscope equipped with a LaB6 emission source. X-Ray diffraction (XRD) patterns of both powder and film samples were obtained using a Siemens D5000 diffractometer. The crystallinity and orientation of the zeolite film were determined at a grazing incidence angle of 1°. Specific surface areas were measured by nitrogen adsorption using a Micromeritics ASAP 2010 surface area/pore size analyzer. Samples were outgassed at 150 °C for 10 h prior to analysis.

Fig. 1 shows the XRD pattern recorded for a ZSM-5 film on a quartz substrate and the corresponding powder diffractogram obtained for ZSM-5 formed in the bulk phase during the synthesis. The latter diffractogram is typical for a MFI powder sample[17] whereas the former confirms that the film consists solely of ZSM-5. This diffractogram also reveals an enhancement of the (0*k*0) peaks and the depression of the other peaks, in comparison with that recorded for the bulk sample, indicating a certain degree of preferential orientation of the crystals constituting the zeolite film. The intensity ratios

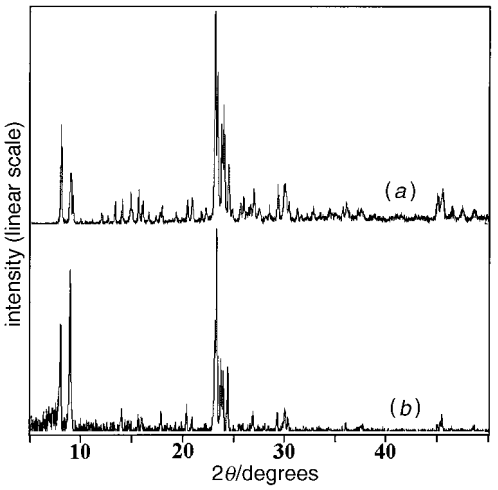

Fig. 1 XRD patterns of a powder sample of ZSM-5 (*a*) and a ZSM-5 film grown on the quartz substrate (*b*)

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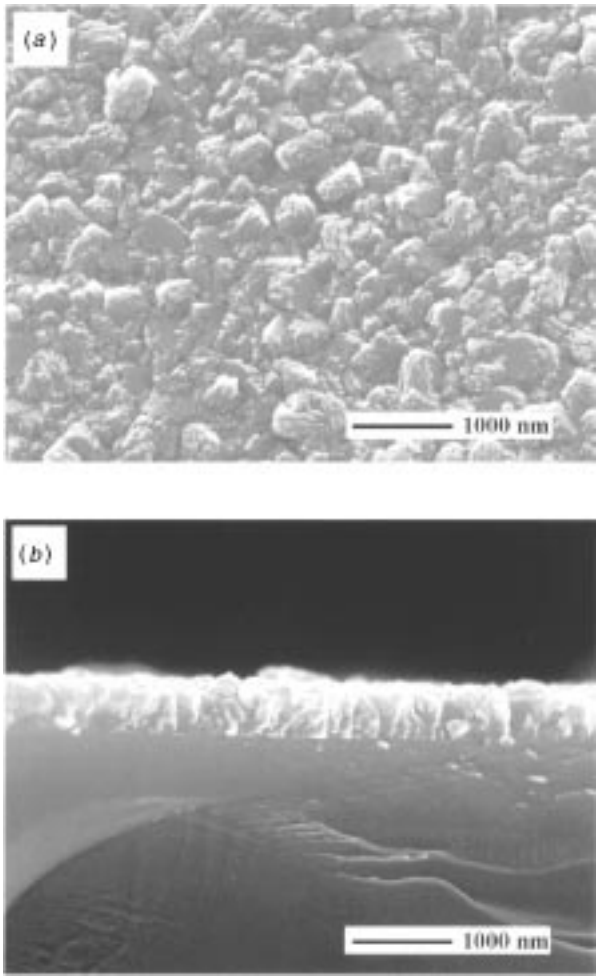

Fig. 2 SEM micrographs of (*a*) the top view and (*b*) the side view of the template free ZSM-5 film

of peaks at 7.95°/8.89°, 23.18°/23.32° and 23.74°/23.99° 2θ are about 0.7, 0.6 and 1.3, which are completely different from those in the powder sample, *i.e.* 2.2, 1.3 and 0.7 respectively.[2,7]

Fig. 2 shows SEM micrographs of a ZSM-5 film on a quartz substrate. From the side view [Fig. 2(*a*)] the thickness of the film can be estimated as approximately 500 nm. This image also shows that the film is continuous with a relatively even thickness. The top view [Fig. 2(*b*)] indicates that the film consists of well intergrown crystals of ZSM-5, of spheroidal shape and with a size of about 60 nm, which form aggregates with a size of approximately 250 nm.

The bonding of the zeolite film to the quartz substrate is strong as substantiated by the fact that the film withstands several hours of ultrasonic treatment in both acetone and water. Bonds between the ZSM-5 film and the substrate are most likely created when the substrate with the adsorbed seed crystals is calcined and perhaps also upon the continued growth and intergrowth of the seeds in the synthesis solution. The exact nature of the interaction between the zeolite and the substrate is, however, not yet fully understood.

The surface area of the ZSM-5 formed in the hydrothermal synthesis was determined as 300 $m^2\ g^{-1}$ without subjecting the sample to a calcination step prior to the analysis. This relatively high surface area shows that a ZSM-5 film with an open pore structure can be obtained without the use of an organic template requiring a calcination step with the accompanying risk of crack formation.

The procedure reported here for the preparation of *ca.* 500 nm ZSM-5 films with a certain degree of crystal orientation is a development of the 'seed-film method' for the preparation of molecular sieve films.[12] This method allows excellent control of the film thickness and is very flexible with regard to the substrate used. Further experimental work is being performed in order to assess the preparative possibilities of this new development as well as for investigating the concept in the preparation of molecular sieve membranes.

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