Continuous films of zeolite ZSM-5 on modified gold surfaces

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Thin continuous films of zeolite ZSM-5 on gold surfaces are prepared by a novel method including silanization, charge modification and seeding of the surface prior to the hydrothermal crystallization of the zeolite.

The preparation of continuous films of molecular sieves on various supports, including metallic and other inorganic as well as organic substrate surfaces, has recently attracted considerable attention.[1–5] The great interest in these materials is primarily motivated by their potential advantages in a number of applications such as membranes for separation and catalysis, chemical sensors, acoustic wave devices, and micro-electronics.[6–10]

Several methods for the preparation of zeolite films on surfaces have been described.[11–14] Most of these methods involve the direct nucleation and crystallization of the desired zeolite on the substrate surface. A novel method for the preparation of thin zeolite films based upon a three-step procedure was recently presented.[15] In this method, the substrate surface is first treated with a cationic polymer in order to obtain a positive surface charge. Colloidal crystals of zeolite are then adsorbed as a monolayer on the surface by electrostatic attraction. Finally, the adsorbed crystals are induced to grow into a continuous film of intergrown crystals under hydrothermal conditions. Although very flexible and easy to control, this method has the disadvantage that it can only be applied on surfaces which have a substantial surface charge in aqueous solutions. This excludes surfaces of noble metals, a fact that significantly reduces the value of the method in several of the potential applications of zeolite films where films on gold or platinum surfaces would be desirable. Modification of this method to render it applicable for noble-metal substrate surfaces is therefore of great interest.

The purpose of this communication is to present a novel method for the controlled preparation of very thin continuous films of ZSM-5 on gold surfaces. Gold substrates consisting of a gold film with a thickness of approximately 50 nm on the surface of silver plates were prepared by sputtering. The surface of the silver plate was first cleaned for 10 min in acetone in an ultrasonic bath and then in a mixture of water, ammonium hydroxide and hydrogen peroxide (molar composition $280H_2O:9H_2O_2:15NH_3$) for 10 min at room temp. The plates were then rinsed with distilled water and, subsequently, sonicated twice for 15 min in distilled water. Application of the gold film was achieved by sputtering in an MED 020 Coating System (BAL-TEC AG). The Au surfaces were silanized by treating the substrates for 3 h in a methanolic 20 mm γ-mercaptopropyltrimethoxysilane (MPT, OSi Specialties) solution and the silane was then hydrolysed in 0.10 m HCl for 15 h at room temp. The surface charge of the silanized gold surface was modified by treating the initially negative surface with a solution containing 1.0 mass% cationic polymer (Berocell 6100, Akzo Nobel) with the repeat unit $[CH_2CHOHCH_2NMe_2)]^+{}_n$ and an average molecular mass of 50 000 g mol^{-1} for 1 h. Substrates were then rinsed twice with a 0.10 m ammonia solution to remove excess polymer. In order to adsorb a monolayer of ZSM-5 seed crystals onto the surface of the substrates, the substrates were treated with a purified colloidal suspension (4.5 mass%, pH = 10.5, average crystal size: d_p = 90 nm) of discrete colloidal crystals of ZSM-5 for 1 h.[16] After this treatment, the substrates were rinsed 3 times with 0.10 m aq. NH_3, air dried and calcined for 1 h at 250 °C. Finally, the substrates were immersed in a synthesis solution with the molar composition $0.35Na_2O:25SiO_2:0.5Al_2O_3:9TPAOH:405H_2O$ for 40 h in order to induce continued growth (and intergrowth into a continuous film) of the crystals on the surface. The type of zeolite structure was confirmed by XRD with a Philips PW1710-00 powder diffractometer.

Particle size analysis and zeta potential measurements of the ZSM-5 seed sol were performed with a Brookhaven Instruments ZetaPlus. Adsorption of MPT was studied by reflection absorption Fourier transform IR spectroscopy (RAIRS, Perkin Elmer PE 2000 FTIR) and by VASE ellipsometry (J. A. Woolam Co). A Philips XL 30 scanning electron microscope (SEM) equipped with an LaB6 emission source was used for studies of surface morphology and to measure zeolite film thickness. Krypton adsorption was measured at liquid nitrogen temperature using a Micromeritics ASAP 2010 surface area and pore volume analyser.

In Fig. 1, a schematic illustration of the process is shown. The silanization of the gold surface by MPT was performed in solution resulting in a very thin silane layer (Fig. 1A). The RAIRS measurements of the silane layer were performed using an unsilanized substrate as the background and silanized samples as probes. The spectra were almost identical to that reported by Kurth and Bein[17] for adsorption of MPT on

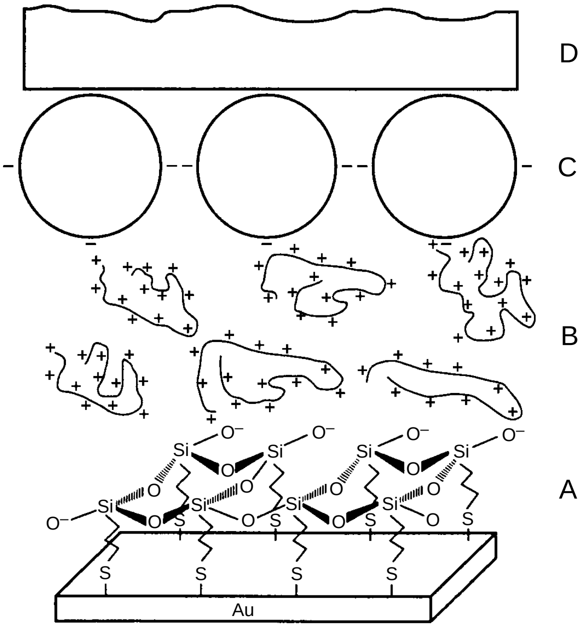

Fig. 1 Schematic representation of the silanization of an Au surface with MPT (A), charge reversal of the negative siliceous interface to a positively charged interface by means of adsorption of a cationic polymer (B), electrostatic adsorption of negatively charged ZSM-5 crystals on silane-polymer modified Au (C) and the formation of a continuous zeolite film after hydrothermal treatment (D)

oxidized aluminium substrates. From their spectrum they concluded that MPT adsorbed on oxidized alumina is vertically oriented. The thickness of the MPT film was determined by ellipsometry to about 10 Å which is in good correspondence with a vertical orientation of MPT on the gold surface. Hydrolysis of the silane results in the formation of dissociated groups on the surface of the substrate resulting in a surface with a negative surface charge in neutral and alkaline aqueous solutions (Fig. 1A). This substrate surface readily adsorbed an excess of the cationic polymer, Fig. 1B, thus reversing the surface charge to a positive one and facilitating electrostatic adsorption of colloidal ZSM-5 crystals, Fig. 1C. The zeta potential of the colloidal ZSM-5 crystals in the purified sol (pH: 10.5) was determined to −54 mV. Fig. 2(*a*) shows an SEM micrograph of colloidal ZSM-5 crystals adsorbed on the gold substrate surface after modification of this surface by silanization, hydrolysis of the silane and charge reversal by treatment with the cationic polymer. The micrograph shows that the crystals are homogeneously adsorbed in a dense layer on the surface. After adsorption of the seed crystals, the sample was calcined in order to decompose the silane and the cationic polymer and to induce a stronger interaction between the adsorbed seed crystals and the substrate surface. Although the nature of the bonding of the seed crystals to the substrate surface is not entirely clear, the attachment of these crystals after the calcination process is strong enough to keep the zeolite firmly on the surface during the crystallization of the zeolite film. The formation of the zeolite film is achieved by contacting the substrate with adsorbed seed crystals with a synthesis solution with a composition suitable for the crystallization of zeolite ZSM-5 at hydrothermal conditions.[16] This treatment results in a continued growth of the seed crystals and eventually to the intergrowth of these crystals into a dense and continuous film, Fig. 1D. Fig. 2(*b*) and (*c*) show top and side views, respectively, of the final film obtained after 40 h of crystallization. From these and numerous other SEM micrographs it is clear that the ZSM-5 films produced are continuous, free from cracks and that they have an almost constant thickness. The film thickness estimated from the micrograph shown in Fig. 2(*c*) is 200–250 nm. The film thickness of this sample was also calculated from Kr adsorption data using the BET equation and the surface area (500 m^2 g^{-1}) and density (1790 kg m^{-3}) of pure ZSM-5 as a reference. The value obtained in this manner is 230 nm which is in very good agreement with that measured from the SEM micrograph.

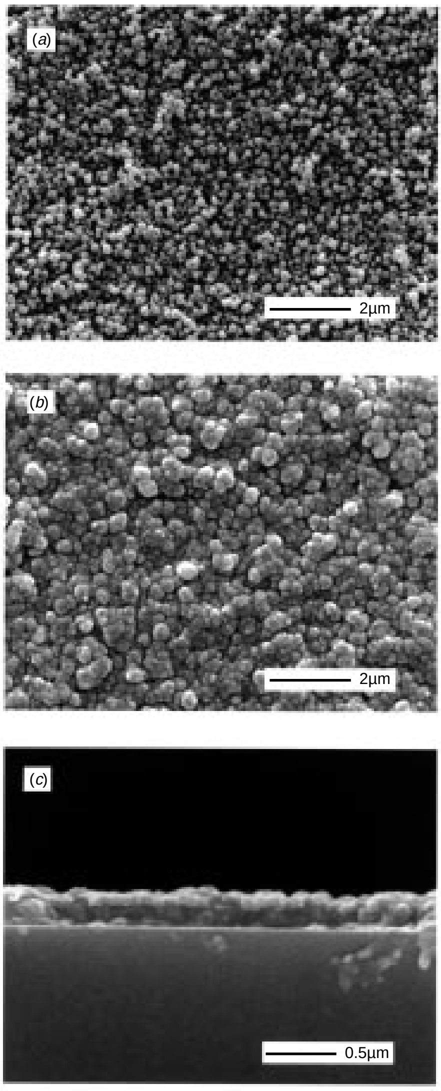

Fig. 2 SEM micrographs showing the adsorbed 90 nm ZSM-5 seeds on the Au surface (*a*), the top view (*b*) and side view (*c*) of the continuous zeolite film after hydrothermal crystallization

The results presented in this communication show that continuous films of ZSM-5 on gold substrates can be prepared by a procedure involving four steps. The gold surface is first covered with a monomolecular layer of MPT which is hydrolysed under acidic conditions. The surface charge is then reversed by adsorption of a cationic polymer and a monolayer of colloidal seed crystals is adsorbed on the positively charged surface by electrostatic attraction. After decomposition of the silane and the cationic polymer by calcination, the seed crystals are grown into a continuous ZSM-5 film by further crystallization in a synthesis solution at hydrothermal conditions. The method is flexible and easy to control and allows for the preparation of films with a desired thickness of *ca*. 50 nm and upwards. Although only demonstrated in this communication for zeolite ZSM-5 on gold substrates, the method permits preparation of thin films of a number of zeolite types, *e.g.* zeolite-β, -A and -X, on various substrates. The flexible nature of the method employed gives new possibilities for the preparation of zeolite films with different physicochemical characteristics which may be of great interest in a number of applications.

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