

Better Ceramics Through Chemistry III

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FORMATION AND CHARACTERIZATION OF INORGANIC MEMBRANES FROM ZEOLITE-SILICA MICROCOMPOSITES

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ABSTRACT

Small crystals of zeolites (500-1000 nm) with two- and three-dimensional channel systems (faujasite and ZSM-5 structures) were embedded in amorphous thin films derived from TEOS hydrolyzed in alcoholic solution. Scanning electron microscopy studies show that the zeolites can be quite evenly dispersed in the membrane, resulting in single layers of zeolite crystals protruding out of the amorphous matrix. In situ FT-IR studies with a series of probe molecules revealed that in most membranes the zeolites were 100% accessible from the gas phase. The membranes excluded molecules which are larger than the pore openings of the zeolite embedded in the composite.

INTRODUCTION

In view of the urgent demand for selective, microscopic sensors^{1,2} which can be integrated into microelectronic circuits, our research program is aimed at the synthesis and characterization of a new generation of well-defined inorganic membrane structures with controlled porosity in the one-nanometer range. These inorganic membranes will ultimately be deposited on the surface of chemical sensors and serve as "molecular sieves" which control access of selected target molecules to the sensor surface.

This communication reports on the design of porous inorganic membranes via the formation of zeolite-amorphous microcomposites. Zeolites are crystalline, porous materials, typically aluminosilicates with charge compensating cations in open channel structures^{3,4} with pore diameters ranging from about 0.3 to 0.8 nm. We expect the following advantages from our zeolite approach: A selection of channel structures with well-defined diameters can be synthesized and acid/base properties can be adjusted within a broad range by ion-exchange⁵, variation of the framework metal⁶, or heat treatments and subsequent doping. The hydrophobicity of the material is tailored by appropriate choice of the framework composition.

A few studies related to zeolite membranes have been reported by other groups, including permeation experiments through single crystals of NaX zeolite⁷, and the preparation of alcohol-selective pervaporation systems by the addition of silicalite to silicone rubber membranes⁸. However, the latter systems function by modification of selectivity and flux through the membrane and do not exclude competing gases. Complete exclusion of all competing gases from the membrane is the goal of the present study.

An important component of the porous, inorganic membranes prepared in this study is the glass or ceramic matrix in which zeolite crystals are incorporated. Synthesis of this inorganic matrix is accomplished through "sol-gel" processing of hydrolyzed tetraethylorthosilicate (TEOS). Depending on the synthesis conditions employed, inorganic polymer growth (via M-O-M bonding) can be biased toward extended, weakly branched structures or compact, fully polymerized colloidal particles^{9,10,11}. Final consolidation of the porous structure to a non-porous, "glass-like" film generally occurs by viscous sintering^{12,13}. When the porous gel phase is completely consolidated, it will serve as an impermeable matrix, allowing permeability through zeolite channels exclusively. We have studied model membranes on Si wafers made with faujasite and ZSM-5 zeolite structures with SEM and adsorption experiments monitored by in situ FT-IR spectroscopy.

EXPERIMENTAL

Zeolite ZSM-5 was synthesized from NaOH, Al₂O₃, colloidal silica (Ludox), and tetrapropylammonium hydroxide (Fluka, 10% solution) according to reference¹⁴ (ZSM₁-5). Sample ZSM₂-5 was refluxed 3 times in 0.1 M HCl. The acid form of commercial ammonium-exchanged faujasite NH₄Y (Linde LZYG2) was obtained by heating under a vacuum of 10⁻⁶ Torr with a rate of 5 Kmin⁻¹ to 720 K in the infrared in-situ cell (see below). Silica gel precursors

were hydrolyzed as described in ref. 9. The acid-catalyzed gel is labeled A2, the base-catalyzed gel B2.

Membrane HY/B2A2. The NH_4Y zeolite powder was dispersed in ethanol, added to the sol phase B2 with a vol.-ratio equal to 2:1, and dispersed using sonication for 5 min. 2 ml of the mixture were spin cast on intrinsic Si wafers (2 mm thickness) at 1000 rpm. The first membrane layer was coated with a thin top layer of A2 gel. ZSM₁-5 and ZSM₂-5 zeolites were dispersed in the A2 sol and dip-coated in one to n layers on the Si wafer to give membranes [ZSM₁/A2]_n. Other sol-dispersions were spray-coated on the Si wafer. The membranes were densified at 570 K for 10 min. after each coating step.

A combination of in-situ FT-IR experiments (Mattson Polaris spectrometer at 4 cm⁻¹ resolution) and temperature-programmed-desorption/MS was used to study adsorption behavior and surface acidity of the zeolite-silica membranes. Small sample wafers (0.5 cm x 1 cm) were mounted in a stainless steel UHV cell equipped with CaF₂ windows and sealed with Conflat flanges. The samples were heated under vacuum at a rate of 5 K/min to 720 K, cooled to 295 K, and exposed to ca. 1 Torr vapor of organic bases. The sample cell was connected to a compact UHV vacuum system pumped by a turbomolecular pump and equipped with a Dycor M200 quadrupole mass spectrometer. Scanning electron micrographs of the as-synthesized zeolite crystals and the zeolite-silica membranes were taken with an Hitachi S450 microscope at the Institute of Meteoritics, Department of Geology, UNM.

RESULTS AND DISCUSSION

1. Study of faujasite-silica membranes.

Crystals of NH_4Y zeolites were embedded in thin-film silica matrices and deposited on silicon wafers. The average crystal size, precursor for the silica film, film layers, and the film thickness are reported in Table 1.

Table 1. Components and Dimensions of Zeolite-Silica Membranes Deposited on Si-Wafers.

Sample name	Zeolite	Crystal size/nm	Gel Precursor	Film thickness/nm ^a
HY/B2A2	NH_4Y	300-1000	B2 then A2 coat	150 + 150
[ZSM ₁ /A2] ₃ ^b	ZSM ₁ -5	500	A2	500
[ZSM ₂ /A2] ₃	ZSM ₂ -5	500-1000	A2	500

^a Thickness determined using ellipsometry and SEM data.

^b This membrane was obtained by stepwise deposition of three layers of [ZSM₁/A2].

Most of the zeolite crystals of the membrane HY/B2A2 protrude slightly out of the silica matrix, thus they can be expected to be accessible to probe molecules adsorbing from the gas phase (Figure 1a). This is an important feature which is required for a successful implementation of these membranes as sensor coatings. The permeability of A2 sol-derived thin films has been examined separately using SAW device adsorption experiments (see Frye et al., this volume). After densification at 670 K, the A2 films alone did not even adsorb nitrogen. Therefore it can safely be assumed that the membrane area between zeolite crystals forms a dense layer that excludes all molecules of interest from the substrate surface.

The central issue of molecular access to the membrane-embedded zeolite crystals was addressed using infrared spectroscopy. Protons which are introduced into the zeolite by ion exchange will typically occupy well-defined positions at zeolite framework Si-O-Al oxygen bridges. Zeolitic bridged hydroxyls can be distinguished spectroscopically from other (terminal) hydroxyls on metal oxide surfaces, because they have O-H stretch vibrations at energies well below those of terminal hydroxyls¹⁵. For instance, the structural hydroxyls of HY zeolite (faujasite structure) appear at ca. 3640 and 3540 cm⁻¹, while terminal Si-OH typically occur at 3720-50 cm⁻¹. The surface hydroxyls observed on the gel-derived matrices (without zeolite) are characterized by a broad, weak IR absorption with a sharp onset at ca. 3750 cm⁻¹ down to ca. 3200 cm⁻¹.

The kinetic diameter of a base molecule will determine if it can react exclusively with acid sites located at external positions of the zeolite crystal, or if it gains access into the zeolite channel system. This principle is demonstrated by comparing the reaction of dehydrated HY zeolite with pyridine (kinetic diameter 5.9 Å) and with perfluorotributylamine (10.2 Å) (Table 2). Only pyridine reacts with the internal, structural hydroxyls of the zeolite. It should be noted that the protonation of pyridine generates a characteristic band at 1545 cm^{-1} which is considered diagnostic for the interaction of pyridine with Bronsted acid sites.

Pyridine and perfluorotributylamine were adsorbed at dehydrated faujasite-silica membranes in the infrared cell. The two probe molecules behave exactly as if they were adsorbed at free zeolite crystals. Pyridine has free access into 100% of the matrix-embedded zeolite channel system and is being protonated to pyridinium ion (indicated by a band at 1545 cm^{-1}), whereas the bulky amine is excluded from the zeolite hydroxyls (Figure 2a). This observation confirms that intact zeolites are embedded in the matrix, and, more importantly, that these crystals are indeed accessible to molecules adsorbing from the gas phase.

2. Study of ZSM-5-silica membranes.

Small crystals of ZSM-5 zeolites were embedded in thin-film silica matrices and deposited on silicon wafers by dip-coating. The sample parameters are reported in Table 1. The morphology of the ZSM-5 thin film samples appears to be more perfect than that of faujasite-silica membranes as demonstrated in Figure 1b. Zeolite crystals which might occur in small agglomerates are embedded in the smooth, *crack-free* film such that the crystals reach partially

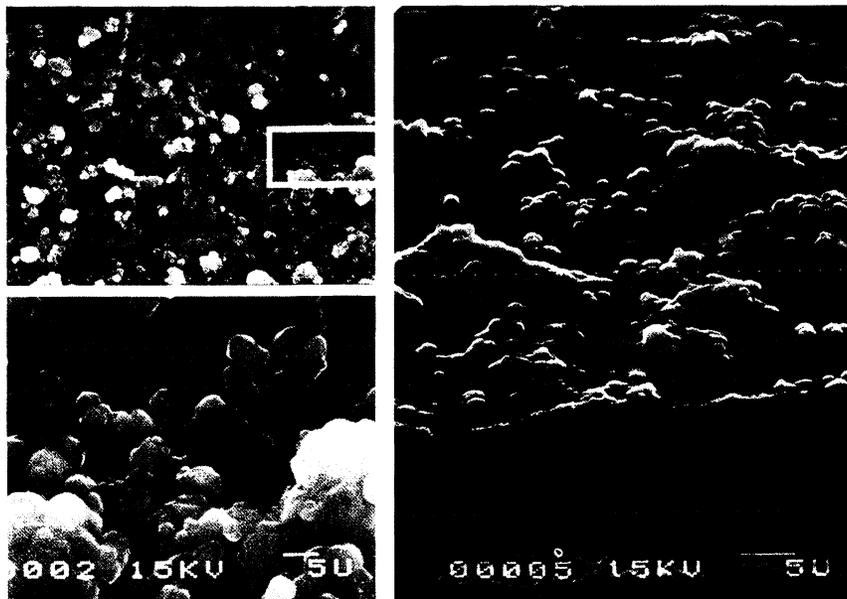


Figure 1. Electron Micrographs of Membrane HY/B2A2 (left) and [ZSM₂/A₂]₃ (right)

Table 2. Remaining Intensity of IR Hydroxyl Bands in Zeolites and Zeolite-Silica Membranes after Adsorption of Organic Species^a.

Probes: Kinetic diameter	Pyridine 5.9	(C ₄ H ₉) ₃ N 8.1	i-octane ^b ca. 6.2	NH ₃ 2.6	(C ₄ F ₉) ₃ N 10.2 (Å)
HY	0%	0%	-	-	100%
HY/B2A2	0%	0%	-	-	100%
ZSM ₁ -5	0%	50%	0% shift	30%	-
[ZSM ₁ /A2] ₃	0%	100%	0% shift	0%	100%
ZSM ₂ -5	-	-	ca. 50% shift	-	-
[ZSM ₂ /A2] ₃	reduced	100%	-	0%	-
[ZSM ₂ /A2] ₃ [*]	reduced	-	-	-	-

^a The spectroscopic observations are summarized by indicating the behavior of the 3640 cm⁻¹ band (HY) or the 3725 cm⁻¹ acidic hydroxyl groups (ZSM-5) upon equilibration at 295 K with 0.2–1.0 torr of the probe molecules. Percentages indicate estimated remaining intensity of the acid bands upon adsorption. Shift percentages: Estimated fraction of 3725 band which is shifted down to 3700 cm⁻¹ upon adsorption of 2,2,4-trimethylpentane. The different probe molecules could be desorbed at temperatures between 370 and 720 K.

^b i-octane: 2,2,4 trimethylpentane.

^{*} [ZSM₂/A2]₃^{*}: Membrane [ZSM₂/A2]₃ refluxed in 0.1 M HCl for 6 h.

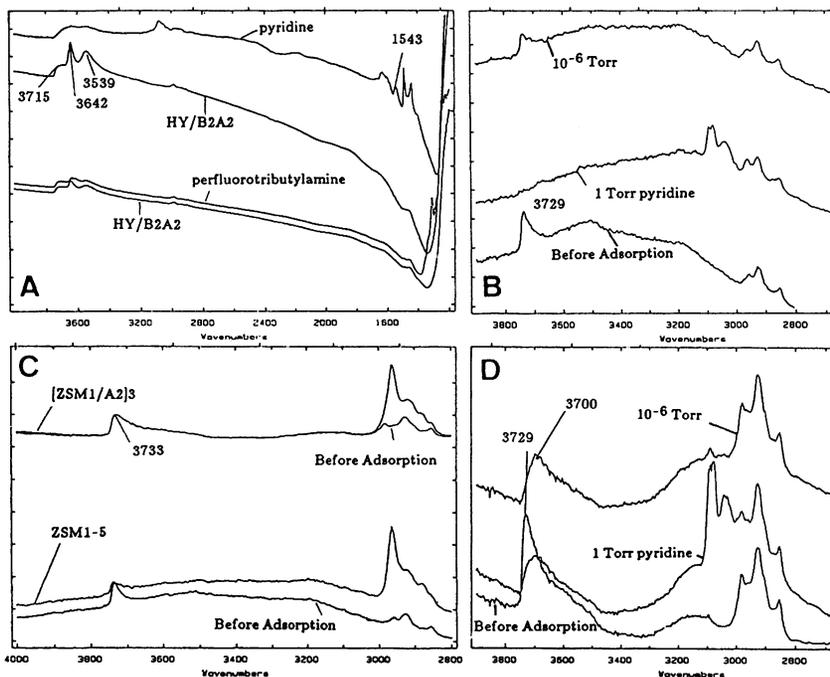


Figure 2. Adsorption of Pyridine and (C₄F₉)₃N on HY/B2A2 (A), Pyridine on ZSM₁-5 (B), (C₄H₉)₃N on ZSM₁-5 and [ZSM₁/A2]₃ (C), and Pyridine on [ZSM₁/A2]₃ (D).

out of the film. This feature is of obvious importance for selective sensor and separations applications, because cracks would open competitive diffusion paths and serve as adsorbing pores for analyte molecules. Adsorption studies similar to those with the faujasite membranes were carried out in order to determine the accessibility of zeolitic pores to different probe molecules.

The hydroxyl groups observed in ZSM-5 zeolites are quite different from the structural hydroxyls in faujasite and have been widely studied. As a result of the lower Al content, far less structural hydroxyls than in faujasite can be expected. Even though there is considerable controversy about the detailed interpretation of experimental observations, several basic results appear to be undisputed: A freshly prepared ZSM-5 sample containing tetrapropylammonium (TPA) and Na cations can be calcined in air at ca. 770 K to yield a zeolite with a small infrared band at ca. 3720-3740 wavenumbers^{16,17}. If the zeolite contains framework Al, subsequent ion exchange with either dilute HCl or NH₄Cl and further degassing yields a second hydroxyl band at ca. 3610 wavenumbers, which is assigned to structural, bridged hydroxyl groups most likely located at channel intersections in the zeolite^{18,19}. The origin of the 3740 band is controversial: it has been related to external Si-OH at the outer surface of the crystal, to contaminations from the synthesis gel²⁰, to amorphous dealumination products, and to dealumination-associated Si-OH ('nests') formed in the interior of the channel system²⁰. The ZSM-5 synthesis conditions in this study were aimed at the formation of very small crystals. This has been achieved by early quenching of the synthesis mixture shortly after nucleation. The ZSM-5 samples examined so far did not exhibit a significant infrared band at 3610 wavenumbers, indicating that no Al was incorporated into the crystals.

Adsorption of probe molecules of different kinetic diameters on ZSM-5 has been reported²¹. The adsorption behavior of vapors of pyridine, 2,2,4-trimethylpentane, tributylamine, and others on free ZSM-5 zeolites and zeolite membranes is summarized in Table 2. Of these molecules, only pyridine and ammonia can enter the channels of ZSM-5.

Based upon the spectroscopic data, the adsorption behavior of the ZSM-5 crystals alone and embedded in the silica matrix can be consistently described with the following model: A large fraction of terminal hydroxyls of the free zeolite ZSM1-5 is not accessible to the bulky tributylamine, thus there is a distribution of internal vs. external (accessible) hydroxyls of ca. 50:50 % (Figure 2c). Pyridine in equilibrium with the zeolite reacts with all hydroxyls, but evacuation at 295 K restores only about 50% which are believed to reside at the external surface of the crystals where the binding energy should be smaller (Figure 2b). Hydrocarbon molecules having access to acid surface sites are known to shift the hydroxyl frequencies by some ten wavenumbers. 2,2,4-trimethylpentane does not appear to react with the hydroxyls of ZSM1-5. If the ZSM2-5 is refluxed in dilute HCl, the number of hydroxyls accessible to 2,2,4-trimethylpentane increases substantially. This is tentatively explained by an increased degree of hydrolysis of the ZSM-5 lattice, creating more hydroxyl 'nests'.

If calcined ZSM-5 crystals are embedded in the silica membrane, most of the terminal hydroxyls (at 3725 cm⁻¹) are still present (Figure 2d). Thus these hydroxyls do *not* completely react with the silica gel in condensation reactions, as might be expected if they were all located at the external crystal surface. This result confirms the assignment of a major fraction of the 3725 band to *internal* hydroxyls which are not accessible to condensation reactions with the silica gel. Pyridine has still unobstructed access to the channel system of the dehydrated zeolite in sample [ZSM1/A2]₃. This is demonstrated in Figure 2d. All observed zeolitic hydroxyl groups react with pyridine at 295 K and show a typical C-C vibration of hydrogen-bonded pyridine at about 1595 cm⁻¹. It should be noticed that the broad infrared features due to hydroxyls of the matrix do not react with any of the probe molecules used here. Complete reaction of NH₃ with [ZSM1/A2]₃ confirms that all of the zeolite hydroxyls are accessible from the gas phase. It can be concluded that the *embedding procedure does not clog the ZSM-5 channel system* towards access from the gas phase. It appears that the very thin coating of silica on the protruding zeolite crystals may retract upon calcination and open up a significant portion of the interconnected pore system.

In contrast to the free ZSM crystals, the membrane-embedded zeolites did not show any reaction of the remaining hydroxyl groups with either 2,2,4-trimethylpentane or tributylamine (Figure 2c). This result is interpreted as follows: the external hydroxyl groups at the ZSM crystal surface link with the silica gel in condensation reactions. Thus, a gas-tight seal between matrix and zeolite is created, and the only molecules being adsorbed are those that can enter the accessible zeolite channels.

The effect of the surface properties of the zeolite crystals was examined by comparing the behavior of HCl-treated ZSM2-5 in the silica membrane [ZSM2/A2]₃ with the above observations. The pyridine adsorption of this membrane appears to be more hindered compared

to [ZSM₁/A2]₃. It is suggested that the HCl treatment of ZSM₂-5 creates more external SiOH groups through hydrolysis and favors extensive 'anchoring' of a thin layer of the A2 gel during the composite formation which prevents complete access from the gas phase. An attempt to etch this coat by reacting the wafer with HCl (membrane [ZSM₂/A2]₃^{*}) appeared to be successful: The pyridine adsorption resembles closely that of the untreated membrane [ZSM₁/A2]₃. (Table 2)

CONCLUSION

We conclude that the immersion of small zeolite microcrystals in sol-gel thin film precursors is a viable route to the rational design of highly selective membranes which discriminate between molecules in the angstrom size range. This type of microcomposite membranes offers future potential for applications on chemical sensor surfaces.

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