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Zeolite Thin Films with Tunable Molecular Sieve Function

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Abstract: We report on tunable zeolite-based thin film nanostructures whose molecular size selectivity can be controlled between 3 and 5 Å by fast ion exchange. The composite films are assembled from molecularly attached zeolite CaA crystals and a silica binding phase on the gold electrodes of piezoelectric quartz crystal microbalances (QCM). Intrazeolitic cations can be reversibly exchanged with other cations from aqueous solution, such as Na^+, K^+, and Rb^+. The mass changes resulting from cation exchange in the film can be measured *ex situ* due to the high stability of the film and the nanogram sensitivity of the piezoelectric crystal. The surface area and microporosity of the films were studied *in situ* on the piezoelectric crystals by measuring sorption isotherms. Distinctive differences in the nitrogen sorption between the CaA films and the Na, K, and Rb forms are due to blocking of the zeolite eight-ring windows. The effective pore sizes of the films were evaluated by measuring isotherms and sorption rates of vapors with different molecular sizes and shapes. Step by step exclusion of progressively smaller molecules from the interior porosity of the film is observed as a function of the cation size and distribution in the zeolitic framework.

The development of inorganic films and membranes with controllable porosity[1] has drawn much attention in view of promising applications in asymmetric membranes, catalytic monoliths,[2] and chemical sensors.[3−9] The interest in microporous thin films is primarily motivated by their potential molecular sieving action, large surface areas, and controlled host−sorbate interactions, especially at low vapor pressures.

Our recent studies of zeolite molecular sieve-based layers have introduced novel strategies for forming well-defined subnanometer pores in inorganic thin films. Zeolite molecular sieves are porous crystalline solids that possess ordered cages and channels of molecular dimensions (ca. 0.3−3 nm), ion exchange capability, and variable hydrophilicity/hydrophobicity.[10,11] The variable pore dimensions and the large pore volume of zeolites make them ideal candidates for sensor designs with effective molecular size discrimination and high sensitivity. The crystal sizes are often between 0.5 and 5 μm. Several strategies have been explored for thin film formation, including dip-coating of zeolite/silica sol suspensions[4,5] and chemical attachment of zeolite crystals via molecular coupling layers.[6−8] Zeolite crystals were also embedded into polymers,[12] covered with glazes,[13] and extruded into composite monoliths.[14] In the above preparations, it is important to control potential blockage of the zeolitic pores and/or formation of non-desirable additional porosity introduced by the matrix in the composites. We have recently discovered the growth of oriented zincophosphate and aluminophosphate molecular sieves on organophosphonate layers.[15,16] In these films, no matrix is required.

Piezoelectric acoustic wave devices are attractive transducers for chemical sensors and for the detailed characterization of thin porous films.[17] *In situ* sorption studies of the above zeolite films have revealed many interesting features regarding porosity, effective pore size, and the isosteric heat of adsorption. For example, we have demonstrated the selective detection of ethanol in the presence of humidity and larger organic molecules.[7]

In order to enhance control of molecular selectivity in sensors, it would be desirable to tune or switch the pore sizes of the zeolite crystals in the film. In this article we demonstrate such a concept by forming zeolite CaA/silica composite thin films and controlling the zeolitic pores through *in situ* cation exchange.

The unit cell of zeolite A is composed of 12 SiO_4 and AlO_4 tetrahedrons, respectively (*Pm*3*m* pseudocell, e.g., $Na_{12}Al_{12}Si_{12}O_{48}$).[10,18] The framework charge is balanced by 12 monovalent or 6 divalent cations. Sodalite cages are linked together

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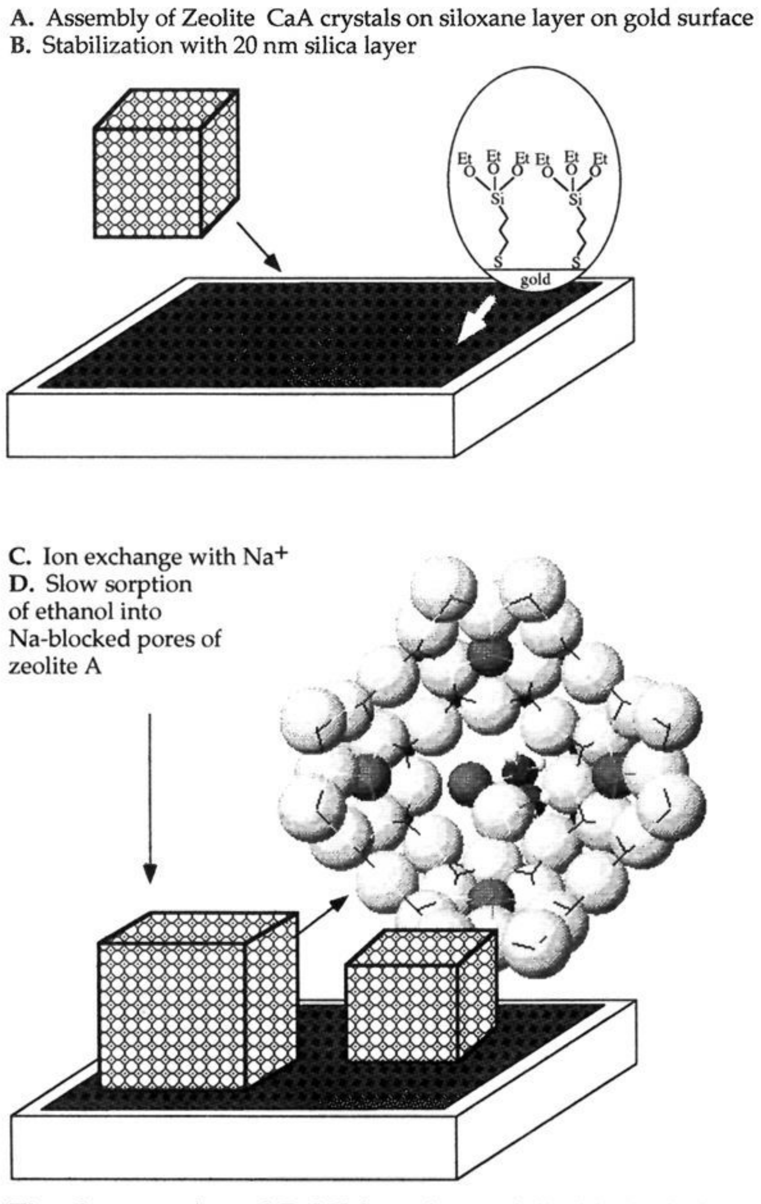
through double four-rings to form a central cage that is accessible through single eight-rings (S8R) with ca. 5 Å effective pore size. In dehydrated CaA zeolite the Ca^{2+} ions are located approximately in the plane of the six-rings of the sodalite cages thus leaving all S8R positions open,[19] and under hydrated conditions the S8R positions are still not occupied by Ca.[20] The effective pore diameter of CaA is close to the crystallographic dimension of the planar eight-oxygen-rings of the zeolite A structure. When the calcium ions are exchanged by 12 sodium ions followed by dehydration, the sodium ions occupy both the six-ring positions (8 per unit cell when fully exchanged) and the S8R windows (about 3−4 per unit cell, off-center in 3-fold coordination).[21] The result of this distribution is obstruction of the entrance of molecules into the central cages. This results in the creation of an effective pore size of about 4 Å. Hydration makes it difficult to crystallographically locate the four ions not positioned in six-rings; this could be due to greater disorder.[22] When the sodium ions are replaced with larger potassium ions, the pore size is further reduced to 3 Å (the ion distribution is similar to that of NaA).[23] The framework of zeolite A shows cation affinity in the following order: $Ca^{2+} > Na^{+} > K^{+} > Rb^{+}$. For many ions, the cation exchange is reversible with no hysteresis.

We now report on *tunable* zeolite-based nanostructures whose molecular shape selectivity can be controlled between 3 and 5 Å by fast ion exchange in the film (Scheme 1). The composite films reported in this study are prepared by using a molecular coupling layer to anchor zeolite crystals on gold that are stabilized with a thin sol-gel derived silica film. Nitrogen sorption is used to evaluate the accessible internal pore volume of the films. The molecular sieving capability of the film is demonstrated with the sorption behavior of different organic vapors.

Scheme 1. Assembly of Zeolite CaA Crystals on Silyl-Modified Gold Electrode, Followed by Silica Stabilization and Ion Exchange with Na^{+} [a]



[a] The slow sorption of EtOH into the partially blocked eight-ring windows is depicted. Sodium ions appear in gray, framework Al, Si in black, and oxygen in light gray.

Experimental Section

Zeolite/Silica Composite Thin Films. The composite films were prepared according to our reported methods.[6,7] Zeolite CaA (Alfa) was two times immersed in a 1 N aqueous solution of $CaCl_2$ for 6 h, centrifuged (2400 rpm, 20 min), and washed with deionized water 5 times. The gold electrodes of quartz crystal microbalances (QCM, AT-cut 6 MHz, Fil-Tech, Boston) were treated with (3-mercaptopropyl)-triethoxysilane in toluene (2 mM) under nitrogen atmosphere for 40 min, to achieve self-assembly of a thiol−organosilane coupling layer.[24,25] The zeolite crystals (1−1.5 μm in size) were attached to the modified gold electrodes by immersing the QCM into a stirred suspension of 0.2 g of zeolite in 30 mL of toluene for 1 h. The zeolite crystals bonded to the QCM electrode were further dip-coated with silica sol at 1 mm/s substrate withdrawal speed. The silica sol was prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol with hydrochloric acid as a catalyst.[26] A mixture of TEOS/EtOH/H_2O/HCl with molar ratios of 1/25/4/0.05 was reacted at 60 °C for 18 h prior to use for the zeolite overlayer coating. The composite films were calcined at 400 °C for 3 h in oxygen atmosphere with heating and cooling rates of 3 °C/min. The composite films typically consist of 100 μg/cm^2 of zeolite crystals and 10 μg/cm^2 of amorphous silica overlayer. The thickness of the silica layer is estimated to be about 20 nm when assuming a density of 2.2 g/cm^3 and a smooth surface.

Cation Exchange in Zeolite/Silica Composite Films. The zeolite film was rinsed with deionized water 5 times after calcination at 400 °C. The QCMs coated with the composite film and dried at 350 °C for 1 h in helium atmosphere show a constant resonance frequency at ambient temperature. To achieve cation exchange, the QCMs coated with the composite film were immersed in a 1 M aqueous solution of NaCl, KCl, or RbCl for 30 min and rinsed with deionized water 5 times. The above procedure was repeated 3 times respectively for different cation exchanges. The mass change resulting from the exchange of different cations in the films was monitored by the shifts of the QCM frequency at 25 °C (in the flow cell under a flow of helium) after the films were dehydrated at 350 °C.[27] Experiments also show that QCMs coated with CaA zeolite composite films recover their original resonance frequency after a $Ca^{2+}-M^{+}-Ca^{2+}$ cation exchange cycle.

Sorption in the Composite Films. Nitrogen sorption isotherms were obtained with QCMs coated with composite films dehydrated at 350 °C for 1 h in helium. The QCM was placed in a 30 mL stainless

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(27) A frequency shift of 1 Hz with the 6-MHz QCM correlates to a mass change of 12.3 ng/cm^2 according to the Sauerbrey relationship. See: Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206. We have measured the frequency changes of many crystals before and after heating to 350 or 400 °C. In most cases the changes after cooling are less than about 5 Hz, which corresponds to a maximum error of ca. 50 ng/cm^2 for the first coverage cycle with zeolites and sol-gel glass. The QCM crystals are not removed from the contact clips during the experiments. However, because in a few instances excursions as high as 50 Hz have been observed, caution is advised in data interpretation when measurements require high temperature heating of samples.

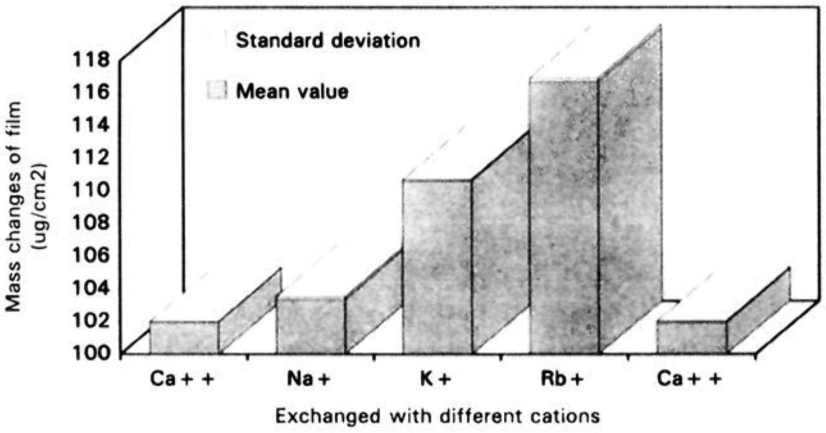

Figure 1. Mass changes of the zeolite silica composite films exchanged with different cations on piezoelectric substrate. The standard deviations of 10 frequency measurements within 20 min on dry films in He flow are indicated.

steel cell that was immersed in liquid nitrogen. The nitrogen partial pressure in helium was regulated by computer controlled mass flow controllers in the range of 0−95%. The mass change on the films caused by sorption or desorption was recorded by the frequency change of the QCM (1 Hz correlates to 12.3 ng/cm^2) through a DAS-16 data acquisition analog−digital I/O board. Vapor concentrations were changed to the next sampling point when the frequency change was less than 1 Hz in 20 s at constant partial pressure. The different concentrations of vapors (water, ethanol, *n*-hexane, 3-methlypentane) were generated from gravimetrically calibrated vapor diffusion tubes at a constant flow of helium (15 mL/min), further diluted with a second helium flow (0−200 mL/min) and passed through a 2 mL flat flow cell holding the QCM. All organic solvents were distilled and stored with dehydrated zeolite 3A prior to use.

Results and Discussion

Cation Exchanges in the Composite Films. When one Ca^{2+} ion (atomic weight 40) is replaced by two Na^+ ions (at. wt 23) in the zeolite pore system, a moderate increase in the mass of the dried composite film is expected. After 3-fold exchange with sodium ions, the mass of CaA zeolite film changed from 102.0 μg/cm^2 (7.9% of amorphous silica, 93.9 μg of CaA) to 103.4 μg/cm^2 (95.3 μg of NaCaA) (Figure 1). The mass per unit cell of zeolite A was changed from 1669.3 in the calcium form to 1694, which shows that about 4.2 of the calcium ions (70%) were replaced by 8.4 sodium ions. The remaining calcium in some of the zeolite crystals (on average, 1.8 Ca per unit cell) is probably blocked by the amorphous silica cover layer. From the nitrogen sorption isotherm (see below) we conclude that complete exclusion of nitrogen results from the ion exchange. This result suggests that the extent of sodium exchanged in the unblocked zeolite crystals must be higher than 75%.[10] A further increase in the mass of the films was observed by exchanging with larger cations, such as K^+ (to 110.6 μg/cm^2) and Rb^+ (to 116.7 μg/cm^2) (Figure 1). If only the 8.4 sodium ions per unit cell are considered exchangeable, these values correspond to 98% exchange with potassium and 64% with rubidium. The lower exchange level for rubidium is similar to the reported maximum exchange level for $Na^+ \rightarrow Rb^+$ in zeolite A (68%; ref 10, p 541). The rubidium-exchanged films can be re-exchanged with Ca ions, and return to the initial mass of the CaA film, which indicates that no detectable mass loss of the films occurs during the ion exchange. If the cation exchanges were performed on amorphous silica films, the frequency changes were less than 3 Hz. The above data show that careful gravimetric QCM measurements can be used to follow ion exchange processes in zeolites.

Nitrogen and Vapor Sorption Isotherms on the Composite Films. Sorption of nitrogen on the CaA zeolite composite film at liquid nitrogen temperature shows type I isotherms suggesting the presence of micropores on the films[28] (Figure 2). More than 90% of the nitrogen uptake in this film occurs at partial pressures below 0.1. In contrast, the composite film exchanged with sodium ions shows type II isotherms indicating the apparent absence of micropores in the films for nitrogen. Similar nitrogen sorption isotherms were obtained on potassium and rubidium exchanged films. These results can be attributed to the blockage of the intrazeolite pores by the larger monovalent ions which reduces the effective pore size at low temperature below the kinetic diameter of nitrogen (3.64 Å). Similar results have been reported for bulk zeolite A.[10,18] Significant absorption of nitrogen was only observed for the CaA form (0.22 g/g at 10 Torr of N_2 (0.013 p/p$_o$)).

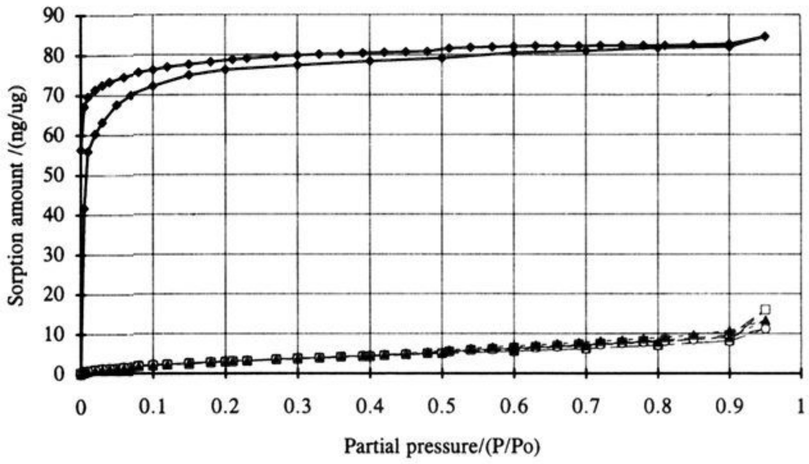

Figure 2. Nitrogen sorption isotherms at liquid nitrogen temperature on the composite films exchanged with different cations: calcium (◆), sodium (○), potassium (△) and rubidium (□).

It can be deduced that the zeolite retains its porosity after formation of the composite film and that the cations in the zeolite pore system act as gates controlling the microporosity of the film. The type II sorption isotherms obtained on the monovalent cation exchanged films result from sorption on the external amorphous silica cover layers. We note that no mesopores are observed in these films. BET plots indicate that the composite film has a nitrogen monolayer capacity of about 4.6 ng/μg of total film mass. Given the 7.9% silica layer in the film, the external silica cover layer has a typical sorption capacity of 58 ng/μg silica,[29] which correlates to a surface area of about 68 m^2 per gram of silica.[30] If one assumes that the composite films exchanged with different cations have similar surface interactions with nitrogen and uses the type II isotherms obtained on the monovalent ion-exchanged films as references, a ∂s plot[28] of the CaA film isotherm suggests that 76 ng/μg (or 0.076 g/g) is absorbed in the micropores and 5 ng/μg on the external silica layer. The micropore nitrogen sorption is less than that of bulk CaA zeolite. This lower sorption could be associated with imperfect acoustic coupling of the liquid intrazeolite phase with the QCM vibrations, and/or with the partial blocking of some zeolite crystals by the silica overlayer. The latter point would also be in agreement with the results of cation exchanges discussed above.

Vapor Sorption. The uptake of different vapors such as water (kinetic diameter 2.65 Å) , ethanol (4.3 Å), and *n*-hexane (4.3 Å) can be observed on the CaA composite films (Figure 3). Uptake of these molecules is also found with bulk CaA zeolite. For example, sorption of water (25 °C) at 0.025 Torr was 0.19 g/g, and sorption of *n*-hexane at 25 °C and 0.2 Torr was 0.13 g/g (ref 10, p 609). However, on the composite film,

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(29) The amount of nitrogen adsorbed on the silica layer is obtained by assuming that the nitrogen covers all of the 7.9 wt % external silica layer of the film.

(30) The calculation is based on dense monolayer packing of nitrogen (0.162 nm^2/molecule) on the silica surface at liquid nitrogen temperature.

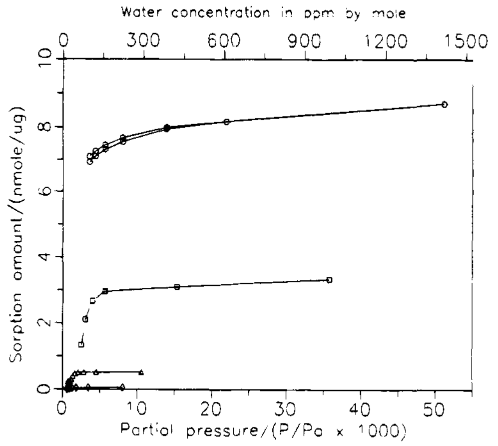

Figure 3. Sorption of different vapors at 23 °C on CaA zeolite composite films. Sorption of water (○), ethanol (□), *n*-hexane (△), and 3-methylpentane (◇).

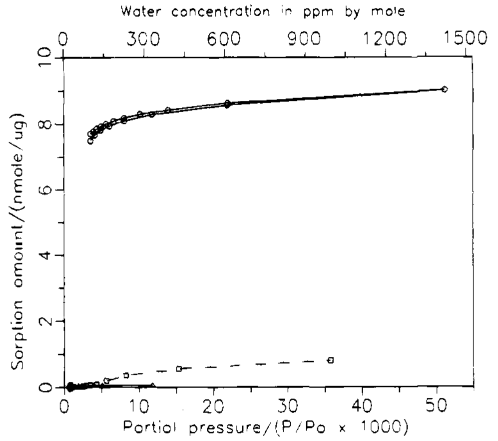

Figure 4. Sorption of different vapors at 23 °C on the zeolite CaA film exchanged with sodium ions. Sorption of water (○), ethanol (□), *n*-hexane (△), and 3-methylpentane (◇).

equilibrium sorption of ethanol and *n*-hexane was not attained below 500 ppm at the experimental conditions (shown as dashed lines in the figures). These results indicate that the molecules adsorbed on the zeolite composite films experience higher diffusion barriers compared to bulk CaA zeolite, and that the effective pore size of zeolite A coated with the amorphous silica layer is slightly smaller than that of the bulk zeolite. The uptake of nitrogen (3.7 Å, P_0 = 760 Torr at −196 °C), ethanol (P_0 = 48 Torr at 23 °C), and water (P_0 = 21 Torr at 23 °C) at a partial pressure of 0.01 is 68.6 (in desorption), 138, and 142 ng/μg of film, respectively. The significant sorption of water can be attributed to its small molecular size, which probably allows it to be absorbed in some of the zeolite crystals partially blocked by the silica cover layer. The relatively high uptake of ethanol at low partial pressure is associated with its polar nature and its molecular size that closely fits into the diameter of the zeolite pore. We also find that a larger molecule such as 3-methylpentane (5.0 Å) is completely excluded from the CaA film because its size exceeds that of the micropores of the zeolite. Previous studies have shown the exclusion of branched hydrocarbons such as isobutane from CaA (ref 10, p 610).

Dramatic changes in the vapor sorption behavior are observed when the CaA film is exchanged with sodium ions (Figure 4). The nonpolar *n*-hexane and 3-methylpentane are now both excluded from uptake into the micropores, while the sorption of water is almost unaffected by the cation exchange in the film. Sorption of ethanol on this film is controlled by a very slow diffusion process and no sorption equilibrium was attained in the entire range of vapor pressure used. These results show that the effective pore size of the composite film is now close to 4 Å, consistent with occupation of the S8R sites by sodium ions. Bulk sorption data indicate exclusion of *n*-hexane from NaA (ref 10, p 608). Furthermore, this result shows that the silica cover layer did not introduce detectable amounts of micropores with larger diameters into the film. This is also in line with the nitrogen sorption isotherms on the films exchanged with different cations.

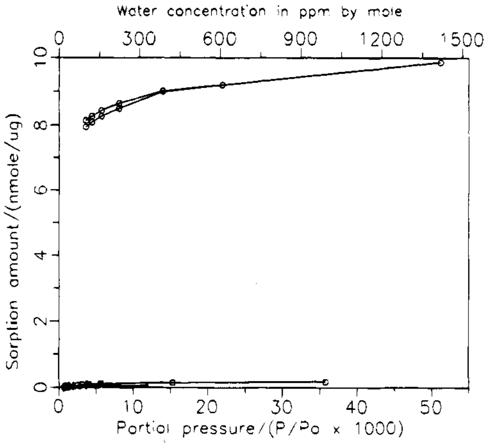

Figure 5. Sorption of different vapors at 23 °C on the composite film exchanged with potassium ions. Sorption of water (○), ethanol (□), *n*-hexane (△), and 3-methylpentane (◇).

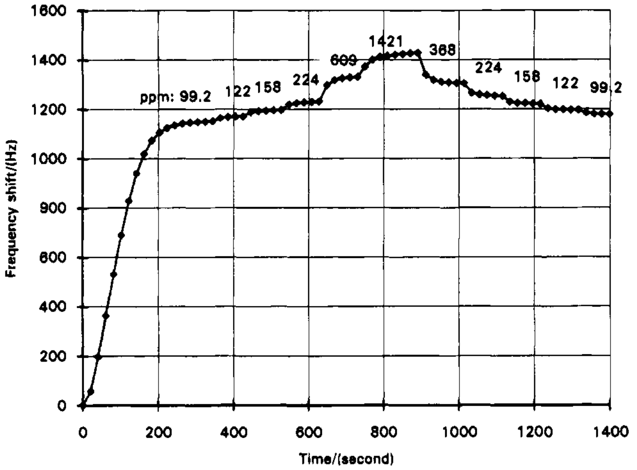

Figure 6. Sorption and desorption as a function of time of different water concentrations at 23 °C on the composite zeolite film exchanged with potassium ions.

When the sodium ions in the film are replaced by larger ions such as potassium, ethanol, *n*-hexane, and 3-methylpentane are completely excluded from the microporosity in the films (Figure 5). Only water is selectively absorbed on the film with a sorption capacity very similar to that of films with smaller cations. The larger cations located at the S8R positions in the zeolite further reduce the pore size of the film to about 3 Å. Similar sorption results were also obtained on the film further exchanged with rubidium ions. Although similar results have been obtained with bulk zeolite A, this is the first study demonstrating that cations in zeolite composite films can act as gates to selectively control the pore size of the film with angstrom precision.

Piezoelectric Molecular Sieve Water Sensor. The piezoelectric crystals coated with zeolite A composite films exchanged with potassium or rubidium show a highly selective response to water over polar or nonpolar organic solvents as discussed above. It is also well-known that such zeolites show very small uptakes of nitrogen, oxygen, hydrogen, carbon dioxide, or larger hydrocarbons at room temperature due to their much larger saturation pressures, or due to the molecular sieving effect of the crystals. The high sensitivity and selectivity of this device suggests a great potential for designing a high-performance humidity sensor. Figure 6 shows the response of the piezoelectric crystals coated with potassium exchanged composite film as a function of time at different water vapor concentrations. For example, when the concentration of water in helium was changed form 0 to 99.2 ppm at a flow rate of 17.1 μg of water per minute, the sorption rate of water on the film at room temperature was about 5 μg/min per square centimeter during the first 2 min of sorption (the entire QCM film surface is 4 cm^2). This value indicates that almost all of the water supplied to the system was captured by the film, and that the sorption is so fast that the sorption rate on the film is controlled by available sorbate in the system. When the water concentration is further increased, sorption equilibrium can be achieved in ca. 20−140 s depending on the concentration changes. During desorption, equilibrium can also be obtained between 20 and 60 s in the range of about 100−1000 ppm. Total desorption of the last water traces at 0 ppm humidity takes much longer, on the order of 30−60 min. This rate is still much faster than desorption from bulk zeolite beds and could be further reduced by decreasing the zeolite crystal sizes.

Conclusions

Thin molecular sieve films prepared by immobilizing zeolite crystals on modified gold electrodes can retain the regular sub-nanometer pores of the zeolite structure even when coated with silica overlayers. The novel composite films coated on piezoelectric substrates permit *ex situ* monitoring of ion exchange with high sensitivity. The surface areas and porosity of the amorphous bonding phases can be independently characterized by selective blocking of the zeolitic channels via cation exchange in the composite films. When the cations are used to adjust the porosity of the composite films, step by step exclusion of progressively smaller molecules from the interior porosity of the film is observed.

In summary, we show that the molecular selectivity of zeolite thin films can be precisely tuned by gating the entry of molecules into the zeolite pores. As demonstrated here, ion exchange is one means to achieve the gating function. This and other powerful strategies to tailor the molecular response of stable, inorganic nanostructures are presently explored in this laboratory.

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