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MOLECULAR RECOGNITION ON ACOUSTIC WAVE DEVICES: MODIFIED ZEOLITE-SILICA THIN FILMS WITH TAILORED ADSORPTION PROPERTIES

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ABSTRACT

Microporous thin films composed either of zeolite crystals embedded in sol-gel derived glass or of a molecular coupling layer, zeolite crystals and a porous silica overlayer, were formed on the gold electrodes of Quartz Crystal Microbalances (QCM). The microporosity of the thin films was characterized by *in situ* nitrogen and vapor sorption isotherms. Both preparation methods result in thin films with substantial microporosity. Selective adsorption based on molecular size exclusion from the microporous films could be achieved.

INTRODUCTION

Growing efforts are being devoted towards the design of chemical microsensors for environmental monitoring and industrial processing [1]. We have recently developed microsensors with molecular sieving functions in chemically selective layers on piezoelectric devices [2,3,4]. The successful design of microporous thin films retaining the molecular sieving capabilities of glass-embedded zeolites requires that several issues be addressed:

- The glass matrix should not introduce additional, undesired porosity.
- The glass matrix should not clog the zeolite pores after deposition, i.e., the zeolite porosity should be accessible from the gas phase.
- The attachment technique should result in a mechanically stable film that provides effective coupling between the zeolite crystals and the oscillating QCM.

In situ nitrogen adsorption data of different zeolite-containing glass films were used to explore some of these aspects. In an extension of the glass-based composite approach we have also explored the attachment of zeolite crystals on sensor substrates by molecular means, i.e., by using a bifunctional coupling layer that binds to the substrate as well as to the zeolite crystals. As an example of such a system, we discuss a chemical microsensor with combined molecular sieve and selective surface interactions, based on novel silicalite-silica composite thin films on the active area of QCMs. The function of this sensor will be discussed in the context of selective responses towards ethanol.

In addition to the high sensitivity and selective size exclusion offered by molecular sieve films, the nature of the chemical surface interactions is important. In the thin films described below, interference from water (2.65Å) which is smaller than ethanol (4.3Å), could be minimized through hydrophobicity of the molecular sieve and the matrix (silica). The interplay of size exclusion and surface affinity thus provides highly selective adsorption suitable for sensor applications.

EXPERIMENTAL SECTION

The QCM crystals used in the present study are AT-cut 5-9 MHz piezoelectric resonators, with 0.20 cm^2 gold electrodes deposited on chromium underlayers on opposite sides of the crystal. The sensitivity of a 6 MHz QCM according to the Sauerbrey relationship [5] is 12.3 ng Hz^{-1} cm^{-2}.

The sol-gel derived, dip-coated composites were prepared from a suspension of silicalite (MFI) and Na-faujasite (FAU) in acid- or base-catalyzed (A2 and B2, respectively) TEOS sols as described previously [2b, 6]. Silicalite is a crystalline molecular sieve of composition SiO_2 with a pore system of zig-zag channels along *A* (free cross-section ca. 5.1 x 5.5 Å), linked by straight channels along *B* (5.3 x 5.6 Å), while FAU is composed of truncated Si/Al octahedra (sodalite cages) that form supercages with 7.5 Å circular openings and 13 Å internal diameter, with typical composition $Na_{58}Al_{58}Si_{134}O_{384}$ [7].

The preparation of the microporous layer for the ethanol sensor (MFI-EtOH) involved two steps: First, silicalite crystals (about 3 μm diameter) were chemically anchored to the QCM gold electrodes via a thiol-organosilane coupling layer [4]. The silicalite crystals bonded to the QCM electrodes were then further coated with an amorphous, porous silica layer, prepared via sol-gel processing from $Si(OEt)_4$ [8], so that stable microporous thin film composites were obtained. Nitrogen sorption at liquid nitrogen temperature on films where the microporosity is presaturated with ethanol revealed a nitrogen monolayer capacity of 0.0028 g/(g film), corresponding to only 9.8 m^2/g external surface area.

The selectivity and sensitivity of the composite film coated QCM devices was determined by measuring the dynamic vapor sorption isotherms in a computer controlled helium vapor flow system. QCM frequency changes of 0.1 Hz could be detected with a Keithley 775A frequency counter interfaced to a 386-based personal computer. Equilibrium of the vapor sorption was assumed when the frequency changes were less than 1.0 Hz in 30 seconds.

RESULTS AND DISCUSSION

Uncoated and glass-coated QCMs. Nitrogen adsorption isotherms of uncoated QCM crystals are Type II and indicate surfaces with no porosity or with macropores. A polished 9 MHz QCM crystal shows a BET surface area of 2.0 cm^2/cm^2 and a C constant of 20. This deviation from a perfectly flat surface is attributed to microscopic roughness of the devices. If the crystal is dip-coated with A2 sol and heated in air at 350°C to result in a coating mass of 1.55 $\mu g/cm^2$, the BET surface area does not increase. However, coating the crystal with a B2-sol derived glass film results in some porosity of the film when heated at the same conditions. The BET surface area increases to 10 cm^2/cm^2.

The conditions of the heat treatment have a profound effect on the porosity of the glass films. Calcination in oxygen at 450 °C further increases the surface area of the films and introduces some microporosity. For instance, if a B2-derived film (45 $\mu g/cm^2$) is treated at 450 °C, the BET surface area increases to 19 cm^2/cm^2 (corresponding to 42 m^2/g; derived from the desorption branch), and micropore filling with 0.019 g N_2/g film is observed. In the sorption branch, the micropore filling is 0.010 g N_2/g. The difference between the adsorption and desorption branches found in several isotherms is probably associated with tortuous porosity of diameter close to that of nitrogen, such that hysteresis results.

Adsorption on Zeolite Sol-Gel Composites. Silicalite (MFI) and faujasite (NaY) type zeolites were embedded in different sol-gel derived glasses by dip-coating a suspension of the zeolites in the corresponding sol. The microporosity and external surface areas of these films were determined from α-plots of the nitrogen adsorption isotherms taken on the QCMs.

In general, the isotherms of the zeolite-glass composites show distinct microporosity as indicated by the initial steep rise of the adsorption at very low partial pressures. However, the isotherms differ from ideal Type I (Langmuir) adsorption which would be expected for zeolite crystals. After the initial steep rise the films are not saturated but continue to adsorb nitrogen in a fashion typical for many porous solids with Type IV isotherms. The continued adsorption indicates the presence of meso- and macroporosity that must result from combining the zeolites with the glass matrix.

Figure **1** shows a comparison of adsorption isotherms of silicalite (MFI) embedded in A2 glass and heated to 350 and 450 °C. Porosity parameters obtained from these isotherms are listed in Table 1. At about the same total coating weight, the adsorption isotherm resulting from lower temperature heating shows clearly much less adsorption in the micropore region (0.015 g N_2/g film at p/p_o=0.10) than that resulting from high temperature heating (0.047 g N_2/g film at p/p_o=0.10). Even if the desorption branch with the hysteresis is evaluated, higher

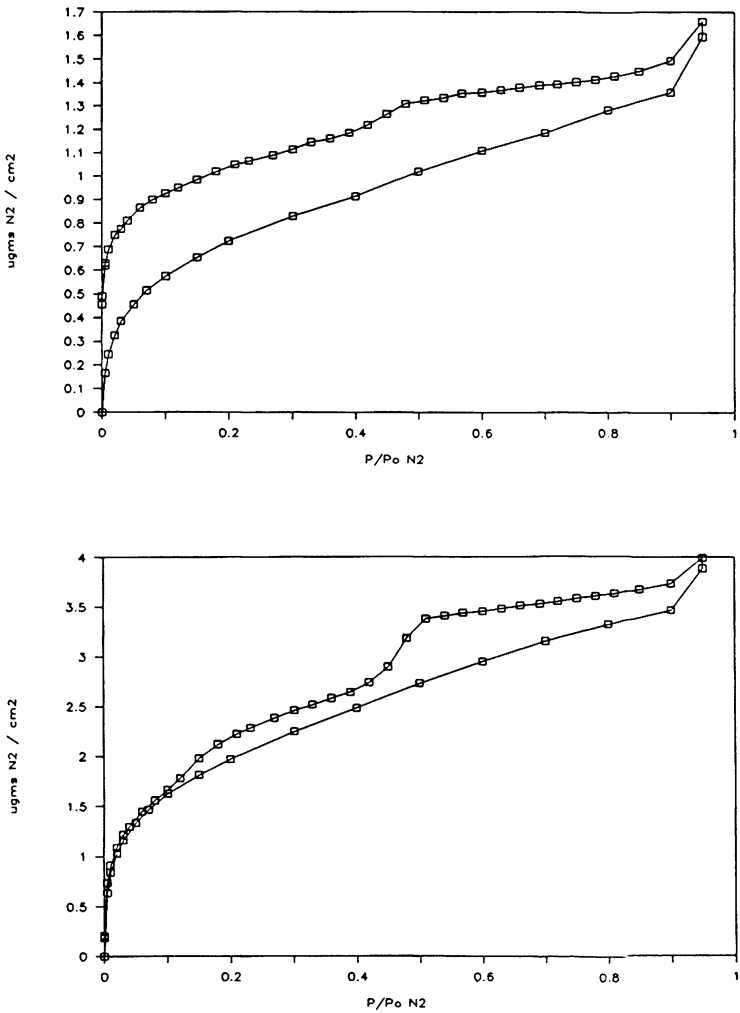

Figure 1. Nitrogen adsorption isotherms on silicalite crystals embedded in A2-derived glass films calcined at 350 °C (top), and calcined at 450 °C (bottom).

microporosity results from heating at higher temperature (0.021 vs. 0.014 g N_2/g). The other important difference between the two isotherms relates to the desorption behavior. After heating at lower temperature, the desorption branch is offset by a strong hysteresis similar to that observed with some of the glass films themselves (see above) which is probably associated with a tortuous pore network of diameters close to that of nitrogen. On heating to 450°C in oxygen, the hysteresis in the low pressure region all but disappears, and some minor hysteresis in the mesopore region remains. Apparently the oxygen treatment removes residual organics from the films such that access to the zeolites is more facile.

The microporosity of these composite films is substantially less than that expected for a film consisting of 100% accessible silicalite (0.17 g N_2/g). Since the weight fraction of the zeolite in the films is not known, it cannot be determined exactly how much of this decrease in microporosity must be attributed to potential pore clogging, ineffective acoustic coupling, or dilution with the glass film. Previous spectroscopic studies have established that zeolite porosity is accessible in similar films [2b].

Table 1. Microporosities and external surface areas of zeolite-glass composite films from nitrogen adsorption isotherms.[a]

Sample	Coating Mass $\mu g/cm^2$	Microporosity g N_2/g film	External Surface m^2/g film	Hysteresis at $p/p_o<0.1$
MFI-A2-350	39	0.014	36	+
MFI-A2-450	35	0.021	110	-
MFI-B2-350	45	0.029	62	+
MFI-B2-450	34	0.029	138	-
FAU-A2-350	55	0.011	64	-
FAU-A2-450	45	0.017	60	-
FAU-B2-350	51	0.020	35	+
FAU-B2-450	41	0.027	55	-

[a] Evaluated from α-plots of the desorption branches; when no hysteresis is present (-), the data are similar to those derived from the adsorption branches.

When the silicalite crystals are embedded in a B2-derived glass film, a comparison of the adsorption isotherms obtained after calcination at 350 and 450 °C show very similar trends as with the A2 glass (Table 1). Again, the adsorption isotherm resulting from lower temperature heating shows clearly much less adsorption in the micropore region (0.027 g N_2/g film at p/p_o=0.10) than that resulting from high temperature heating (0.059 g N_2/g film at p/p_o=0.10). The strong hysteresis disappears only on calcination at 450 °C. The B2-derived glass matrix results in more porous composites than the A2-derived films, as reflected in the higher microporosities and external surface areas, determined at both calcination temperatures. This is consistent with the known behavior of base-catalyzed TEOS sols which retain greater porosity on condensation due to their more compact aggregate structure.

Films derived from faujasite crystals show a different behavior with respect to calcination temperature, compared to silicalite. Figure 2 shows nitrogen sorption isotherms of FAU in A2-derived films. At both temperatures, no hysteresis is observed in the micropore region, but the microporosity still increases on heating to 450 °C, from 0.011 to 0.017 g N_2/g film. Similarly, little hysteresis is observed if a B2-derived FAU composite is heated to 350 °C, in contrast to the silicalite B2-film. As shown in Table 1, the microporosity of the FAU-B2 films is higher than that of the A2-derived films, but the external surface areas remain similar.

These results suggest that the sols do not affect the access to the larger FAU pores as much as they limit access into silicalite pores at low calcination temperatures where the glass may still contain residual organics. Thus, the adsorption behavior of the FAU films is not much affected by the different calcination treatments. Relative to the bulk micro-porosity (0.25 g N_2/g), that of the FAU-containing films is reduced more than that of the MFI films, possibly due to increased penetration of the sol into the larger FAU pores.

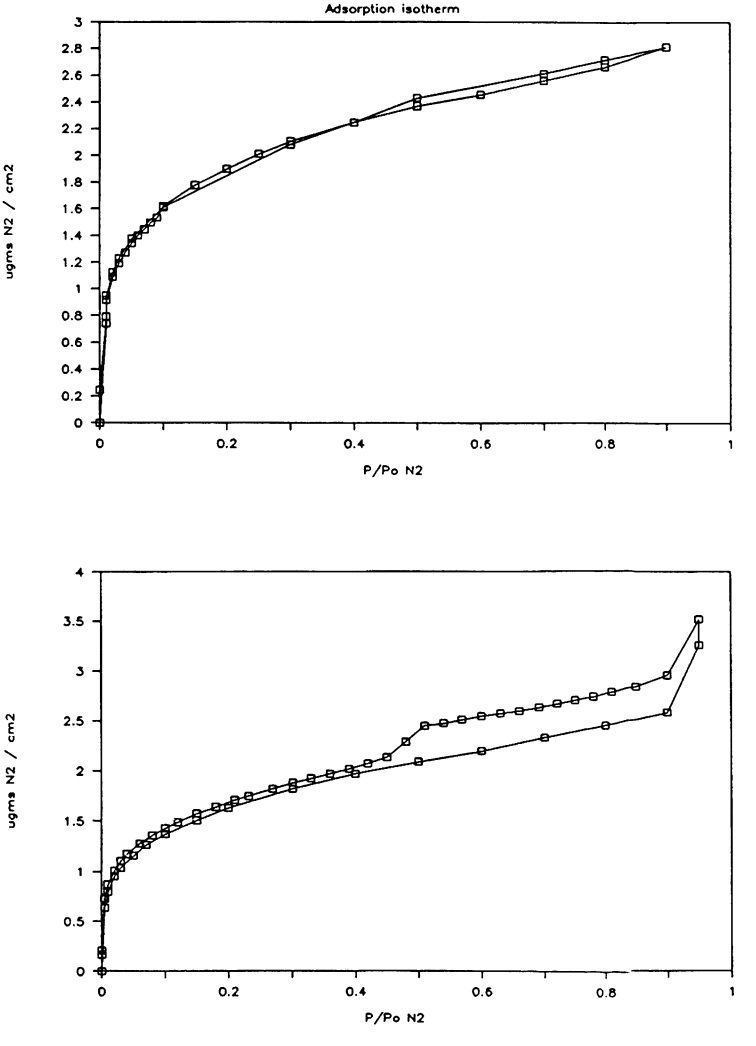

Figure 2. Nitrogen adsorption isotherms on faujasite crystals embedded in A2-derived glass films calcined at 350 °C (top), and calcined at 450 °C (bottom).

Ethanol selectivity. The selective vapor responses of a QCM coated with the microporous, hydrophobic silicalite composite layer (MFI-EtOH) are illustrated by the sorption of pure vapors of ethanol (ca. 4.3 Å diameter), 2,2,3-trimethylpentane (iso-octane, ca. 6.2 Å) and water (2.65 Å) in the range of 0-2000 parts per million (ppm) in moles (Figure 3). The QCMs were pre-degassed at 170 °C in a helium flow for 20 min. The sorption of ethanol (top curve) shows the largest and fairly linear response as a function of vapor concentration. A 50.4 ppm ethanol vapor concentration results in 0.024 μg sorption per μg coating layer, 309 ppm cause further mass increase to 0.050 μg/μg, and 722 ppm to 0.076 μg/μg, which is about 1000 times higher than the alcohol response of a bare QCM.

In contrast, the response of the microdevice to iso-octane (bottom line) exhibits an almost negligible change with increasing vapor concentration. As the concentration of iso-octane is varied from 200 ppm to 700 ppm, the amount adsorbed changes from 1.66 ng/μg to 1.87 ng/μg, which is a mass increment of only 0.6% of that of alcohol sorption at the same concentrations. The results show that novel sensing layers with highly effective molecular sieving functions and very low external surface areas can be designed. Sorption of the small water molecules (middle line) shows also a small response. Although water sorption slightly increases with increasing concentration (at the two concentrations given above, the capacity is respectively 12.2 and 15.5 ng/μg), it already approaches a rectilinear isotherm at these low concentrations. This behavior differs drastically from the sorption of ethanol.

The microsensor design discussed in this communication shows that highly selective responses can be achieved when microporous adsorption is combined with tailored surface interactions in composite films. Exploration of additional selective interactions in microporous glass composites is in progress.

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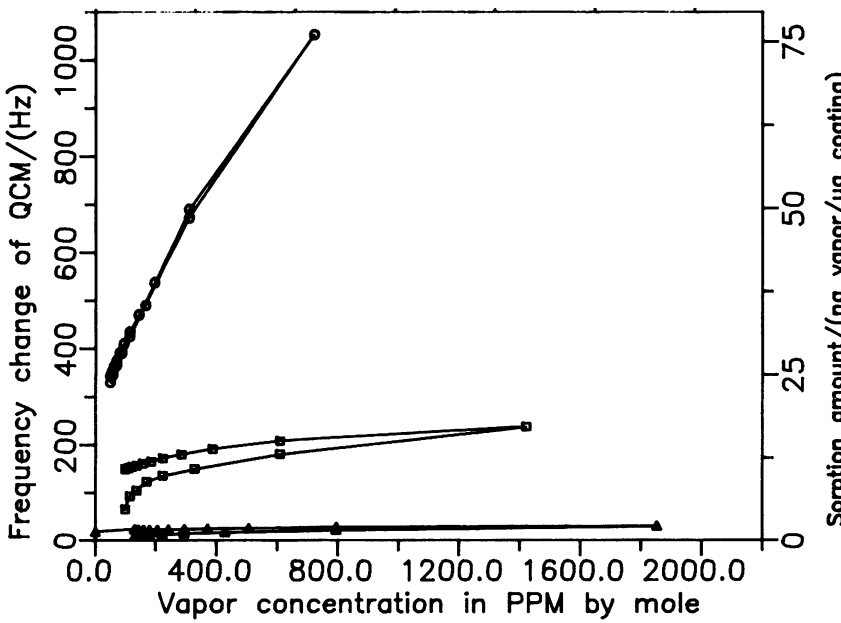

Figure 3. Sorption isotherms of ethanol (O), water (□) and isooctane (Δ) on a QCM coated with 168 μg/cm^2 of MFI-EtOH composite at 20 °C.

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