Molecular recognition on acoustic wave devices: zeolite thin films coated with organosilane gate layers

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Abstract

Microporous thin films composed of a molecular coupling layer, zeolite crystals, and a porous silica overlayer, were formed on the gold electrodes of quartz crystal microbalances (QCMs). The silica overlayer enhances the mechanical stability of the zeolite films, and results in additional surface area and porosity as characterized by the sorption isotherms and transient sorption of vapors with different molecular diameters and different polarities. The protecting silica glass layer is gas permeable such that the regular zeolite micropores with molecular sieving capability are still accessible in the composite film. A novel surface tailoring technique for the microporous thin films was developed, in which organosilane molecules were chemisorbed on the silica overlayer via siloxane linkages, forming a molecular "gate" at the gas thin film interface. The adsorption of vapors into the microporous zeolite films is therefore controlled by the permeability of the gate layer. Selective adsorption based on kinetic or equilibrium exclusion from the microporous films could be achieved, as demonstrated by discrimination of molecules with similar polarity but different molecular diameters (water vs. ethanol), and effective exclusion of larger molecules such as n-hexane. As a result of the increase in the vapor sorption selectivity and reduction of the external surface area of the thin films, the modified QCMs show high selectivity towards water over other molecules.

Keywords: acoustic wave device; sensor; zeolite film; organosilane coating; humidity sensing

Introduction

The design of microporous thin films and membranes has attracted increasing attention. These systems offer many potential applications in such diverse fields as catalysis, separation, microelectronics and chemical sensors. We have previously reported molecular selectivity on molecular sieve-coated piezoelectric devices. The combination of mass sensitivity at the nano- or picogram level [1,2] with the molecular shape and size selectivity of zeolites [3-5] presents a promising area of research in molecular recognition and interfacial chemistry. The microporous framework of the zeolite films endows the active region of the sensors with extensive surface area and volume

for vapor sorption, and provides for molecular exclusion and recognition sites. Vapor sorption experiments with microporous thin films coated on quartz crystal microbalances (QCMs) have demonstrated that molecular selectivity of over 100:1 could be achieved based on the molecular sieving and sorption affinity of the particular zeolite crystals used [4,5]. The sorption behavior and ultimate selectivity of the films is also influenced by the nature of the external surface. For example, the presence of external silanol groups will result in non-selective interactions with polar and polarizable molecules, hence reducing the molecular recognition ability due to the zeolite pores of such a device.

The focus of the present study is to design mechanically stable zeolite composite thin films on QCM devices, and to enhance their molecular

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recognition capability, for example by eliminating silanol–adsorbate interactions. Our approach is to coat the composite surface with an organosilane monolayer via siloxane linkages [6]. Such a monolayer should (i) neutralize the non-selective sorption sites of the surface silanol groups and (ii) potentially act as a gate layer that controls transport of the species of interest into the zeolite film. Fig. 1 depicts a schematic cross section of the microporous composite films. The films are characterized by nitrogen sorption isotherms at liquid nitrogen temperature, transient sorption of vapor pulses, vapor sorption isotherms, and sorption kinetics. A detailed investigation shows that different gate layers (in which the organosilane precursors have single, double or triple organic groups protruding from the surface) have a profound effect on both the sorption selectivity and kinetics.
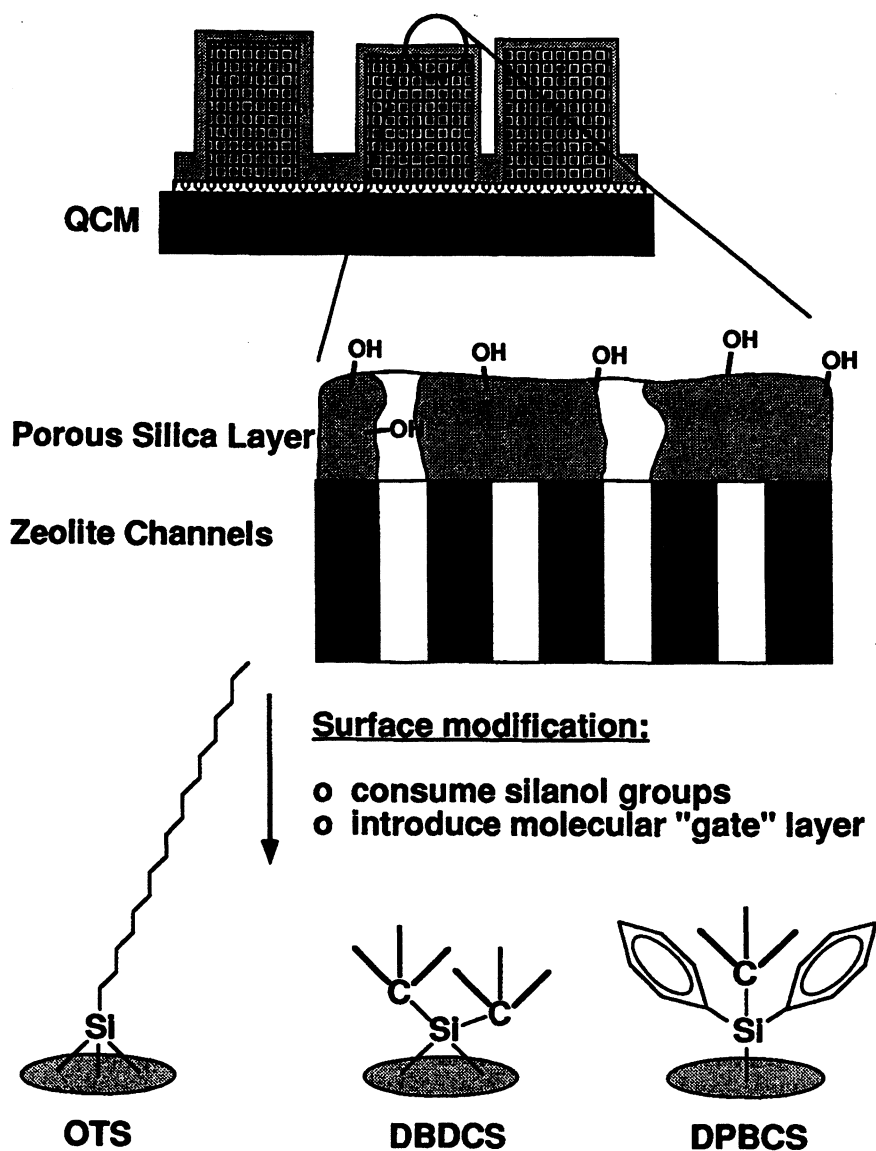

Fig. 1. Schematic cross section of composite microporous film formed on the gold electrode of a QCM crystal.

Experimental

Materials

Sodium A zeolite was obtained by threefold ion exchange of 5A zeolite (Alfa) with 1 N aqueous solution of NaCl, and subsequently filtered and washed with water and dried at 50°C before use. (3-Mercaptopropyl)trimethoxysilane (MPS, $HS(CH_2)_3Si(OCH_3)_3$) and tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) (Petrarch) were used without further purification. AT-cut 6 MHz QCMs with vacuum-deposited keyhole patterned gold electrodes on both sides, acquired from Cold Springs Research (New York), were coated with zeolite thin films and used for porosity characterization, and in situ monitoring of silane chemisorption. Toluene (Fisher) was stored over dehydrated 3A zeolite and deoxygenated by bubbling nitrogen for 30 min when employed as solvent for the formation of the MPS coupling layers on the gold electrodes of the QCMs. The silane precursors for the formation of the gate layers, such as octadecyltrichlorosilane (OTS), di(tert-butyl)dichlorosilane (DBDCS) and diphenyl(tert-butyl)chlorosilane (DPBCS) (Petrarch) were used as received. UHP grade (>99.999%) nitrogen and helium purified in dry zeolite traps were used as carrier gases for the flow adsorption experiments.

Formation of zeolite composite thin films on QCM sensors

The zeolite thin films were prepared in two steps (see Fig. 1): (i) The NaA zeolite crystals were chemically anchored to the gold electrodes via thiol-organosilane coupling layers, in which the thiol head groups of the MPS bind to the gold surface and the triethoxylsilyl groups are oriented towards the solvent, similar to other bifunctional thiols [5,7,8]. (ii) A porous silica protecting layer on top of the zeolite crystals was subsequently formed.

The MPS coupling layer was self-assembled by immersing the QCM with gold electrodes into 1.0 mM MPS solutions in dry and deoxygenated toluene for 60 min. We have found by reflection-absorption infrared (RAIR) spectroscopy and contact angle measurements that a surface cleaning

process (e.g., an oxygen plasma at 4–8 Torr for 5–10 min) is necessary to prepare a contaminant-free gold surface immediately before use. After reaction with MPS, the QCMs were rinsed with toluene and purged with nitrogen to remove excess adsorbate, and transferred to a pre-sonicated zeolite–toluene suspension. A single zeolite crystal layer forms on the electrodes [5]. The amount of zeolite coupled onto the QCM electrodes can be varied in the range of about 10–100 µg/cm² by controlling the stirring time, the zeolite concentration in the suspension, the temperature of the suspension and the density of the thiol-silane layer. The zeolite-coated QCMs were then heated in air at 150°C for 1 h before further treatment.

A protecting silica layer was subsequently formed by transferring the zeolite-coated QCM into an acid-catalyzed [9,10] TEOS-derived sol. For its preparation, 15 ml TEOS and 1 ml 0.05 N HNO_3 were added dropwise into 100 ml ethanol at 50°C. Before use, this stock solution was further diluted to 10% by adding ethanol. The silica sol was coated on the zeolite-containing electrode by dipping the QCM into the solution for 10 s and pulling it out at a rate of 1 mm/s. The coated zeolite composite thin films were heated in oxygen at 350°C overnight prior to further characterization and modification.

Formation of the gate layer

The silica film on the zeolite crystals was modified by chemisorption of organosilane vapors at 100°C. The organosilane vapors were generated by passing nitrogen (100 ml/min) through organosilane solutions in a saturator at ambient temperature. The gate layer formation was monitored in real time by recording the resonance frequency changes of the QCM during sorption of the organosilane vapors. The QCMs coated with organosilanes were heated to 150°C and washed with hexane and methanol to eliminate material physically sorbed on the surface.

Porosity characterization of the composite thin films

Three different vapor sorption techniques were used to study the thin film porosity and sorption selectivity.

Transient sorption of vapor pulses

This experiment was performed in a modified gas chromatograph. The QCM crystal was placed in a 1 ml sealed cell connected to the injector by open steel tubing instead of a column. Nitrogen gas continually purged the injector (at 150°C) and the QCM cell (at 100°C) at a flow rate of 100 ml/min. Doses of pure liquids (0.5 μl) were injected into the injector and the sorption/desorption responses of the coated QCMs were recorded. The frequency variation of the QCM was converted into an analog voltage through a frequency mixer. A thermal conductivity detector was connected downstream from the QCM to monitor the peak width and signal intensity of the dosing pulses.

Nitrogen sorption isotherms

Nitrogen sorption isotherms were obtained at liquid nitrogen temperature in a computer-adjusted mass flow controller system (Unit Instruments Inc.). Nitrogen partial pressures in helium were adjusted over the range 0–0.95. QCMs coated with zeolite thin films were pretreated at 200°C in helium for 2 h. The zeolites were dehydrated under these conditions, as shown by stabilization of the QCM frequency and from related FTIR experiments of similar films. Data acquisition and analysis was performed with DAS-16 analog-digital I/O boards (Keithley MetraByte Co.). The frequency changes of the coated QCMs upon nitrogen sorption/desorption and the nitrogen partial pressures were monitored at intervals of 1 s. The amounts of vapors sorbed in the thin films were calculated according to the Sauerbrey equation [1] in units of ng of sorbate/μg of zeolite composite film.

Dynamic vapor sorption kinetics and isotherms

Generation of different vapor concentrations was achieved with gravimetrically calibrated vapor diffusion tubes at 25°C under constant flow of carrier gas (15 ml/min helium) [11]. Different vapor concentrations were produced by dilution with a second computer controlled helium flow (0–200 ml/min). Changes in flow rates of pure helium between 15 and 250 ml/min produced only frequency changes in the range of $0 < \Delta f < 1.6$ Hz with the zeolite-coated, dehydrated QCMs. Sorption measurements were carried out similar to

those described above for nitrogen. Equilibrium was usually assumed and the next partial pressure was adjusted when the frequency change of the QCM was less than 1 Hz in 90 s (corresponding to a sorption of 12.1 ng/ cm² of QCM electrode area). The close coincidence of adsorption and desorption branches of many isotherms shows that the measurements are close to true equilibrium (but see section on sorption kinetics for exceptions).

Results and discussion

Characterization of NaA/silica composite thin films

The NaA zeolite-coated QCMs had a typical composition of 0.29 μg/cm² MPS coupling layer and 53 μg/cm² dry zeolite crystals anchored on the electrodes (the coating weights are given in amount of material per cm² of QCM electrode surface). After coating the zeolite film with the silica glass layer derived from TEOS sol and thermal treatment at 350°C in oxygen, a further mass increase of ~12 μg/cm² was obtained on the dehydrated thin film.

The adhesion and mechanical stability of the thermally treated NaA/silica film on the QCM electrode was tested using a scotch tape peel test [12]. In this test, the tape was applied to less than a quarter of the electrode and then peeled off. After each peel test the mass on the electrode was reduced by only 0.1–0.2 μg/cm², indicating no significant loss of composite. In contrast, for the non-thermally treated film, each peel test resulted in a mass loss of 4–5 μg/cm².

The external surface area and porosity of the QCMs were determined by evaluating the nitrogen sorption isotherms at liquid nitrogen temperature. The corresponding isotherms of zeolite NaA composite film (consisting of MPS coupling layer, zeolite crystal and silica overlayer) and of a reference silica thin film are shown in Fig. 2. The steep rise of the isotherms at low P/P_0 for the films (except the one coated with DPBCS) indicates a small amount of microporosity. The external surface areas were estimated from BET plots [13–16] (Fig. 3) and are listed in Table 1. The reference silica film has a slightly larger surface area for
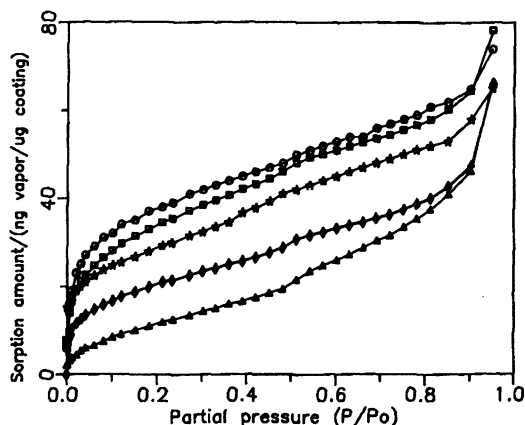
Fig. 2. Nitrogen sorption isotherms at liquid nitrogen temperature on QCMs coated with: (O) silica layer; (□) NaA/silica film; (☆) modified with OTS; (◇) modified with DBDCS; and (△) modified with DPBCS.
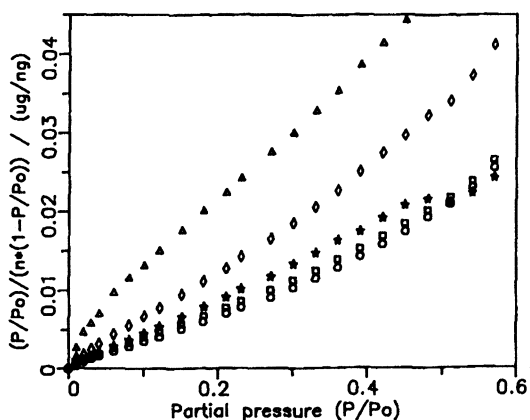

Fig. 3. BET plot of nitrogen sorption isotherms at liquid nitrogen temperature on QCMs coated with: (O) silica layer; (□) NaA/silica film; (☆) modified with OTS; (◇) modified with DBDCS; and (△) modified with DPBCS.

nitrogen (129 m²/g of film) than the zeolite composite film (115 m²/g). In comparison, a film containing only zeolite NaA on MPS (isotherm not shown) has no microporosity and a surface area of 26 m²/g. This fairly high external area must result from the presence of small zeolite crystallites and agglomerates on the substrate. Zeolite A has a large cavity at the center of its unit cell which is surrounded by 8-membered oxygen rings. These 8 rings constitute the channels to the cavity. In the NaA form, the channels are partially blocked by the Na⁺ ions, resulting in a pore diameter of 4.2 Å. As shown

above, nitrogen cannot permeate easily into the cavities at 77 K [17].

The kinetics of vapor sorption/desorption, and the molecular selectivity in the NaA/silica composite film are shown by the transient sorption of vapor pulses (Fig. 4). Upon injection of water vapor, the coated QCM shows a large frequency shift of about 2200 Hz compared to 6–7 Hz on the uncoated and 64 Hz on the silica-coated QCMs. The transient responses are characterized by fast sorption followed by slower desorption. The composite film shows large responses to polar molecules such as water, alcohol and methylene chloride in comparison to nonpolar organic molecules, such as n-hexane and isooctane. Table 2 shows the transient responses of vapors on the uncoated QCM, compared to those on silica film over the MPS coupling layer, zeolite crystals on the MPS coupling layer, and zeolite composite film covered with silica. The large mass sorption in the NaA/silica film indicates that the zeolite-coated electrode presents an extensive surface area accessible to the sorbate. It should be noted that although the films are coated with a silica layer exposed to the vapor phase, the composite films exhibit a strong affinity towards water. One of the effects of the silica layer on the composite films is to increase the response to alcohols and chlorinated methanes. In contrast to the behavior of QCMs coated with ZSM-5 zeolite reported previously [5], the NaA zeolite composite film does not show very pronounced molecular sieving (exclusion) effects towards molecules larger than its pore size, such as chlorinated methanes and even isooctane. We associate this less selective sorption with the presence of significant external surface area and additional porosity in the amorphous silica layer. It is therefore of interest to further tailor the composite surface to enhance the molecular recognition in such a microporous system.

Enhancement of molecular recognition in organosilane-modified NaA/silica films

Several methods to control the surface properties and pore opening sizes of zeolite crystals have been reported, including intra-zeolite channel silanation and chemical vapor deposition on the zeolite exter-

TABLE 1

Surface areas derived from BET plots of nitrogen sorption isotherms at $-196°C$

Surface	Monolayer capacity, n_m (ng/µg)	Surface area, S (m²/g)	Range of linearity of BET plot (P/Po)
Bare QCM electrode	150[a]	2.61[b]	0.01-0.45
Silica coating over MPS	36.9	129	0.05-0.33
Zeolite coating over MPS	7.58	26	0.01-0.40
Zeolite/silica composite	32.9	115	0.01-0.30
OTS-modified composite	27.5	96	0.01-0.33
DBDCS-modified composite	19.8	69	0.01-0.30
DPBCS-modified composite	9.9	33	0.05-0.36

[a] ng/cm²; [b] cm²/per side.
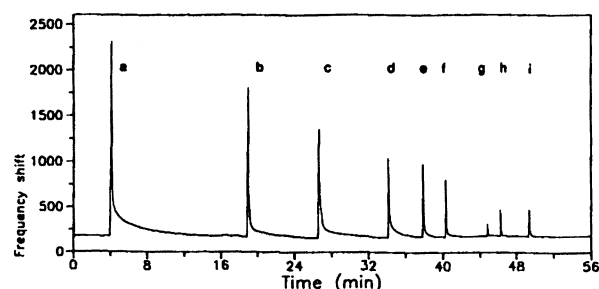
Fig. 4. Transient sorption of vapor pulses on composite thin film (56 µg/cm² zeolite + 13 µg/cm² silica) at 100°C. Analytes from left to right: (a), water; (b), methanol; (c), ethanol; (d), methylene chloride; (e), chloroform; (f), carbon tetrachloride; (g), n-pentane; (h), n-hexane; and (i), isooctane. Frequency shifts are in Hz.

nal surface [18-22]. The former can effectively reduce the zeolite pore size but also introduces an undesirable decrease of internal surface area and pore volume. With the latter technique, the internal zeolite surface is not affected but the modification is limited by a smaller decrease of the zeolite pore size. As the access to the zeolite crystals in the composite films described in this study is mediated by the porous silica layer, an additional modification technique would be desirable. Several requirements can be identified for such a modification: (1) Effective reduction of the non-selective external surface area, (2) neutralization and reduction of external chemisorption sites such as silanols, and (3) the molecular size of the modifying precursor should be larger than the zeolite pore size such

TABLE 2

Transient sorption of vapor pulses on zeolite/silica composite films and reference QCMs[a]

	Bare QCMs with gold electrodes (ng/cm²)		Silica-coated QCMs (ng/µg)		NaA-coated QCMs (ng/µg)		NaA/silica-coated QCMs (ng/µg zeolite)	
	1	2[b]	1	2	1	2	1	2
Water	43	43	65	63	180	174	198	200
Methanol	43	43	72	72	96	101	153	147
Ethanol	49	43	76	72	88	90	118	120
Methylene chloride	44	46	59	59	40	44	99	95
Chloroform	49	55	61	59	11	11	61	62
Carbon tetrachloride	49	49	59	61	12	12	23	19
n-Pentane	37	30	54	54	62	60	44	44
n-Hexane	37	37	62	62	78	69	50	52
2,2,4-Trimethylpentane (isooctane)	37	37	70	74	8	8	30	31

[a] 0.5 µl of liquid were injected; nitrogen flow rate was 100 ml/min. [b] Results from two experiments are compared.

that the zeolite void volume remains unchanged after the modification. Our approach in this study is to react the film surface with organosilane coupling agents from the gas phase. In order to adjust the molecular packing density and thus the residual porosity, chemisorption of silane coupling agents with different organic substituents and with different numbers of hydrolyzable groups was carried out.

Fig. 5 shows the mass increases upon chemisorption of different silanes on the NaA/silica composite films as a function of time at 100°C. All experiments show fast initial sorption followed by slow irregular mass increases. After a period of reaction, the frequency of the QCMs exposed to the silane vapor stabilized completely, indicating saturation of the surface. The period of irregular mass increase might be attributed to the desorption of byproducts while more silane was sorbed. After exposure of the silica surface to the silanes for 200 min at elevated temperature, the surface coverage remained constant when purging in nitrogen. Apparently, once a saturated silane layer has formed on the surface, the surface with its remaining silanol groups underneath is shielded from further reaction. The silane treatment was completed by purging with solvent (such as toluene) and heating in air at 150°C to complete the condensation of the silanes with the surface.
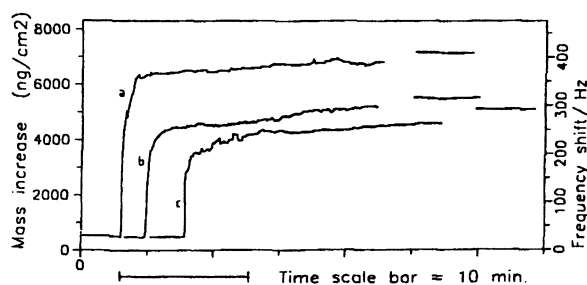
The mass changes observed upon adsorption of

Fig. 5. Mass changes on zeolite NaA/silica films monitored in situ upon adsorption of silane layers from the vapor phase at 100°C (on 5 MHz QCMs; the mass increase is given for the QCM area with two faces). (a, left), chemisorption of octadecyltrichlorosilane (OTS) (on 56 μg/cm² zeolite + 13 μg/cm² silica); (b, middle) chemisorption of di(tert-butyl)dichlorosilane (DBDCS) (on 51 μg/cm² zeolite + 12 μg/cm² silica); and (c, right), chemisorption of diphenyl(tert-butyl)chlorosilane (DPBCS) (on 45 μg/cm² zeolite + 11 μg/cm² silica).

OTS, DBDCS and DPBCS layers, together with the estimated surface areas occupied by the silanes on the zeolite/silica films are listed in Table 3. We note that the areal densities of the three silanes are quite similar, although the minimal cross section of OTS is much smaller than that of the other two molecules. We suggest that this effect may be based on a more spherical average shape of OTS in the gas phase, and its low mobility and a coiled structure on the silica surface. If the amount of silane chemisorbed is divided by the zeolite/silica film external surface area (115 m²/g from Table 1), the average area per molecule occupied by the silane coupling monolayer can be obtained. The residual areas obtained by subtracting the silane Van der Waals cross sections from the average occupied areas are in the sequence of: OTS ≫ DPBCS > DBDCS. These different residual areas are expected to have a significant effect on the sorption properties of the modified films.

One of the results of the silane monolayer modification on the zeolite/silica thin films is a significant reduction of their external surface areas as evaluated by the nitrogen sorption isotherms (Figs. 2 and 3, and Table 1). The surface areas decrease in the sequence unmodified film > modified with OTS > DBDCS > DPBCS. On chemisorption of DPBCS (with the largest cross section), the external surface area was reduced to one third of that of the NaA/silica film. As will be seen below, the chemisorbed organosilane molecules fill many of the small pores in the silica layer, thus reducing the nitrogen surface area, and enhancing molecular selectivity.

The silane surface treatments dramatically change the response of the coated QCMs towards the transient sorption of vapor pulses (Fig. 6). For the thin film modified with a long single C_{18} alkyl chain (OTS) (Fig. 6A), the frequency shifts on adsorption of large molecules, such as chlorinated methanes and hydrocarbons, are strongly reduced compared to the non-modified NaA/silica film, while sorption of methanol and ethanol is less affected. The sorption of polar molecules on this modified QCM increases with decreasing molecular size. Fig. 7 summarizes the relative sorption of vapor pulses by taking the water response as 100%. It appears that the silane layer formed on the silica

TABLE 3

Chemisorption of organosilanes on NaA/silica thin films

Silane	Δm silane chemisorbed (ng/μg film)	n_m^d silane areal density (nmol/cm^2)	S_o occupied area per molecule (Å^2/silane)	S_v Van der Waals cross section (Å^2)	$S_r(S_o - S_v)$ residual area (Å^2)
OTS[a]	49	0.152	109	20	89
DBDCS[b]	40	0.24	68	49	19
DPBCS[c]	42	0.153	109	75	34

[a]The mass change upon chemisorption of OTS varies ca. ±13% on different zeolite/silica composite films; [b]mass change varies ca. ±11%, and [c]mass change varies ca. ±7%. [d]Areal density in nmol per cm^2 of film surface as determined from BET data. It is assumed that all chloride ligands have been substituted at the silane molecules.

film surface acts as a "gate" which allows only some molecules to pass through the residual pores in the silica film into the zeolite volume. This additional selectivity based on molecular size and sorption affinity can be further enhanced when coating the NaA/silica film with a silane with a larger cross section, i.e., DBDCS (Fig. 6B), and even more with DPBCS (Fig. 6C), which significantly reduces sorption of all molecules except water (see Fig. 7 for relative responses). In the latter film, response to water (2.65 Å diameter) is 120 times greater than to isooctane (2,2,4-trimethylpentane, 6.2 Å). This dramatic effect is apparently caused by molecular size sieving in the thicket of the silane gate layer that allows water penetration even though the layer should be hydrophobic. Comparison of the response of the DPBCS-modified thin films toward molecules with similar polarity but with slightly different molecular sizes, such as ethanol (3.8 Å) and water (2.65 Å), shows a much larger response for the smaller molecule. Extended water desorption tails in the case of the modified films also suggest the formation of diffusional barriers as a result of narrowing the pores of the silica film.

The selective responses of the modified NaA/silica films can be confirmed on examining the *vapor sorption isotherms* at low partial pressures, shown in Fig. 8. As water and ethanol have similar physical properties, both molecules should be adsorbed in the unmodified zeolite/silica film. The response ratio towards water vs. ethanol varies from 1.1 to 1.4 in the range of experimental partial pressures. The ratio of vapor sorption on zeolite/silica films vs. the reference silica film becomes

larger as the vapor concentration decreases, in agreement with preferential filling of micropores vs. external surface adsorption [23]. The uptake of the larger molecule ethanol is remarkably reduced when the NaA/silica film is modified with the DPBCS monolayer, while water sorption is barely affected. Finally, while ethanol and n-hexane can both be adsorbed on the unmodified NaA/silica films, hexane is effectively excluded from all silane-modified films. As the later discussion on sorption kinetics will show, sorption of both ethanol and hexane into the unmodified zeolite films is very slow (saturation takes longer than 2500 s), thus some isotherms discussed here (ethanol and hexane on unmodified NaA/silica film and ethanol on silane-modified films) are not at equilibrium. The silane layers slow ethanol sorption even further and completely block hexane sorption.

Sorption kinetics and selective water sorption in the modified microporous films

More insight into the influence of the silane "gate" layers on the molecular recognition capability of the zeolite thin films is obtained from the vapor sorption kinetics shown in Fig. 9. The amounts adsorbed in the films are plotted as a function of the square root of time. The apparent diffusion coefficients D in these films at constant pressure can be estimated according to the equation [24,25]

$$M_t/M_\infty = (2A/V)(Dt/\pi)^{1/2}$$

where M_t and M_∞ are the sorbed amounts in the zeolite films at time t and at equilibrium, respec-
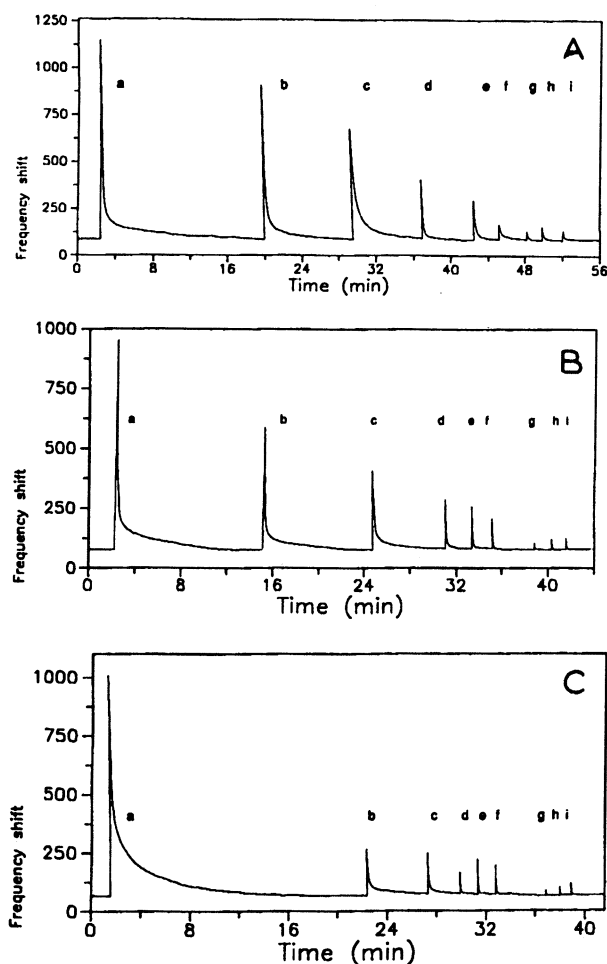
Fig. 6. Transient sorption of vapor pulses on NaA/silica films modified with different monolayers at 100°C. Analytes from left to right: (a), water; (b), methanol; (c), ethanol; (d), methylene chloride; (e), chloroform; (f), carbon tetrachloride; (g), n-pentane; (h), n-hexane; and (i), isooctane. Frequency shifts are in Hz. (A) Modified with OTS (56 $\mu g/cm^2$ zeolite + 13 $\mu g/cm^2$ silica); (B) modified with DBDCS (51 $\mu g/cm^2$ zeolite + 12 $\mu g/cm^2$ silica); (C) modified with DPBCS (50 $\mu g/cm^2$ zeolite + 12 $\mu g/cm^2$ silica).

tively. A is the total external surface area and V is the total volume of the zeolite crystals. This relation holds for the low loading regime, for uniform crystal size and for small t. Based on SEM images, the NaA zeolite crystals in the films have a regular cubic shape and a size of ~ 2 μm (plus a small fraction of small crystals). Sorption of both ethanol and hexane into the unmodified zeolite films is very slow (saturation takes longer than 2500 s),

therefore for these cases an approximate equilibrium sorption of 120 ng/μg of film was assumed.

The diffusion rate of water into the zeolite films is not strongly affected by modification with organosilanes, as shown by the moderate decrease of D, from 6×10^{-12} cm^2 s^{-1} for the NaA/silica film, to 3×10^{-12} cm^2 s^{-1} for the DPBCS-treated film. In contrast, the sorption processes of ethanol and n-hexane are quite different from water, and they are drastically changed after treating the films with silanes, as shown in Figs. 9B and 9C. Ethanol sorption in the untreated NaA/silica film shows an initial jump followed by a slow (slightly sigmoidal) increase in loading. This can be understood with fast sorption in the porous silica top layer followed by slow filling of the zeolite crystals through their partially blocked oxygen 8-rings. The diffusion coefficient for ethanol sorption into this film is two orders of magnitude lower than that for water (if saturation at 120 ng/μg is assumed). When silane gate layers are coated on the NaA/silica films, the initial jump for ethanol sorption *disappears*, and diffusion into the zeolite crystals is slowed down by another factor of ten (with DPBCS as gate layer). This shows the effective coating of silica film porosity by the silane gate layer, and the increasingly difficult access into the zeolite crystals. In contrast to ethanol, hexane sorption does not show an initial fast jump in the NaA/silica film, but slow sorption into the zeolite volume is still observed (D is of the order of 10^{-14} cm^2 s^{-1}). Apparently, the silica porosity is too small to adsorb much hexane. On coating the films with the silane gate layers, effective exclusion of hexane is achieved, and equilibrium is already reached after about 400 s. This remaining small sorption of hexane must be on the surface of the modified silica films.

Conclusion

The results discussed in this article demonstrate the drastic effects of silane gate layers on kinetics and equilibrium sorption behavior of polar and non-polar molecules in NaA/silica films. This study highlights the potential for molecular recognition
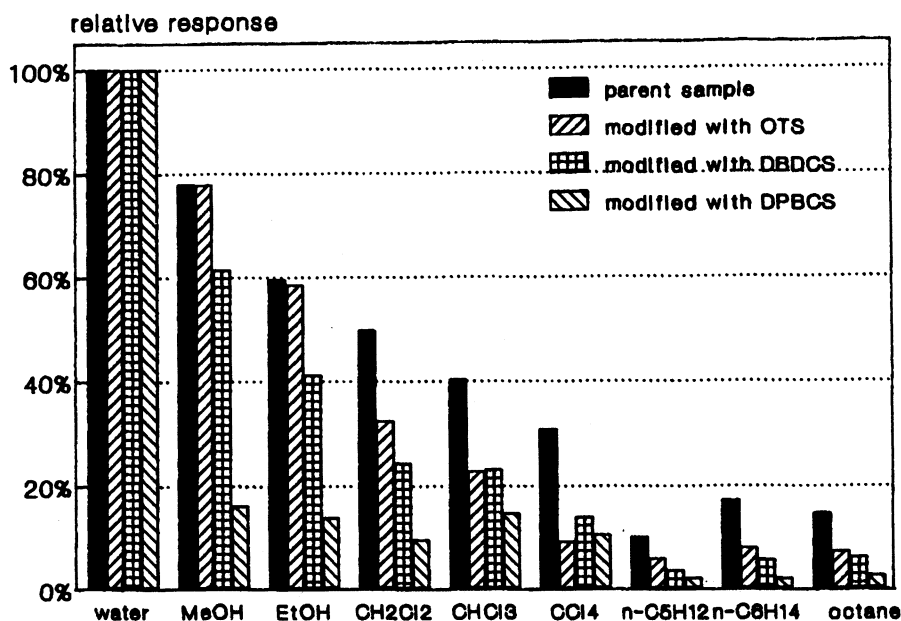
Fig. 7. Relative QCM frequency changes (normalized to the response to water) in transient vapor sorption experiments on NaA/silica and silane-modified thin films.
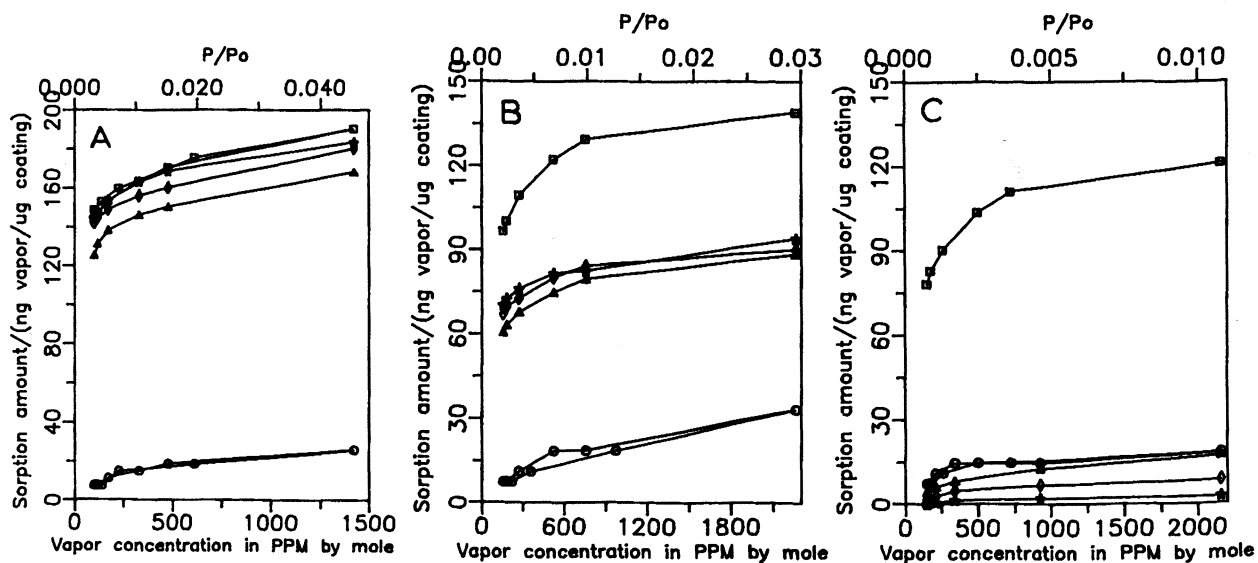

Fig. 8. Vapor sorption isotherms on NaA/silica and silane-modified films at 25°C of (A) water; (B) ethanol; and (C) n-hexane. (O) Silica layer; (□) NaA/silica film; (☆) modified with OTS; (◇) modified with DBDCS; and (△) modified with DPBCS. The sorption of ethanol and hexane in NaA/silica film, and of ethanol in the silane-modified films, did not attain equilibrium under experimental conditions.

via selective sorption processes in microporous thin films. Selectivity can be enhanced by tailoring the surface and interfacial interactions with molecular layers of silane coupling agents. As water has

one of the smallest kinetic diameters compared to other molecules, these modified microporous systems show a promising potential as water sensors with very high sensitivity and selectivity.
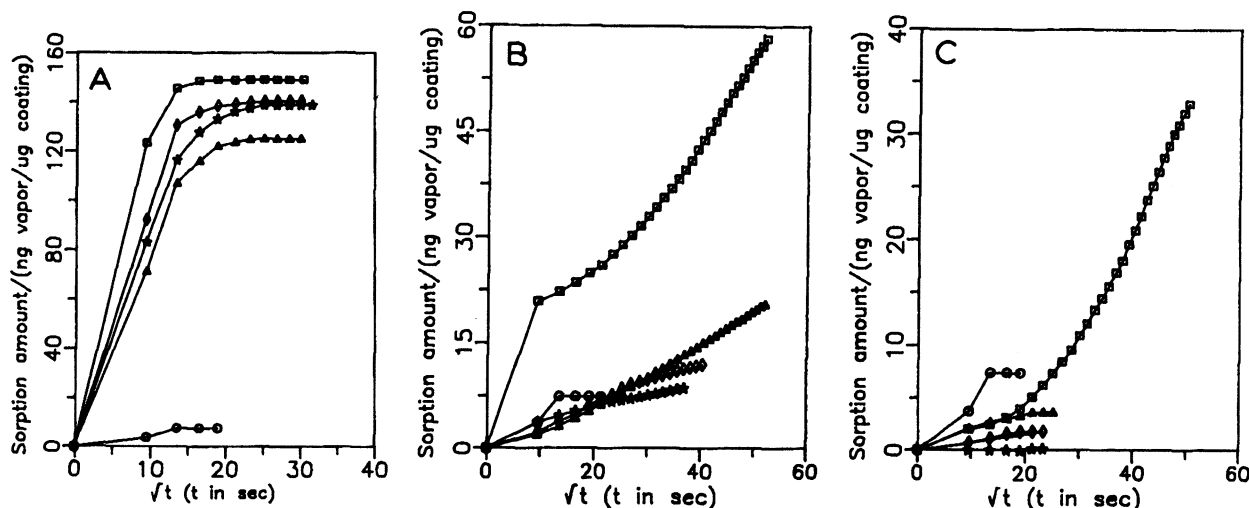
Fig. 9. Vapor sorption kinetics on the NaA/silica and silane-modified films at 25°C of (A) water; (B) ethanol; and (C) n-hexane. (O) Silica layer; (□) NaA/silica film; (☆) modified with OTS; (◊) modified with DBDCS; and (△) modified with DPBCS.

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