Humidity Sensing with Ultrathin LTA-Type Molecular Sieve Films Grown on Piezoelectric Devices

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LTA-type zeolite films on mass sensors (quartz crystal microbalances) were prepared using secondary growth on a precursor seed layer. Zeolite seeds with a mean size of 40 nm were obtained at room temperature and used to form precursor layers via several identical adsorption steps on silane-modified sensor surfaces. Oriented LTA-type films with thicknesses in the range of 65–980 nm were prepared after additional hydrothermal treatment of the precursor seed layers at elevated temperature (100 °C) for different crystallization times (from 3 to 24 h). The application of LTA-type zeolite films in humidity microsensors is presented. The importance of film thickness, type of zeolite structure, and the preparation parameters of the sensor layers with respect to the sensitivity of the humidity sensors at different water vapor concentrations are discussed. The zeolite films are hydrophilic and thermally stable and show reproducible response. On the basis of these results, it was concluded that the above LTA zeolite films can be used effectively as humidity sensor materials for water vapor sensing purposes. High sensitivity, good reversibility, and long life were demonstrated for thin LTA-type zeolite films at low water concentrations.

Introduction

In recent years the development of humidity sensors has acquired significant technological importance in different applications such as medical instrumentation, the food and paper industry, automobiles, electric appliances, and agriculture.[1-2] Several new materials have been developed during the past 2 decades, some of which exhibit desirable properties, such as high sensitivity and selectivity toward water, stability, reproducibility, reliability, quick response, long life, resistance to contaminants, and simple structure.[3-8] Among different types of humidity sensors, the ceramic type and metal oxide sensors have shown significant advantages for applications because of high mechanical strength, temperature stability, and chemical resistance.[9-11] However, there are the limitations regarding the appropriate humidity ranges for different materials, which leads to the development and investigation of various kinds of humidity sensors that do not always completely meet all requirements mentioned above.

The use of zeolites as the sensing material opens up an interesting possibility for improving the selectivity of chemical sensors. Recently, molecular sieve films have been used in sensor applications for the detection of various organic vapors.[12-15] The controlled pore size and large specific surface area of molecular sieves make them suitable materials for sensors with high selectivity and sensitivity.[16-17] Most of the published work concerns the preparation of molecular sieve films with MFI-, LTA-, LTL-, and AFI-type structures.[18-30] Several strategies have been applied for zeolite film formation,[12,15,17-26] and recently a very effective method was established for the preparation of ultrathin MFI-type

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Table 1. Synthetic Conditions for the Preparation of LTA-Type Zeolites

sample	number of adsorption steps	crystallization time, t_{cr}(h)	$\Delta F_{ads}{}^a$	$\Delta F_{synth}{}^a$	thickness (nm)^b
QCM1	1	3	965	3033	65
QCM2	3	9	2239	21433	470
QCM3	3	24	2150	44288	980

^{a} ΔF_{ads}, ΔF_{synth}: QCM frequency shift after adsorption of seeds and synthesis of zeolite film, respectively. ^{b} Thickness data were calculated based on mass changes of the QCM; these cause proportional shifts of the fundamental resonance frequency: $\Delta f = -2.3 \times 10^{-6} F^2 \Delta m/A$; density $\rho = 2.0$ g/cm³.

zeolite films on the gold electrode of sensor devices (QCM).[15] Both MFI and AFI ultrathin zeolite films were applied for sensing organic vapors,[15,27] such as *n*-hexane.

The sorption rate of different vapors is controlled by the choice of zeolite structure, by changing of the size of zeolite crystals, and by variation of the thickness of the zeolite film. For applications such as chemical sensors, the perfect configuration would be a very thin and oriented zeolite film.

The work presented here demonstrates the suitability of ultrathin films of colloidal LTA-type zeolite for the preparation of very sensitive humidity sensors at low water concentrations. Measurements of the sensor responses as a function of film thickness are presented.

Experimental Section

The synthesis mixtures used for the preparation of both zeolite seed sols and films of LTA-type molecular sieve had the following chemical composition: 0.12:5.0:0.72:5.8:250 Na₂O: SiO₂:Al₂O₃:(TMA)₂O:H₂O. Aluminum isopropoxide (Aldrich), silica sol (30%, Aldrich), tetramethylammonium hydroxide pentahydrate (Aldrich), sodium hydroxide (Aldrich), and distilled water were mixed under vigorous stirring to obtain a clear aluminosilicate solution for the synthesis of colloidal LTA-type zeolite. LTA-type zeolite is a small pore molecular sieve with eight-membered ring openings (~4.1 Å) and cubic symmetry. Colloidal seed crystals of LTA-type zeolites were prepared at room temperature for 7 days according to the method described in ref 31. The seed crystals were purified by repeated centrifugation followed by redispersion in water to obtain a seed sol with a dry content of 3.5% and pH of 10.

Quartz crystal microbalance devices (10 MHz QCM, Cold Springs R&D, Marcellus, NY) were used to monitor zeolite film formation and for the preparation of humidity sensors. The zeolite films were prepared using the seed method by chemical anchoring of LTA crystals on (3-mercaptopropyl)trimethoxysilane (MPS) coupling layers bound to the gold surface of a QCM.[29] The initial mixture used for the preparation of films was allowed to age for 1 day at room temperature before immersing the QCM device into the solution. Additional hydrothermal treatment of this solution at 100 °C for 3, 9, and 24 h was performed to obtain zeolite films with thicknesses of about 65, 470, and 980 nm, respectively. The amount of zeolite crystals bound to the QCM electrodes was varied by controlling the adsorption steps and duration of film formation.

The synthetic conditions for the preparation of three films with different thicknesses are presented in Table 1. After synthesis, the zeolite films were rinsed with water, acetone, and 0.1 M ammonia. The frequency shifts after each step of film formation are presented in Table 1; these data were used to estimate the thickness of the zeolite layers. The zeolite-coated QCM samples were heated in O₂ at 300 °C for 3 h prior to further sorption measurements. The colloidal seeds and the
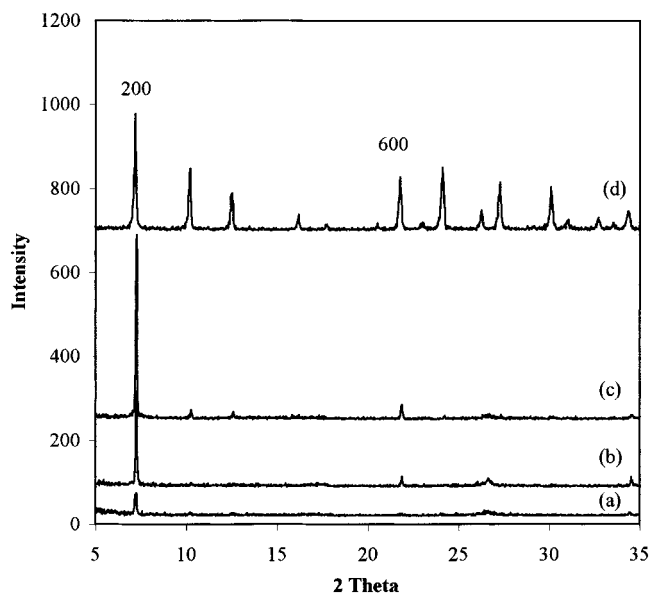
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Figure 1. XRD patterns of LTA-type films after hydrothermal growth for (a) 3 h, (b) 9 h, (c) 24 h, and (d) powder bulk LTA-type zeolite seeds. (Scanning time for films: 6 h; slits: 0.1, 0.2, 0.5, 0.3; 30 kV).

film samples were characterized with SEM (Philips Electro-Scan 3.2), X-ray diffraction (Scintag XDS 2000, cooled Ge detector, Cu Kα radiation, $\theta-\theta$ geometry), dynamic light scattering (DLS, Coulter N4 Plus Submicron Particle Analyzer), and transmission electron microscopy (Philips CM 200 FEG TEM, 200 kV). Vapor sorption measurements on LTA-type zeolite films at 23 °C were performed with a computer-controlled gas flow system using a PPT Residual Gas Analyzer (MKS Instruments) for calibration. The generation of water vapor was achieved with a vapor diffusion tube under a constant flow of nitrogen carrier gas. The concentrations were adjusted by incremental dilution after a predetermined number of frequency points were measured at a certain partial pressure. The mass changes of the films caused by sorption and desorption of water vapor were automatically recorded as frequency changes of the QCM. Mass spectrometric measurements indicate that the water base pressure of the flow system is 10 ppm in nitrogen.

Results and Discussion

General Characterization of LTA-Type Films. A specially developed technique was used to produce thin and homogeneous films from colloidal LTA-type zeolite with thicknesses in the range of 65–980 nm. The LTA-type zeolite seed sols used for the preparation of adsorbed crystal layers on MPS-modified QCM surfaces were obtained by synthesis at room temperature (RT) for 7 days. The XRD pattern of the seeds shows fully crystalline LTA-type materials and no presence of amorphous phase (Figure 1d). The average crystal size of the seeds was determined to be 40 nm by DLS. TEM was used to confirm both the size and the crystallinity of particles in the initial solution and in the seed sol. Figure 2 shows spheroidal aggregates with sizes of about 40 nm, which become fully crystalline particles after 7 days at room temperature. Well-formed visible fringes of a LTA crystalline lattice in the TEM image confirm the crystalline structure of the seed particles. TEM shows that all particles are nanoscale single crystals of zeolite LTA (Figure 2b). The size determined by DLS was in good agreement with that found by TEM.
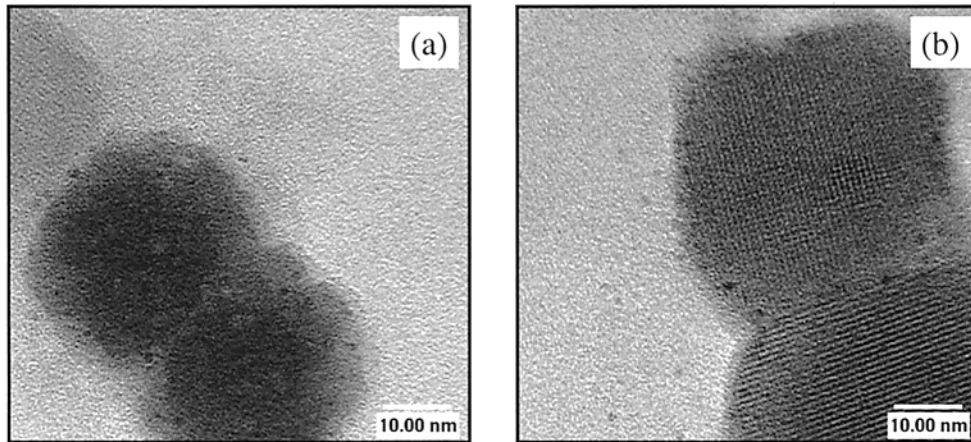
Figure 2. TEM photographs of (a) initial solution for crystallization of LTA-type zeolite and (b) crystalline LTA seeds obtained at room temperature after 7 days.
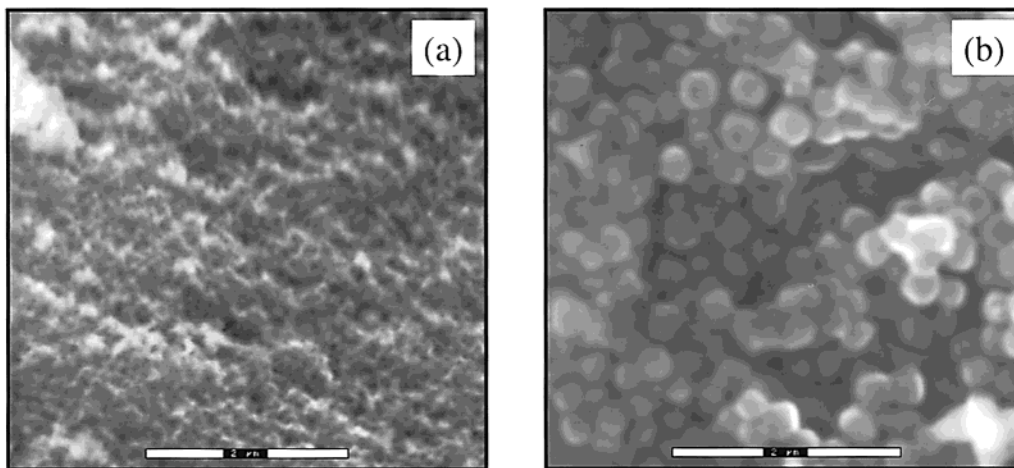

Figure 3. SEM photographs of LTA-type crystals obtained after hydrothermal growth for 9 h in (a) the film of sample QCM2 and (b) in the corresponding bulk sample.

To prepare humidity sensors, sequential adsorption of colloidal seed layers was followed by further growth under hydrothermal conditions. The adsorption layer on the QCM1 sample was obtained after one adsorption step, after which the whole QCM surface is covered with about one seed monolayer. After three adsorption steps a higher coverage of zeolite seeds was obtained on QCM2 and QCM3, as seen in changes in the sensor frequencies (Table 1). Films of LTA-type zeolites were then grown on the QCM having adsorbed layers of seeds by hydrothermal treatment in the same synthesis solution, but at elevated temperature (100 °C), to increase the film growth rate. On sample QCM1 the thickness of the LTA film is about 65 nm after only 3 h of hydrothermal treatment. After prolonged crystallization time (9 h), the zeolite particles grow larger and the thickness achieved is about 470 nm. Zeolite films in samples QCM2 and QCM3 are found to exhibit a multilayer structure. Figure 3 shows the SEM images of LTA-type zeolite particles in both QCM2 film and bulk samples taken from the synthesis solution. The particle size in the bulk reaches 200 nm and most of the crystals have a well-defined cubic shape, while the smaller crystals in the film exhibit a rounded-off shape. After 24 h of synthesis, the size of the crystals formed in the bulk has reached its final value, 400 nm (Figure 4), and the film thickness has increased substantially from 470 to 980 nm. This result can be attributed to
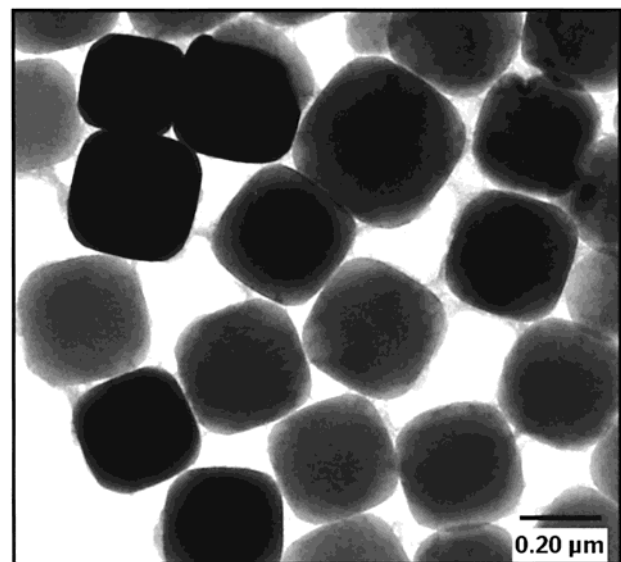

Figure 4. TEM photograph of LTA-type crystals after hydrothermal growth for 24 h in the solution used for sample QCM3.

the formation of a multilayer film of LTA-type crystals, noting that the size of individual zeolite grains is only about 400 nm. The average growth rate of LTA-type film, as estimated from the frequency change of the sensor devices with three seed layers, is ≈40 nm/h at
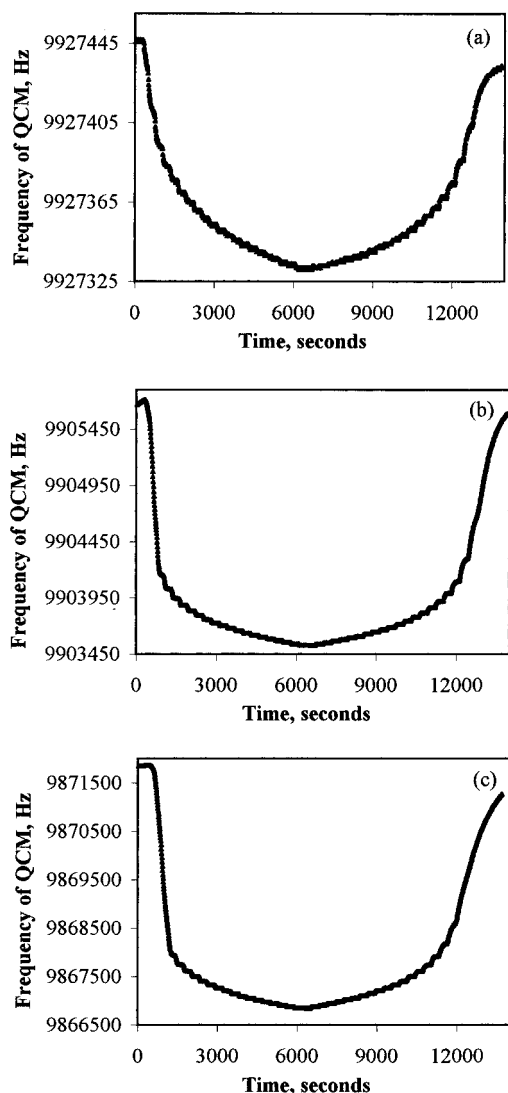
Figure 5. Frequency response upon sorption and desorption as a function of time at different water concentrations (30–180 ppm) at 23 °C on zeolite A films with different thicknesses: (a) QCM1 65 nm, (b) QCM2 470 nm, and (c) QCM3 980 nm.

Figure 6. Frequency change upon sorption of low water concentration (up to 45 ppm) for (a) QCM1, (b) QCM2, and (c) QCM3 films.

100 °C. The thicker films are obtained when using longer crystallization times or when starting from a multilayer of seeds. Similar observations were made in our previous studies, where seeded substrates have been used for the growth of MFI-type films and where the growth rate appears to be constant after a short induction time.[15,29] The linear growth rate of colloidal zeolite A crystals was equal to about 19 nm/h for crystals growing in the presence of seeded QCM. The SEM images show that the zeolite crystals cover the whole QCM surface after performing the additional hydrothermal synthesis.

The type and orientation of the resulting molecular sieve films was evaluated with XRD measurements. Figure 1 shows the XRD patterns of films with different thicknesses compared to a powder sample of LTA-type zeolite. The (200) peak is the only one present in the film patterns of the QCM1 and QCM2 samples, and its intensity increases with increasing film thickness. The (600) peak appears during prolonged crystallization time in the QCM3 sample, which clearly shows that the films are oriented with the (*h*00) plane of the crystals parallel to the substrate. These LTA films are highly oriented,
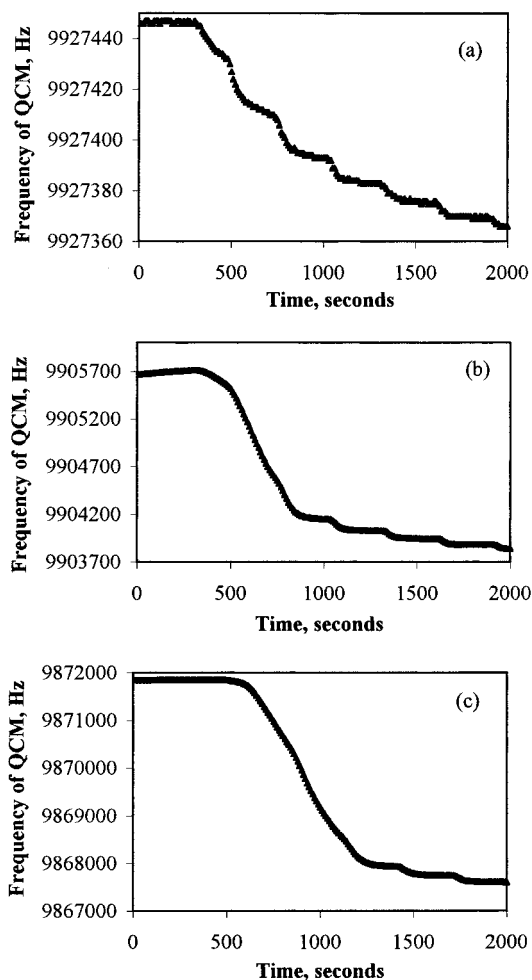
and therefore the micropores are oriented parallel and perpendicular to the QCM surfaces. The SEM images reveal that the LTA-type films cover the entire surface of the QCM substrates. The formation of zeolite films on layers of adsorbed seed crystals (40 nm) on silane-modified sensor surfaces results in the formation of uniformly intergrown compact films. Similar results were reported recently by Boudreau and Tsapatsis[24] and Hedlund et al.[25] for the preparation of highly oriented zeolite LTA films using two different techniques.

Water Vapor Sorption Measurements. Exposing LTA films to different concentrations of water vapor caused frequency shifts in the sensor devices. Figure 5 shows the frequency changes upon sorption of water on 65-, 470-, and 980-nm-thick zeolite films grown on the QCM devices. At different water vapor concentrations (30–180 ppm), the devices QCM1, QCM2, and QCM3 show large frequency shifts of about 200 Hz (at 150 ppm), 2000 Hz (at 150 ppm), and 5000 Hz (at 180 ppm), respectively. Equilibration of the thinner films on QCM1 and QCM2 is much faster than equilibration with QCM3. This is illustrated in Figure 6. Equilibration steps for the same changes in vapor pressure (45 ppm) are much better resolved with the thinner films. It should also be mentioned that, at 20 ppm for samples QCM1 and QCM2, sorption equilibrium was achieved in 60–100 s, while with increasing concentration the
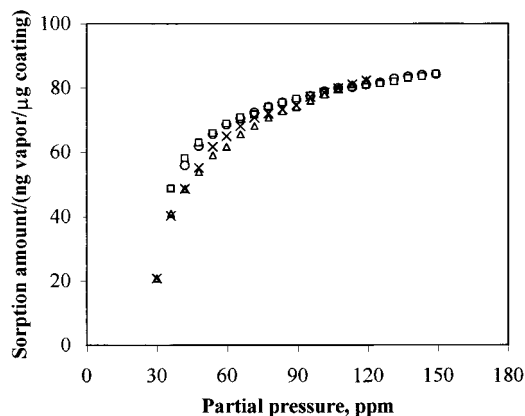
Figure 7. Vapor sorption isotherms for water on QCM1 film (adsorption, ○; desorption, □) and QCM2 film (adsorption, △; desorption, ×) at 23 °C.

Figure 8. Vapor sorption response for water on QCM3 film (adsorption, ●; desorption, □) at 23 °C. (These responses did not show complete equilibration after the given exposure time.)

sorption equilibrium can be achieved within <20 s. During desorption, the equilibration was obtained in a similar time range for samples QCM1 and QCM 2 (Figure 5a,b). Sample QCM3 shows high sorption capacity but the adsorption and desorption rates are notably different (Figure 5c). At the last desorption points it can be seen that the total desorption of the last water traces takes a much longer time than the uptake at the same amount of water during the adsorption stage. The adsorption and desorption loadings in QCM3 at high water concentration (>100 ppm) are identicaly equilibrated, while at low water concentration equilibration is not achieved within the given holding periods of 4 min. In general, the desorption rate of water is much faster in the thinner films (QCM1 and QCM2) than in the thicker one (QCM3). The kinetic diameter of a water molecule is about 2.65 Å (fitting into the LTA pore system) and the zeolite is hydrophilic, which explains the sensitivity of the thin LTA-type zeolite film. These data show that the equilibration rate of water is affected by the size of zeolite particles as well as by the thickness of the molecular sieve films, where the orientation of the zeolite crystals in the films is similar, that is, parallel to the (200) plane.

The sorption isotherms are obtained from the last data points of the frequency change curves for the individual concentration steps. Figure 7 shows the responses of QCM1 and QCM2, covered with molecular sieve films having different thicknesses, as a function of time at different water vapor concentrations. A water vapor concentration of 80 ppm causes a mass increase by 0.075 μg of sorbate/μg of film and a concentration of 140 ppm leads to a mass increase by 0.085 μg of sorbate/μg of film. The sorption and desorption curves are almost identical for the devices QCM1 and QCM2 (Figure 7), indicating equilibration of the sensors. For
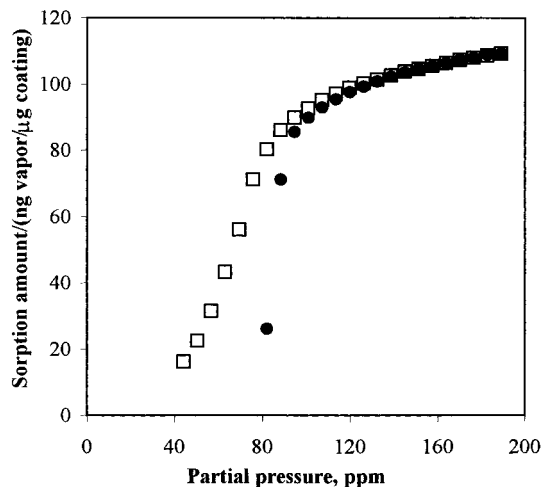
QCM3 the desorption takes longer than the adsorption, and desorption equilibrium was not achieved within the exposure time used here (330 s). Only above about 90 ppm did equilibration occur within 70 s (Figure 8).

To examine the reproducibility of these film responses, continuous experiments were performed for the duration of 1 month. The data obtained were nearly identical, which suggests reproducibility of the sensor properties.

Conclusions

The results presented here show that oriented LTA-type films can be prepared with different thicknesses (65−980 nm), depending upon the number of seed adsorption steps and time of crystallization. Preparation of zeolite seeds at room temperature allows for substantially decreased grain size and the formation of very thin films within 3 h of secondary hydrothermal treatment. The zeolite crystals in the films are highly oriented with their (*h*00) faces parallel to the sensor surfaces.

We also report on the development of a humidity microsensor based on the ultrathin molecular films grown on a QCM. Fairly rapid response times as well as reversibility at room temperature were obtained with ultrathin LTA-type zeolite films, which possess remarkable sensitivity at low water vapor concentrations.