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Design And Investigation Of A Novel Zeolite Coated Films In Sensor Applications

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Abstract

Thin zeolite films have great potential in several novel application areassuch as: structured catalysts, membranes and sensors. To fully exploit theadvantages of these films it is of great importance to determine theproperties of the films. A powerful technique for studies of phenomena atsurfaces or in thin films is FTIR/ATR-spectroscopy (Fourier TransformInfra-Red / Attenuated Total Reflection). Furthermore, thin zeolite filmsmay be utilized for enhanced selectivity and sensitivity for this technique.In this work films with a thickness of 200 nm of the zeolites ZSM^{-5} andsilicalite-1 were grown on ZnSe, ZnS, ZrO_2, Si and Ge ATR elements usinga method that had been developed previously.The coated elements were evaluated in a gas sensor application bycomparing the sensitivity for a hydrocarbon of zeolite-coated elementsversus a standard 10 cm gas cell. The sensitivity was approximately 85times higher for the coated elements compared to the gas cell at lowhydrocarbon concentration. The response time was investigated by exposingthe coated element to a step increase of an analyte and recording theresponse as a function of time. The response was relatively fast, equilibriumwas achieved after approximately 250 s, but already after a few seconds astrong signal could be detected.The coated elements were also used to determine single gas adsorptionisotherms. The systems studied were n-hexane/silicalite-1 and pxylene/silicalite-1. Adsorption isothermsdetermined at varyingtemperatures were typical for microporous materials. Capillary condensationwas observed at higher concentration of the adsorbate. Henry constants andheats of adsorption determined from low-pressure data agreed well withpreviously reported data in the literature.

1. Introduction

Zeolites and zeolite filmsZeolites are a group of minerals of great scientific and

industrial importance.The first zeolite mineral was discovered in the middle of the 18th century bythe Swedish mineralogist A. Cronstedt found that the mineral lostwater rapidly upon heating, thus seeming to boil. The name zeolite stemsfrom the greek words zeo (to boil) and lithos (stone).Zeolites are crystalline, hydrated aluminosilicates consisting of a threedimensional network of $[SiO_4]^{4-}$ and$[AlO_4]^{5-}$ tetrahedra. The tetrahedra arelinked by sharing oxygen atoms. More than 150 different zeolite andzeolite-like frameworks are known today, both natural and synthetic [1].

In membrane applications, a thin, defect free film is desirable. The thinnerthe film the smallerthe mass transport resistance, and obviously a defectfree film is necessary to obtain as highselectivity as possible [3, 4]. Incatalysis, the product composition is dependent on the film thickness,controlling the film thickness could then alter the product composition [5].Zeolitesin sensor applications may be beneficial for selectivity andsensitivity and thin films assure afast response time of the sensor [6-8].Zeolite films are most often grown on some kind of support formechanical strength, although non-supported films also have been reportedin theliterature [9, 10]. Several methods for preparing zeolite films havebeen developed. The seedfilm method was developed at our division [11-13]. In this method, the surface of the supportis first positively charged byadsorbing a cationic polymer. Negatively charged colloidal zeolite seedcrystals are subsequently electrostatically adsorbed to the charged surface.Finally, theseeded support is placed in a synthesis solution to grow the seedcrystals into a continuous film.

Knudsen diffusivity in defects in the form of mesopores is several orders ofmagnitude larger than diffusivity in zeolite pores [14]. Defects are usuallyclassified as pinholes, cracks and open grain boundaries. Pinholes arebelieved to be a result of incomplete seeding or insufficient film thicknessand may occur at certain growth conditions [15, 16]. Several reports oncrack formation in zeolite films are available [17-19].Cracks may form during calcination of the film, most likely due to thatthe unit cell in MFI zeolite shrinks during template removal [19].It is likely that some grain boundaries remain “open” after synthesis ofthe zeolite film. In this case, “open” has the meaning “pathway with a widthexceeding the diameter of the zeolite pores. Since zeolite pores are sonarrow, “open” may mean that the opening is about a nanometer wide. Itmay be impossible to close grain boundaries completely, since buildingblocks during zeolite crystallisation have a certain size [20].

Chemical bonds involving chemical reactions are stronger than the onesinvolving van der Waal forces. The heat of adsorption is a direct measure ofthe bond strength between the surface and the adsorbate. This parameter willyield information on which adsorption process is taking place. For physicaladsorption the heat of adsorption is approximately 2-3 times smaller thanthe heat of vaporization [21]. Physical adsorption from gas phase is alwaysan exothermic process.

Infrared spectra can be recorded using several experimental techniques suchas transmission, diffuse reflectance, infrared micro spectroscopy etc [32].A technique specially suited for studying processes at surfaces and inthin films is the ATR (Attenuated Total Reflection) technique [33, 34].Ninnes et al., Lu et al. and Han et al. [35-37] studied and reported theadsorption of hydrocarbons from aqueous solution

whilst Chittur [38]reported adsorption of proteins. Göbel et al. [39] have used the ATRtechnique to study the diffusion of chlorinated hydrocarbons in thin polymermembranes. Wolf et al. and Süer et al. [40, 41] both used the ATRtechnique for in-situ reaction monitoring. In Süer's case, an uncoatedcylindrical ATRelement was placed in the center of a packed bed reactorfor studying n-heptane cracking over a commercial Y-type zeolite.

Scope of the work

Adsorption, diffusion and reactions are important processes taking placewithin zeolites. Although much effort has been devoted to gain a deeperunderstanding about these processes, there is still a lack of knowledge,especially within the fields of multi-component- adsorption, diffusion andreactions in zeolites.The present work aims at evaluating ATR elements coated with welldefined, thin zeolite films as a tool for studying the processes taking place inzeolites, as well as investigating the films in sensor applications.

2. Experimental

Film synthesis

Trapezoidal ATR elements of ZnS, Ge, ZnSe and ZrO_2(50x20x2 mm) andSi (50x20x1 mm) having 45º cut edges were used in this study. Some of thematerial properties for the elements are reported in Table 1.

Table 1. Properties of the ATR elements.

Material	Refreactive index at 1000 cm^{-1} (n)	Melting point (°C)	Spectral range (cm^{-1})
ZnSe	2.4	1520	20000-650
ZnS	2.2	1830	17000-950
ZrO_2	2.4	2700	25000-1800
Si	3.4	1420	9500-950
Ge	4.0	936	5500-870

In order to obtain a free path for the IR beam entering and leaving the ATRelement the cut edges of the element were protected in order to preventzeolite growth on these surfaces. This was achieved by coating the surfaceswith an epoxy polymer. To obtain a surface suitable for seeding theelements were cleaned. The ZnS, ZnSe and ZrO_2 elements were immersedin acetone and treated in an ultrasonic bath for ten minutes and subsequentlyrinsed with distilled water. An alternative procedure was used for the Sielements. The Si elements were first treated in the same way as the ZnSelements, followed by five minutes of boiling in a solution having thevolume composition $5H_2O$: $1H_2O_2$: $1NH_3$, and then boiled another fiveminutes in asolution having a volume composition of $6H_2O$: $1H_2O_2$: 1HCl.Finally, the elements wererinsed in distilled water. The Ge element wastreated differently. The element was first

treatedin the same way as the ZnSelementsand then dipped in a 38 wt% HF solution for 5-10 s andwashedwith distilled water. The element was subsequently dipped in a 27 wt%H_2O_2 solution for 10- 15 s and then rinsed in distilled water. These twoprocedures were repeated four times toremove several atom layers of Ge.Finally, the element was oxidized by dipping the element in a 27 wt% H_2O_2solution for 10-15 seconds.To render the surface of the elements positively charged the elementswere treated in a 0.4 wt-% solution of a cationic polymer for five minutes.To remove excess polymer the elements were rinsed with a 0.1 M ammoniasolution. Subsequently, the charged reversed elements were immersed in asol containing 60 nmsilicalite-1 seeds. Finally, the seeds were grown into acontinuous, polycrystalline silicalite-1 film by hydrothermal treatment at100ºC for 24 h using a synthesis solution with molar composition 3TPAOH:25SiO_2: 1450H_2O: 100EtOH. Following film growth, the elementswererinsed with a 0.1 M ammonia solution and then dried in an oven at 50ºC.The TPA molecules used as template molecules and the protective polymerused were removed by calcination at 500ºC.

3. Results

General characterization of the films

Continuous thin ZSM-5 and silicalite-1 films were successfully grown onZinc Sulphide (ZnS), Zirconia (ZrO2), Silicon (Si) and Germanium (Ge)ATR elements.Top (a) and side view (b) SEM images of a silicalite-1 film on a Sisubstrate are presented in Figure 1. The thickness of the film isapproximately 200 nm. The silicalite-1 films on a ZnS substrate appearedvery similar.

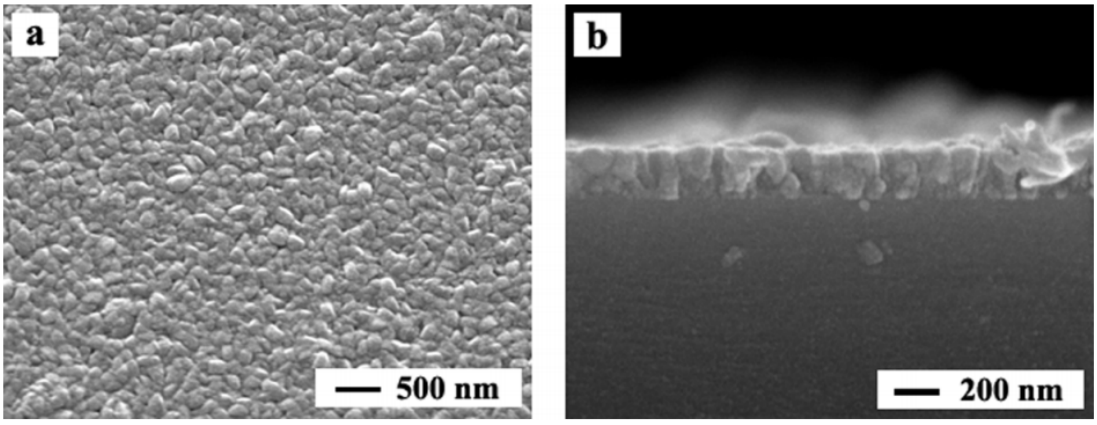

Figure 1. SEM top (a) and side (b) view images of a silicalite-1 film on a Si substrate after 24 hours of hydrothermal treatment at 100ºC.

During synthesis of the films, MFI crystals are formed in the bulk of the synthesis solution. An XRD pattern of purified crystals formed in the bulk is shown in Figure 1 (a), the pattern is typical for randomly oriented silicalite-1 crystals.

The XRD pattern of a silicalite-1 coated ZnS substrate is shown in Figure 2 (b), the reflection labeled with a star stems from the ZnS substrate. It can be concluded that the film consists of MFI crystals. XRD pattern of silicalite-1 films on Si substrates were very similar.

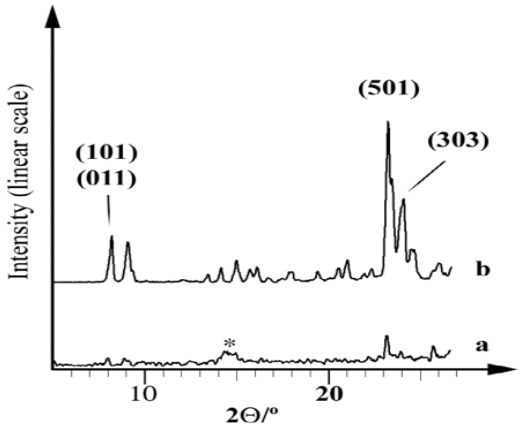

Figure 2. X-ray diffraction patterns of (a) purified bulk product powder, used as reference, and (b) a silicalite-1 film on a ZnS element after 24 hours of hydrothermal treatment at 100°C. The peak labelled with a star stems from the ZnS substrate.

The films were further characterized using FTIR/ATR – spectroscopy. A spectrum of a silicalite-1 film on a Si ATR element is shown in Figure 3. The spectrum shows some absorption bands in the region 2000-1600 cm^{-1}, which are assigned to overtones of vibrations in the silicalite-1 lattice. Moreover, a band is observed at 3743 cm^{-1}, which is a typical band for terminal SiOH - groups in silicalite-1.

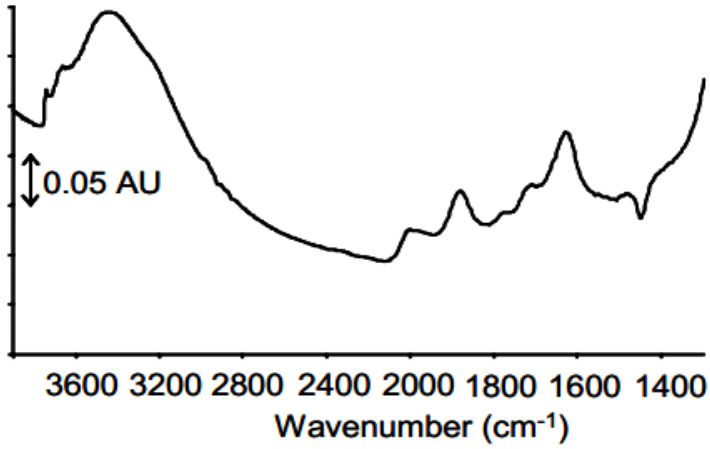

Figure 3. IR spectrum of a silicalite-1 film on a Si element.

Films on ZnSe were damaged and discontinuous, probably due to oxidation of the elements to ZnO during calcination, as supported by the appearance of ZnO reflections in the XRD pattern.

Sensitivity of a silicalite-1 coated ATR element compared to an uncoated element

The sensitivity of a silicalite-1 coated ZnS element for the detection of nhexane in gas phase was compared to an uncoated element. The absorbance from the coated element was compared with the absorbance obtained from the uncoated element. The experiments were carried out at room temperature and the elements were exposed on both sides to a gas mixture of n-hexane in helium with a relative pressure of n-hexane of $6*10^{-5}$. Figure 4 presents the C-H stretching region of the two spectra.

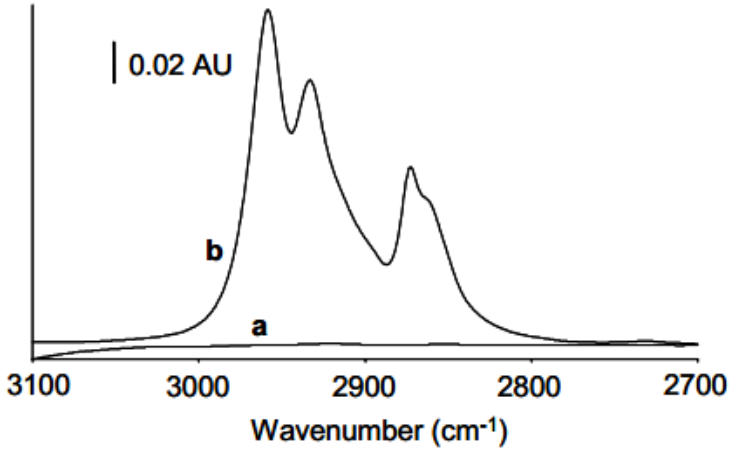

Figure 4. IR spectra of n-hexane using an uncoated ZnS element (a) and a silicalite-1coated element (b). The experiment was performed at room temperature with a n-hexanecontent in the feed of 0.006 % of saturation.

Spectra were recorded by accumulating 250 scans. The uncoated element (a)showed only weak absorption bands, slightly above noise level, whilstdistinct bands were obtained using the coated element (b). The peak heightof the 2960 cm^{-1} absorption band was approximately 180 times higher forthe coated element.

Sensitivity of a silicalite-1 coated ATR element compared to agas cell

Experiments were carried out to compare the sensitivity of coated elementswith a 10 cm gas cell. The experiments were performed at room temperatureusing a Si element coated with a silicalite-1 film on one side. The cells werefed with a gas containing n-hexane in helium with a relative pressure of nhexane corresponding to $6*10^{-5}$. Figure5 (a) shows the spectrum whena10 cm gas cell was used and spectrum (b) was recorded using the coatedATR element. The peak height of the 2967 cm^{-1} band was used forcomparison. The silicalite-1 coated element has approximately 85 timesstronger absorbance.

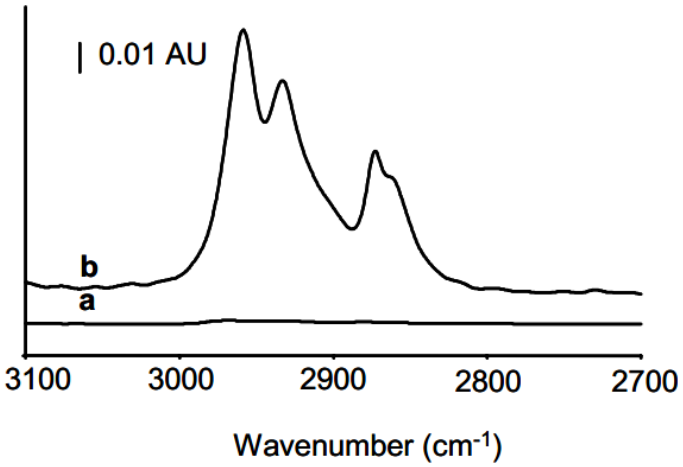

Figure 5. IR spectra of n-hexane recorded using (a) a 10 cm gas cell, and (b) a Si element coated on one side with a silicalite-1 film. The experiment was performed at room temperature with n-hexane content in the feed of 0.006 % of saturation.

Increasing the path length in the gas cell would yield a higher absorbance. On the other hand, several methods could be used for increasing the absorbance in ATR spectroscopy. Coating both sides of the ATR element would yield a stronger absorbance; another method would be to increase the angle of incidence since this would give more reflections inside the waveguide. Further, increasing the film thickness would result in stronger absorbance since more of the analyte would be available for detection by the evanescent field (this option would only be possible up to a certain limit depending on the penetration depth). Using longer and thinner waveguides such as optical fibers would also yield a higher absorbance.

Response time

The response time for the silicalite-1 coated ATR element was also investigated. A ZnS element coated on both sides was used in the experiment. The number of scans was reduced to 10 because of the shorter data acquisition time needed in this experiment. The element was subjected to a step increase of n-hexane from $P/P_0 = 0$ to $P/P_0 = 0.01$ at 27ºC. By following the progression of the 2960 cm^{-1} band the response time was estimated, see Figure 6.

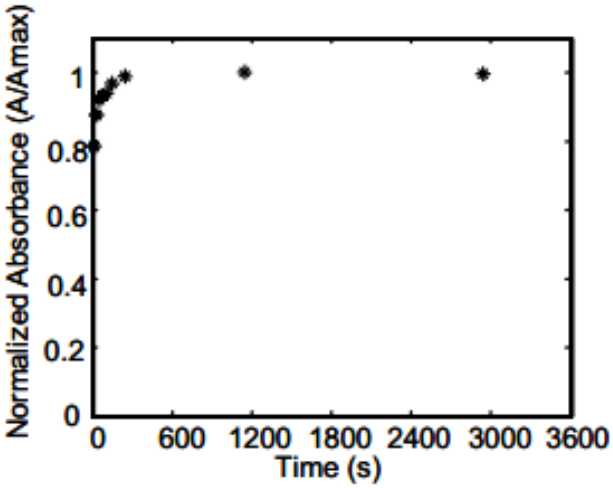

Figure 6. Plot of the normalized absorbance (A/Amax) as function of time for the systemn-hexane adsorbed in a silicalite-1 film. The experiment was carried out at 27°C and theabsorbance was measured at 2960 cm-1.

It can be concluded that equilibrium is achieved after approximately 250 s, but already at the first point, averaged between approximately t=5 s to t=15 s, the absorbance was 79% of the value at equilibrium, which indicates a relatively fast sensor response time. It is likely that the response time will be even shorter for thinner films, higher temperatures and molecules with higher diffusivity in the adsorbent. High sensitivity towards hydrocarbons combined with a fast response time and the versatility of FTIR spectroscopy, makes zeolite coated ATR elements a very interesting choice for studying adsorption, diffusion and reactions taking place within the films. The sensor seems ideal for detection of low concentrations of hydrocarbons in gas.

Conclusions

Silicalite-1 and ZSM-5 films have been successfully grown on waveguides of various crystals for use in ATR spectroscopy. The thicknesses of the films were independent of the substrate. The coated ATR crystals were very sensitive for hydrocarbons (nhexane). The sensitivity was also compared with a standard 10 cm gas cell. It was also shown that the response time of the sensor was relatively fast. Adsorption isotherms for n-hexane and p-xylene in silicalite-1 were determined at various temperatures. Henry constants adsorption heats determined from the isotherms at low pressures agreed well with previously reported data. Capillary condensation in defects was observed at higher pressures. Zeolite coated waveguides in combination with FTIR spectroscopy are extremely promising tools for studying adsorption, diffusion and reaction in zeolites under well defined conditions. The novel sensors show promising sensitivity and response time and are possibly very selective as well.