

## A Narrative Experimental View for Zeolite in Molecular Orientation

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### ABSTRACT

In this paper, FTIR spectroscopy in understanding with polarized light and an ATR look into coated with a b-oriented ZSM-5 film was the first time used to conclude the point of reference of adsorbed molecules in the ZSM-5 structure. Two adsorbents were studied, n-hexane and p-xylene and the results decided with formerly reported results obtained by other investigational techniques.

**Keywords:** Zeolite; Attenuated Total Reflection; adsorbates; dichroic ratio ; gas sensing; silanol ; guest/host materials; absorption.

### I. INTRODUCTION

Zeolites are widely used in industry as ion exchangers, sorbents and catalysts and several novel applications such as membranes for separations and chemical sensors have been planned. A thorough facts of the adsorption is basic in all these applications. In the present work, two systems that have been widely studied previously, viz. n-hexane/MFI and p-xylene/MFI were selected for inquiry by a novel technique. An overview of the previously reported results for these systems is given below. Several groups have studied the n-hexane/MFI system, and an inflection in the adsorption isotherm has been reported at a concentration of ca. 0.7 mmol/g, corresponding to about half the saturation loading [1,2]. The inflection was credited to adsorption on dissimilar sites by Smit and Maesen [3], who studied the system using Monte Carlo simulations.

They observed a redeployment of n-hexane as the concentration in the adsorbent increased. At low concentrations, the molecules are evenly spread in the intersections and in the channels. At higher concentrations, the molecules migrate into the sinusoidal channels exit the intersections free, enabling a complete filling of the straight channels. Mentzen [4] employed powder x-ray diffraction (XRD) and observed a similar redistribution of n-hexane at room temperature. On the contrary, Morell et al. [5] could not observe any redistribution of the adsorbate at room temperature nor any favored sites when investigating the nhexane/silicalite-1 system with powder and single crystal XRD as well as <sup>29</sup>Si MAS NMR and molecular modelling. However, clear ordering of n-hexane appeared when the temperature was lowered to 180 K, with molecules only adsorbed in the channels leaving the intersections unoccupied.

A type IV isotherm has been observed for p-xylene when adsorbed in MFI powder and unsupported

films at temperatures around- and slightly above room temperature [6,7]. For the case of a type IV isotherm, the saturation capacity is 8 molecules/unit cell (or ~1.4 mmol/g). When the temperature is increased, a type I isotherm with a saturation capacity of only 4 molecules per unit cell is observed. The location and orientation of p-xylene molecules in MFI have been studied by means of XRD [8,9], FTIR microscopy, [10] Monte Carlo simulations [11] and NMR [12]. The initial step in the type IV isotherm has been assigned to adsorption of p-xylene in the intersections with the long axis (going through the CH<sub>3</sub>- groups) mainly oriented in the b-direction of the crystals. Further, the second step in the type IV isotherm has been assigned to p-xylene adsorbed in the sinusoidal channels [9]. FTIR/ATR (Attenuated Total Reflection) has emerged as a powerful tool for studying surfaces and thin films of various systems, e.g. polymers [13], mineral flotation [14], membrane peptides [15], and catalysts [16]. An advantage with the technique is that, by applying polarized radiation, it is possible to gain information on orientation of adsorbed molecules [13-15]. This work aims at illustrating the utility of FTIR/ATR spectroscopy combined with polarized radiation and oriented MFI films for determining the arrangement of molecules in MFI crystals for the first time. In this context, an advantage with p-xylene as adsorbate is that the molecule is rigid, in that it cannot take on different conformers. This makes it possible to determine an average tilt angle of the molecule relative the surface normal.

### II. EXPERIMENTAL METHOD

Trapezoidal (50x20x2 mm, 45° cut edges) ZnS Attenuated Total Reflection (ATR) elements were coated with b-oriented ZSM-5 films using an in-situ method [17]. The films were subsequently characterized by Scanning Electron Microscopy (SEM)

and XRD [17]. The infrared measurements were conducted using a Bruker IFS 66v/S spectrometer prepared with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Polarized radiation was achieved by applying a rotatable ZnSe wire grid polarizer. A gas delivery system and an insitucell were used for exposing the film to a controlled environment, details of the equipment have been reported previously [18]. Helium (AGA 99.99990%) was used as carrier gas and n-hexane (Sigma 99+%) and p-xylene (Aldrich 99+%) were used as adsorbates. Prior to each measurement, the film was heated in-situ to 573 K for 4 hours at a heating/cooling rate of 1°/min. under a flow of pure helium to remove any molecules adsorbed in the zeolite. Subsequently, the cell was mounted in the spectrometer and background spectra without polarizer, and with 0° and 90° division were recorded by averaging 128 scans. After that the hydrocarbon was introduced and spectra were recorded at equilibrium by averaging 64 scans. First one spectrum was recorded without polarizer, and then spectra with 0°, 90° and 0° polarization were recorded. Two spectra were recorded at 0° to ensure that the system was stable. In the evaluation, the mean value of the two measurements at 0° was used. IR spectra recorded without polarizer were used for determining the concentration of the adsorbate in the film, whereas spectra recorded with polarized radiation were used for determining the dichroic ratio. For n-hexane, the peak height of the methylene asymmetric stretching vibration band (2934 /cm) was used for determining the dichroic ratio, whereas for p-xylene, the integrated absorbance of a band assigned to a ring stretching vibration (1518 /cm) was used for formative the dichroic ratio.

**2.1 The ATR-technique**

In the ATR sampling technique, the infrared radiation is reflected inside a waveguide, also denoted an ATR element. At each reflection, a standing wave of the electromagnetic field is created. This field penetrates a short detachment outside the element surface and interacts with molecules situated close to the element surface. The concentration of the electromagnetic field decays exponentially with distance from the surface and a penetration depth,  $d_p$ , has been introduced to estimate the surface sensitivity of the technique [19]:

$$d_p = \frac{\lambda_1}{2\pi(\sin^2 \theta - n_{21}^2)^{1/2}} \quad (1)$$

The wavelength of the radiation in the element is  $\lambda_1$ ,  $\theta$  is the angle of incidence (45° in this work), and  $n_{21} = n_2/n_1$  is the ratio of the refractive indices in the film ( $n_2$ ), and element ( $n_1$ ), respectively. The penetration depth is usually in the range from a couple of hundred nm to a few  $\mu\text{m}$ , making the ATR

technique especially well suited for studying thin films.

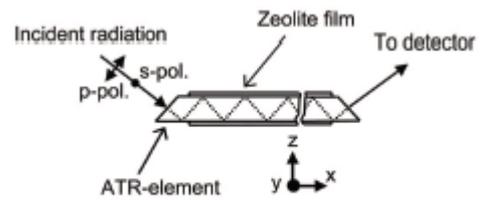


Fig.1. Geometry of the ATR setup

As pointed out in the foreword, an benefit with the ATR-technique is that it is possible to conclude average molecular orientation by applying polarized radiation. The key parameter when determining the direction of molecules is the dichroic ratio,  $D$ , and by assuming an uniaxial distribution of the adsorbates, the dichroic ratio is given by [20]:

$$D = \frac{A_s}{A_p} = \frac{E_y^2(\sin^2 \gamma (2 - 3 \sin^2 \Theta) + 2 \sin^2 \Theta)}{(E_x^2 + E_z^2)2 \sin^2 \Theta + (2 - 3 \sin^2 \Theta)E_x^2 \sin^2 \gamma + 2E_z^2 \cos^2 \gamma} \quad (2)$$

The absorbance for a certain band resolute with radiation polarized in the plane of the element surface is denoted  $A_s$  (s-polarized) and  $A_p$  is the absorbance for the same band recorded with radiation polarized in the plane normal to the element surface, see Figure 1. Moreover,  $\square$  is the angle between the transition moment of the vibration of interest and the main axis of the molecule, for p-xylene,  $\square = 0^\circ$  for the ring stretching vibration observed at 1518 /cm. Further,  $\gamma$  is the tilt angle of the main molecule axis from the surface normal.

The electric field amplitudes,  $E_x$ ,  $E_y$  and  $E_z$ , in the x-,y- and z-directions are given for a three layer system (ATR-element, film and gas) by equations, 3, 4 and 5.

$$E_x = \frac{2(\cos \theta)(\sin^2 \theta - n_{31}^2)^{0.5}}{(1 - n_{31}^2)^{0.5}[(1 + n_{31}^2)\sin^2 \theta - n_{31}^2]^{0.5}} \quad (3)$$

$$E_y = \frac{2 \cos \theta}{(1 - n_{31}^2)^{0.5}} \quad (4)$$

$$E_z = \frac{2n_{32}^2 \sin \theta \cos \theta}{(1 - n_{31}^2)^{0.5}[(1 + n_{31}^2)\sin^2 \theta - n_{31}^2]^{0.5}} \quad (5)$$

The refractive index of the gas is denoted  $n_3$  and  $n_{31} = n_3/n_1$  and  $n_{32} = n_3/n_2$ . By inserting  $\square = 0^\circ$  in equation.2 a simplified version of the equation is obtained:

$$D = \frac{E_y^2 \sin^2 \gamma}{E_x^2 \sin^2 \gamma + 2E_z^2 \cos^2 \gamma} \quad (6)$$

From this expression,  $\gamma$  can be determined after measuring the dichroic ratio and calculating  $E_x$ ,  $E_y$  and  $E_z$  from equation 3 to equation 5.

### III. RESULTS AND DISCUSSION

Figures 2 (a) and (b) show top- and side view images of a ZSM-5 film on a ZnS element. The images indicate that the film mostly consists of inter grown b-oriented crystals with tablet habit, and a slight fraction

of a-oriented crystals. Further, a few b-oriented crystals are deposited on top of the film. The images also show that the film did not cover the element entirely.

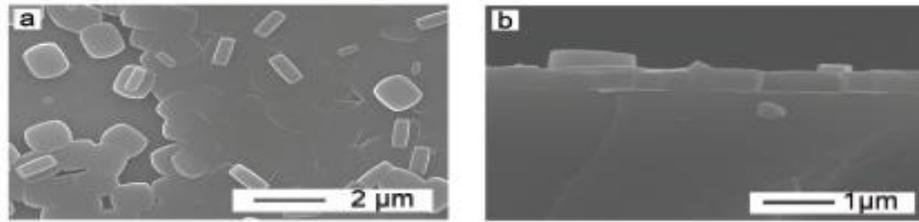


Fig.2. SEM images of the top ( a ) and side ( b ) of a MFI film on ZnS

The adsorption of n-hexane in a silicalite-1 film developed from seeds and found that the saturation capacity was in superior agreement with standards reported for powders. By assuming that the result reported by Bjorklund et al. is valid also for the films used in this study, a parameter accounting for discrepancies both due to deficient surface coverage

and to any differences in molar absorptivity between the experimental value determined in  $CCl_4$  and the real value in the zeolite can be defined. The parameter,  $k_{hexane}$ , was determined to about 0.43. Spectra recorded without polarizer of n-hexane and p-xylene adsorbed in the film were very similar to previously reported spectra, examples are shown in Fig.3.

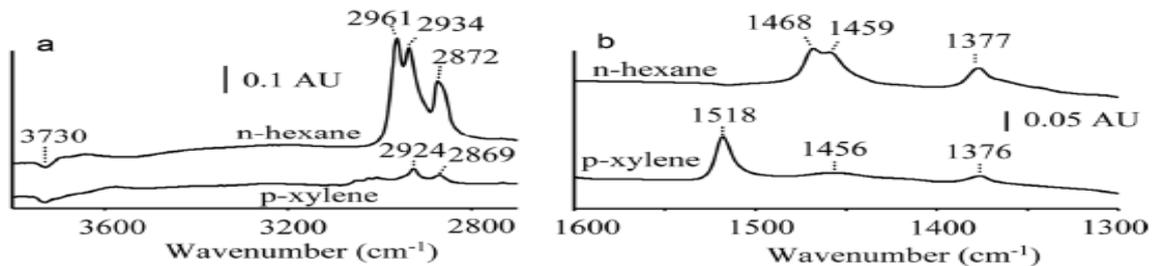


Figure 3. Spectra of n-hexane and p-xylene adsorbed in ZSM-5. The spectrum of n-hexane was recorded at 303 K and a n-hexane pressure of 12.92 kPa whereas the spectrum of p-xylene was recorded at 323 K and a p-xylene pressure of 652 Pa.

As expected, for n-hexane, bands appear in the CH stretching region between 3000-2700 /cm and in the CH deformation vibration region between 1500-1300 /cm. In the p-xylene spectrum, several overlapping bands appear in the region 3200-2700 /cm, from which the most prominent are the bands at 2924 and 2869 /cm, assigned as symmetric methyl stretching vibration and asymmetric methyl deformation overtone [10]. At lower wave numbers, bands appear at 1518, 1456 and 1376 /cm, these bands are assigned to benzene ring stretching vibration, asymmetric and

symmetric methyl deformation vibrations, respectively. In addition, for both spectra, a negative band appears at 3730 /cm in combination with the appearance of a new band at lower wave numbers. This band is assigned to silanol groups perturbed by adsorbate molecules resulting in a shift to lower wave numbers.

Spectra recorded with the polarized radiation showed significant polarization of several bands and examples are shown in Fig. 4.

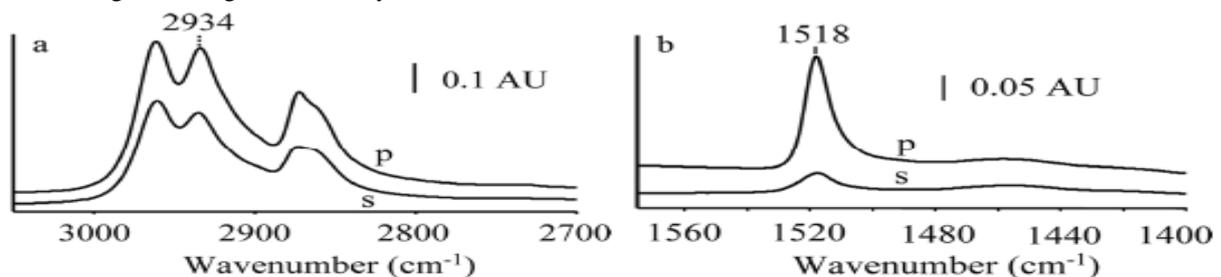


Fig.4. Parts of spectra recorded with polarized radiation of n-hexane (a) and p-xylene (b).

The bands indicated in the spectra were the ones used for determining the dichroic ratio, and in all cases, higher absorbance was observed with p-polarized radiation. The strong polarization, mostly

observed in spectra of p-xylene, indicate a preferential orientation of the molecules. Dichroic ratios determined at different concentrations are presented in Table 1 together with calculated tilt angles for p-

xylene. The dichroic ratio for n-hexane changes significantly when the concentration changes from 0.60 to 0.85 mmol/g, i.e. in the region where the

inflection have been reported, while the ratio changes less in the concentration range 0.85 – 1.42 mmol/g.

Table 1. Dichroic ratio at different adsorbate concentrations in the film.

N – hexane		P – xylene (323 K)		
Concentration (mmol/g)	Dichroic ratio	Concentration (mmol/g)	Dichroic ratio	Tilt angle (in degree)
0.60	0.68	0.15	0.30	34
0.85	0.59	0.29	0.26	28
1.12	0.60	0.52	0.16	22
1.42	0.63	0.73	0.14	20

The change in dichroic ratio in the concentration range 0.66 – 0.84 mmol/g indicates that some kind of molecular reorientation takes place. A change in the conformer distribution, i.e. the number of trans C-C bonds, could cause a change in the dichroic ratio for alkanes. However, the positions of the CH<sub>2</sub>-stretching vibrations bands are known to be sensitive to the conformation of alkanes. Shifts to lower wave numbers indicate that the number of trans bonds increases whereas a shift to higher wave numbers is a sign of an increased number of gauche bonds. In the present study, the position of the asymmetric CH<sub>2</sub>-stretching vibration band was fairly constant at 2934 /cm throughout the concentration range studied.

Hence, the change in the dichroic ratio observed in the present work at about half the saturation loading is attributed to a redistribution of n-hexane in concert with the findings of Smit and Maesen [3] and Mentzen [4]. Further, if all n-hexane molecules were in all-trans conformation it would have been possible to determine an average molecular orientation, however previous studies have shown that this is not the case for n-hexane in MFI, hence no average tilt angles for n-hexane were determined in the present work.

For p-xylene, we observe a decrease in dichroic ratio and average tilt angle with increasing concentration. The tilt angle 20° obtained at a concentration of 0.73 mmol/g is very close to the one reported by Schüth (18°), as determined by FTIR microscopy on large single crystals at ca 310 K [10]. van Koningsveld et al. [9] investigated the p-xylene/MFI system at room temperature using XRD and found a tilt angle of 7.5° for p-xylene adsorbed in the channel intersections. Fyfe et al. [12] employed <sup>1</sup>H/<sup>29</sup>Si CP MAS NMR spectroscopy to study the p-xylene/ ZSM-5 system and found that the orientation of p-xylene in the intersection that best fitted experimental data is with the long axis parallel to the crystallographic b-direction. However, the authors states that completely reliable data was only obtained below 213 K and data recorded above room temperature could not be used for distance and structure determinations due to extensive molecular motions averaging the interactions. The difference in tilt angle between the measurements in this report and

the ones by van Koningsveld et al and Fyfe et al. may, at least partially, be explained by molecules being more mobile at the higher temperatures used in the present study. Further, some involvement may also create from p-xylene adsorbed on silanol groups, as indicated in Figure 3. Aggressive adsorption on silanol groups may also explain the observed decrease in tilt angle with increasing concentration in the present work.

In addition to being a tool for studying molecular orientation, the FTIR/ATR technique has high sensitivity, making it appropriate for studying the properties of very thin films. Moreover, since FTIR spectroscopy is sensitive to the species adsorbed, it should be possible to determine the orientation of adsorbed molecules from a multi component mixture as long as the direction of the transition moments are known and the corresponding absorption bands are separated. Another interesting application would be to use the technique to study anisotropic diffusion in zeolites. A challenge for quantitative measurements is the need of a molar extinction coefficient for the adsorbate in the zeolite film. Furthermore, the small size of the crystals constituting the film introduces some problems. Firstly, the large external surface area/volume ratio leads to relatively high concentration of external silanol groups, which may affect the quantitative measurements as well as the determination of adsorbate orientation. A second effect is that small crystals in a dense film results in more grain boundaries and some of these will always be open, enabling capillary compression to occur may also influence the data.

#### IV. CONCLUSIONS

A novel technique for studying the orientation of adsorbates in zeolite at various concentrations of the adsorbate was developed. The method utilizes ATR elements coated with oriented zeolite films in mixture with FTIR spectroscopy and was demonstrated by studying the adsorption of n-hexane and p-xylene in a b-oriented ZSM-5 film. The obtained results agreed with previous findings.

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