



Infrared reflectance measurements of zeolite film thickness, refractive index and other characteristics

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Abstract

We present a method for the non-destructive measurement of zeolite membrane characteristics by means of infrared (IR) reflectance measurements in the non-absorbing frequency range. A rigorous expression for the IR reflectivity of an isotropic layered structure is combined with a polynomial expansion for the refractive index function, to interpret reflectance measurements from zeolite MFI membranes grown on α -alumina substrates by the seeded growth technique. The optical refractive index function, the membrane thickness, and the RMS roughness of the membrane surface can be extracted from non-linear least squares fitting of the measurement model. The method can also be used to detect the loading of organic species by measuring changes in the optical characteristics. The utility of the method in studying adsorption and transport in zeolite membranes is discussed.

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1. Introduction

Zeolite membranes have been a topic of much research in recent years, as a possible means of performing efficient and low-cost separations of organic molecules and gases [1]. Several synthesis methods exist for fabricating supported zeolite membranes in the thickness range of 0.5–100 μm , and many challenging separations have been demonstrated using zeolite membranes [1]. In addition, zeolite films are candidates for low dielec-

tric constant (or low refractive index) insulators [2] (of interest in microelectronics) and are also being considered as hosts for various types of nano-structured materials [3,4].

Reliable and non-destructive measurements of zeolite film characteristics such as the film thickness and dielectric constant (or refractive index) are beneficial for estimating the performance of zeolite films in the above mentioned applications. Thickness measurements are usually made by a destructive technique such as scanning electron microscopy (SEM), wherein the sample is cross-sectioned for viewing in the microscope. The effective thickness of a zeolite membrane grown on a permeable substrate can also be estimated by

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interpreting transient gas permeation data in terms of the Maxwell–Stefan equations for transport in zeolitic materials [5]. Impedance measurements have recently been employed to obtain the dielectric properties of zeolite films [2]. This technique involves sputtering of metallic contacts on the membrane surface, and also may suffer from problems such as current leakage through defects and other non-zeolitic charge transport pathways. On the other hand, the ‘bulk’ or ‘average’ film properties can also be measured from the diffraction of electromagnetic radiation in an appropriate wavelength range. Given the thickness range of zeolite membranes, IR radiation (whose wavelength is in the μm range) is a good choice for performing such measurements. Owing to the easy availability of FTIR spectrometers and various types of reflectance stages, it is also possible to conduct these measurements in situ during transport or adsorption experiments. In this paper, we report a method for extracting zeolite membrane characteristics from FTIR reflectance measurements in the non-absorbing frequency range. A rigorous theory of optical reflection from a non-absorbing layered medium (such as a zeolite membrane on a substrate) is used in combination with a polynomial expansion for the refractive index as a function of the frequency. The membrane characteristics are obtained by non-linear least squares (NLS) fitting of the model to the experimental data. The results are evaluated by comparison with other techniques for measuring the membrane characteristics.

2. Theory

The dielectric function ε of an isotropic material is in general a complex number, and is written as [6]:

$$\varepsilon(k) = \varepsilon_1(k) + i\varepsilon_2(k) \quad (1)$$

where k is the frequency (commonly expressed in cm^{-1}). For non-magnetic materials, the refractive index n , is the square root of the dielectric function:

$$n(k) = n_1(k) + in_2(k) = \sqrt{\varepsilon(k)} \quad (2)$$

The real part of the dielectric function describes phenomena such as the refraction of light at any frequency, whereas the imaginary part is significant only near the characteristic resonance frequencies of the material at which it absorbs electromagnetic radiation. In insulating solids, such resonances in the IR frequency range can arise from the vibrational modes of the atoms in the solid. The complex dielectric function and complex refractive index of a material can be obtained from surface reflectance measurements taken over a large frequency range, from an optically smooth surface of the bulk material. These measurements allow extraction of the complex dielectric function by the well-known Kramers–Kronig relations [7]. However, these relations cannot be easily extended to describe the optical properties of materials deposited in the form of thin layers on a substrate.

In zeolite frameworks, the lattice vibrational mode of highest frequency is the Si–O asymmetric stretching mode [8] which occurs between 1100 and 1250 cm^{-1} . Therefore, zeolite frameworks can be considered as transparent to IR radiation above 1250 cm^{-1} , especially in the case of zeolites whose pores contain little or no adsorbed water or other molecules. In this case, the refractive index can be approximated as a real function (i.e., the imaginary part, $n_2 = 0$). The imaginary part of the refractive index can be parametrized [9,10] as a summation of peak functions (such as Gaussians), each centered on a lattice vibrational frequency. However, the theory of optical reflection from a layered structure is greatly simplified if absorption can be neglected. We choose the IR frequency range 1500–3000 cm^{-1} for the present measurements, in which case this assumption is reasonable.

Fig. 1 shows a schematic of the interaction of light (incident from air, denoted as a) with a general layered structure, consisting of N layers of varying refractive index (n_m) and thickness (L_m) supported on a substrate (denoted as s). The substrate is assumed to be infinitely thick in comparison to the layers. The reflectivity (r) of such a structure can be obtained by solution of Maxwell’s equations with the appropriate boundary conditions applied at each interface [11]. The reflectivity is obtained from the following recursive expression:

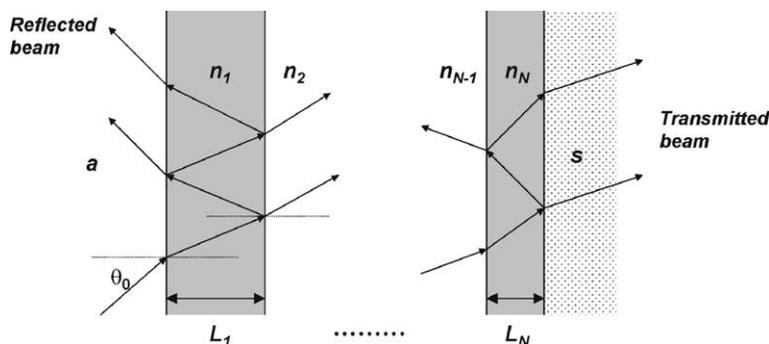


Fig. 1. Reflection and transmission of light from a layered structure composed of N refracting layers supported on a surface.

$$r_{m..s} = \frac{f_{(m,m+1)} + r_{m+1..s} e^{-2i\phi_{m+1}}}{1 + f_{(m,m+1)} r_{m+1..s} e^{-2i\phi_{m+1}}} \quad (3)$$

where $m = a, 1, 2, \dots, N - 1, N$. The quantity $r_{m..s}$ is an effective reflectivity from a structure composed of layers $m + 1, \dots, N$ supported on the substrate s . Thus the quantity of physical interest in this case, is the total reflectivity $r_{a..s}$. The recursive calculation is terminated when the interface between layers $N - 1$ and N is reached, at which point we use the closed expression for the reflectivity of the single layer N supported on s :

$$r_{N-1..s} = \frac{f_{(N-1,N)} + f_{(N,s)} e^{-2i\phi_N}}{1 + f_{(N-1,N)} f_{(N,s)} e^{-2i\phi_N}} \quad (4)$$

The factors $f_{(m,m+1)}$, defined for each interface, are given by:

$$f_{(m,m+1)} = \frac{\sqrt{n_m^2 - \sin^2 \theta_0} - \sqrt{n_{m+1}^2 - \sin^2 \theta_0}}{\sqrt{n_m^2 - \sin^2 \theta_0} + \sqrt{n_{m+1}^2 - \sin^2 \theta_0}} \quad (5)$$

Here, θ_0 is the angle of incidence from air (Fig. 1). The phase factors for each layer (ϕ_m) are given by:

$$\phi_m = 2\pi L_m k \sqrt{n_m^2 - \sin^2 \theta_0} \quad (6)$$

The measured quantity in the FTIR experiments is the *reflectance* (R), which is the fraction of the incident light intensity that is reflected, and is related to the complex reflectivity (r) by:

$$R = |r|^2 e^{-(4\pi\sigma k)^2} \quad (7)$$

In this expression, a frequency-dependent correction factor has been applied to account for the RMS roughness (σ) of the surface [12]. The RMS roughness of a surface is measured as:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (l_i - L)^2} \quad (8)$$

where l_i are the local depths of the surface at a number of points N , and L is the mean depth (or centerline) of the surface. The RMS roughness can be estimated by a technique such as scanning probe microscopy (SPM). Since the phase factors (Eq. (6)) are linear functions of the frequency, we expect (from Eqs. (3)–(8)) that the reflectance in the non-absorbing region would be an oscillatory function of the frequency.

An accurate theoretical determination of the refractive index of a material as a function of the incident light frequency, requires quantum mechanical calculations. On the other hand, we can experimentally determine the refractive index, thickness and RMS roughness by fitting Eqs. (3)–(7) to experimental reflectance data. A functional form for the refractive index has to be assumed for this purpose. In the present case, we first determine the refractive index function for the substrate. An expression for the reflectivity of the bare substrate is obtained trivially from Eqs. (3)–(7), by setting the refractive indices of all the layers to n_s . This gives the reflectivity of the substrate as identical to $r_{(a,s)}$ which is given by Eq. (5) with $n_m = n_a = 1$ (air) and $n_{m+1} = n_s$. Thus, the refractive index

function of the substrate can be obtained directly without any fitting parameters, if the RMS roughness of the polished substrate is assumed to be negligible. Upon performing this analysis (see Section 4), the effective refractive index function of the substrate in the given frequency range is found to be well fitted by a five-coefficient polynomial function:

$$n_s(k) = \sum_{i=0}^4 C_i k^i \quad (9)$$

The experimentally determined substrate refractive index function is then used in subsequent data analysis of spectra from the zeolite films on the substrate. The five-coefficient polynomial form is also used for the refractive index function of the zeolite. Thus, the fitting parameters for the model consist of the layer thicknesses, the refractive index polynomial coefficients, and the RMS roughness. For a single-layered zeolite membrane on a substrate, we have $N = 1$, so that the total number of fitted parameters equals 7.

3. Experimental methods and data analysis

Zeolite MFI membranes were grown on several α -alumina substrate disks. These 1 in.-diameter, 2 mm-thick disks were first polished with 600 grit silicon carbide paper. They were then coated three times with calcined zeolite MFI seed crystals (~ 100 nm in size) from a 2 g/L colloidal suspension. Membranes of various thicknesses were made by carrying out hydrothermal seeded growth [13–16] for different times between 7 and 27 h, using a synthesis composition described elsewhere [13]. The membranes were washed in hot deionized water, dried at 363 K and then calcined in air at 773 K for 6 h to remove the organic SDA. Reflectance FTIR spectra were obtained in the frequency range 500–6500 cm^{-1} on a Perkin–Elmer 2100 spectrometer equipped with a Specac reflectance stage. The frequency resolution used was 0.5 cm^{-1} , and a total of 256 scans were measured for each sample. An incidence angle of $\theta_0 = 10^\circ$ is used in all cases. All measurements are

referenced to a highly reflecting gold mirror, taken as a standard for normalizing the reflectance from the membrane samples. FTIR reflectance spectra were collected from the polished bare substrate and from the calcined zeolite membranes of varying thicknesses. One of the membrane samples was measured both before and after calcination. This sample was then exposed to saturated *p*-xylene vapor (with a helium carrier) in a closed chamber for 48 h at room temperature. FTIR spectra were also measured from this membrane loaded with *p*-xylene. The thicknesses of the membranes were determined (after cross-sectioning) by SEM (JEOL 100CX), for comparison with the fitted values. RMS roughness measurements were carried out using a scanning probe microscope (digital instruments). Several 5 $\mu\text{m} \times 5 \mu\text{m}$ areas of each membrane sample were scanned in tapping mode using a crystalline silicon probe. The roughness values obtained from each area were averaged.

The as-measured reflectance spectra in the region 1500–3000 cm^{-1} are coarsened (by rebinning and averaging) to 5 cm^{-1} resolution. This gives 301 data points for fitting seven parameters. Since the FTIR spectra in this frequency region are of an oscillatory nature with periods greater than 200 cm^{-1} (Fig. 2), there is negligible loss of information by coarsening the data to 5 cm^{-1} resolution, with the benefit of much faster data fitting. The data were fitted by NLS to the general model described above (with $N = 1$), using a locally developed data analysis code based on the Levenberg–Marquardt NLS algorithm [17]. The data fits were started with a single-coefficient (constant) zeolite refractive index and the membrane thickness as parameters, and subsequently refined by the progressive addition of the remaining four polynomial coefficients (Eq. (9)). The roughness parameter in Eq. (7) was introduced towards the end of the fitting procedure. The estimated statistical errors on the final fitted parameters were calculated from the covariance matrix [17]. As with all fitting procedures of this type, there is no guarantee that the global minimum has been obtained. However, the validity of the fit is checked by starting from different initial estimates of the parameters.

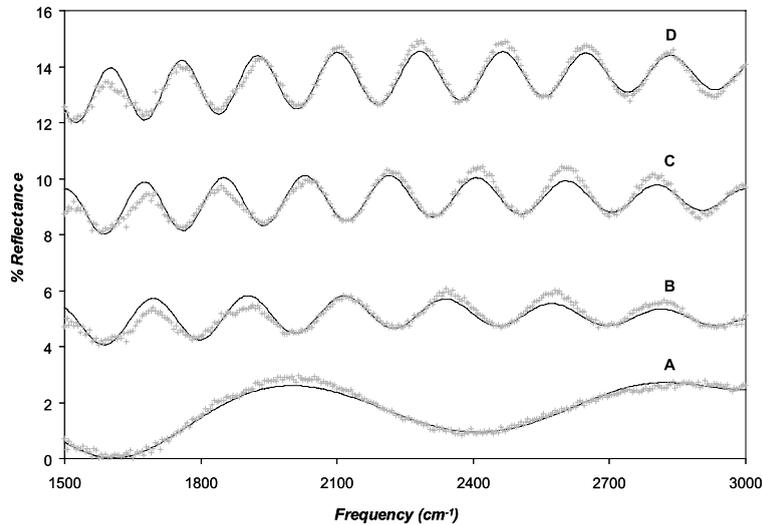


Fig. 2. Reflectance spectra (expressed in units of percent incident light reflected) for MFI membrane samples A–D. SEM cross-sections of these samples are shown in Fig. 3. The measured data are indicated by + symbols and the fits by smooth curves. The spectra for sample A are shown as is, while the remaining spectra are progressively shifted upwards by 4% units each.

4. Results and discussion

Fig. 2 shows the measured and calculated IR reflectance spectra from four MFI membrane samples. The measured data are shown as + symbols, while the spectra calculated from the fitted parameters are shown as smooth curves. In this figure, the reflectance is expressed as the percentage of incident light that is reflected, i.e., $100 \times R$. The measured data and the fitted curve for sample A are shown as measured (or calculated), whereas the data for the remaining samples are progressively shifted upward by 4 percentage units on the y -axis, for clarity. The fitted curves represent a good fit to the experimental data and capture well the essential features of the measured

spectra. Table 1 gives the values of the thickness (μm) and RMS roughness (μm) obtained from the data fitting, and the estimated uncertainties of these parameters. The thicknesses obtained from the FTIR data may be compared with the thicknesses obtained from Fig. 3, which shows SEM images of the four membrane samples after cross-sectioning. Clearly, the FTIR data fits lead to values of the optical thickness of the samples which are close to the apparent thickness observed by SEM. The RMS roughness values obtained from the FTIR fits are also physically reasonable, and are quite small when compared to the membrane thickness. These values are in the same physical range as those estimated from the SPM measurements. The membrane sample A has the

Table 1

Optical thickness and root-mean-square (RMS) roughness of membrane MFI samples extracted from FTIR measurements, and comparison with the thickness as estimated by SEM and the RMS roughness as estimated by scanning probe microscopy (SPM)

Sample	FTIR thickness (μm)	SEM thickness (μm)	FTIR roughness (μm)	SPM roughness (μm)	Residual ^a (%)
A	4.0 ± 0.2	3.3	0.00 ± 0.03	0.04 ± 0.02	9.53
B	14.8 ± 0.4	13.6	0.24 ± 0.07	0.12 ± 0.02	18.92
C	17.8 ± 0.4	16.6	0.19 ± 0.02	0.10 ± 0.02	18.08
D	18.9 ± 0.6	17.1	0.10 ± 0.05	0.11 ± 0.02	14.92

^a Percentage residual for reflectance (R) is calculated as $100 \times [\sum (R_{\text{calculated}} - R_{\text{measured}})^2 / \sum R_{\text{measured}}^2]^{1/2}$.

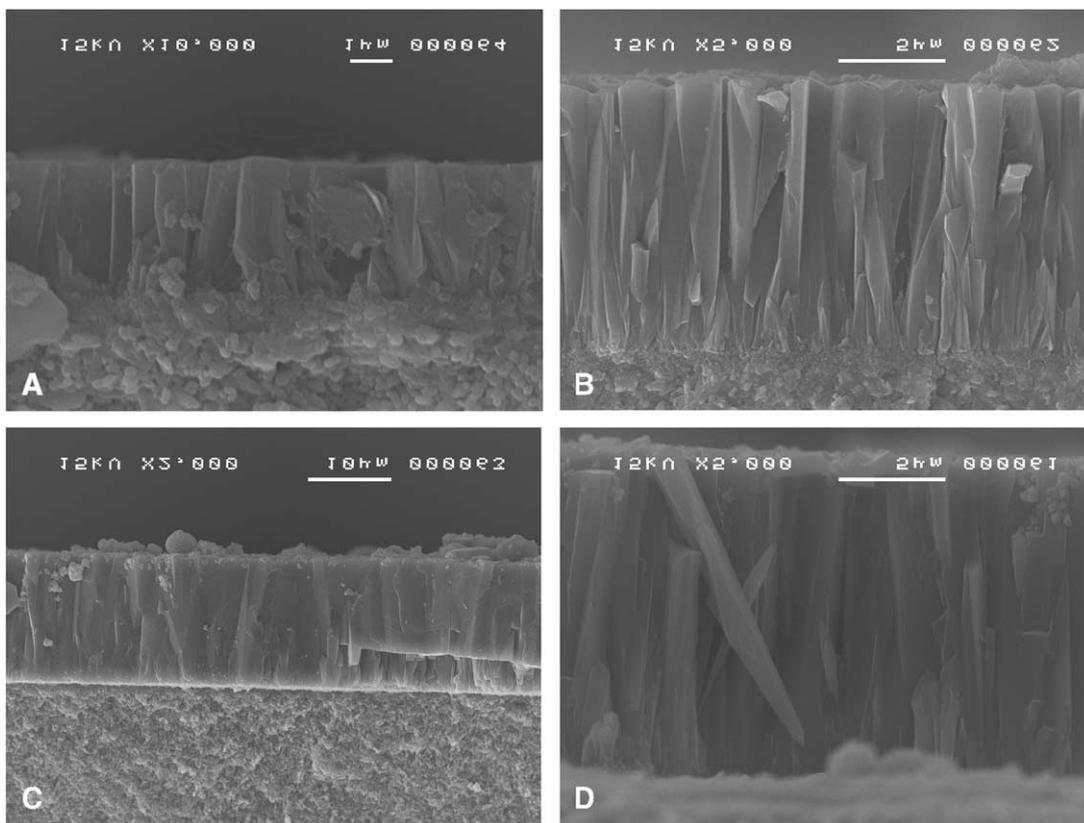


Fig. 3. SEM cross-sections for MFI membrane samples A–D on α -alumina substrates. The scale bars are 1, 5, 10, and 5 μm respectively, and are used to determine the thickness of the membranes.

smallest thickness and also the smallest RMS roughness, whereas the remaining membrane samples have rougher surfaces. This is related to the evolution of the membrane microstructure (Fig. 3) during secondary growth [16]. Under the synthesis conditions used in the study, film growth proceeds from a relatively smooth layer of small (~ 100 nm) zeolite crystals. At low growth times, the (101) crystal plane facets (observed on the surface of thick, [001]-oriented MFI films) are not pronounced and the film surface has low roughness. Upon increasing the growth time, the membrane becomes strongly [001]-oriented with well-defined (101) facets on the surface [16], due to which the roughness increases. The roughness may also be influenced by the presence of deposited crystals or other debris on the surface. Though the NLS fits to the data are overall of good quality, the per-

centage residuals (Table 1) are moderately high. This may reflect the simplifying assumption of a perfectly non-absorbing zeolite film. In reality, some IR absorption may take place from weak lattice vibrational overtones or surface impurities. To achieve better fits, absorption effects should be taken into account, as discussed in more detail below.

Fig. 4 shows the effective refractive indices as a function of frequency, for the bare alumina substrate and the membrane samples A–D. In the case of the bare substrate, the refractive index of the porous alumina is calculated directly from the reflectance at any frequency (using Eq. (5)) without any fitted parameters. These calculated values are shown in Fig. 4, as well as the fit to a five-coefficient polynomial. In the case of the zeolite membrane samples, the fitted refractive index functions

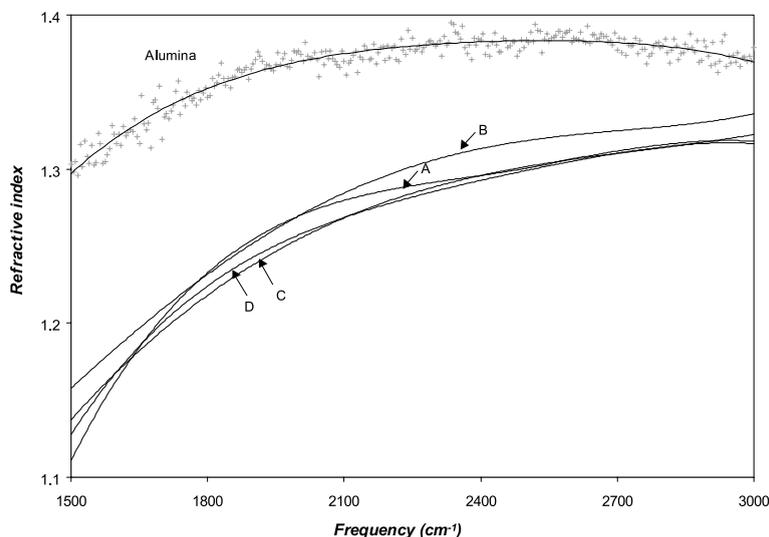


Fig. 4. Fitted refractive index functions (solid lines) of MFI membranes A–D shown in Fig. 3, and with properties tabulated in Table 1. The refractive index of the alumina substrate (+ symbols) is determined directly using Eq. (5), and is fitted (solid line) using Eq. (9).

are shown. There is a clear contrast between the refractive indices of the alumina substrate and the zeolite membranes. At the same time, there appears to be no significant difference between the refractive index functions of the various zeolite membrane samples. This is physically the expected behavior, as all the membrane samples A–D are made from the same zeolite material, MFI. The refractive indices of the zeolite membranes increase with increasing frequency in the present spectral region, as is expected for silica polymorphs [10].

As mentioned earlier, another membrane sample was measured before and after calcination, and also after loading with *p*-xylene. The refractive indices obtained from these fits are shown in Fig. 5. The empty microporous zeolite membrane has the lowest refractive index, whereas the uncalcined zeolite membrane, which contains four tetrapropylammonium (TPA) cations per unit cell [14], has a significantly higher refractive index. The refractive index increases further when the calcined membrane is loaded with *p*-xylene (to a loading of eight molecules per unit cell, as is known from crystallography [18,19] and adsorption measurements [20]). This behavior is qualitatively explained as being due to the filling of the empty

zeolite pores, leading to a denser material that has different optical properties from the empty zeolite. It is for similar reasons that the porous α -alumina substrate has a lower refractive index than bulk (dense) alumina, and zeolites have lower refractive indices than dense silica glass. Thus, the technique is sensitive to changes in the composition of the membrane, induced by organic species adsorbed/occluded in the pore space of the zeolite. It is suggested that this fact can be used to perform concentration profiling of molecules diffusing through zeolite membranes. The theory of optical reflection from inhomogeneous layers (i.e., layers having a refractive index that varies continuously with depth) is well-developed [11], since such layers are of importance in optical applications as spectral filters and anti-reflection coatings. A zeolite membrane which is under a concentration gradient of a diffusing species (such as *p*-xylene) is an optically inhomogeneous layer. In situ IR reflectance measurements during permeation under a concentration gradient, can be used to extract the refractive index profile of the membrane as a function of depth. On the other hand, reflectance measurements made at various equilibrium conditions (wherein the membrane is uniformly loaded with no concentration gradients, such as the

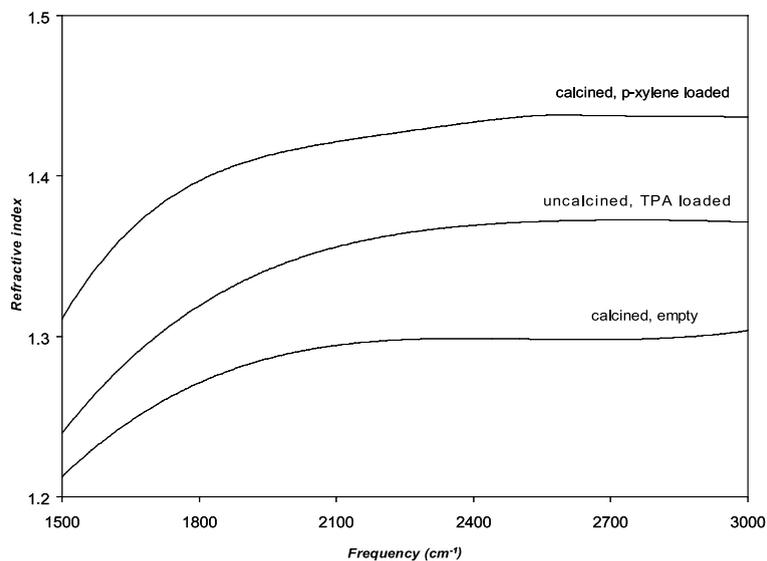


Fig. 5. Fitted refractive index functions for an uncalcined MFI membrane containing TPA cations (middle), the same membrane after calcination (bottom), and after loading with *p*-xylene (top).

p-xylene loaded membrane used in this study) give the dependence of the refractive index on the concentration. The two types of data can be used together to construct experimental concentration profiles of species diffusing through zeolite mem-

branes. The process is analogous in some respects to a concentration profiling technique such as neutron reflectometry, which however is not effective beyond depths of several hundred nanometers.

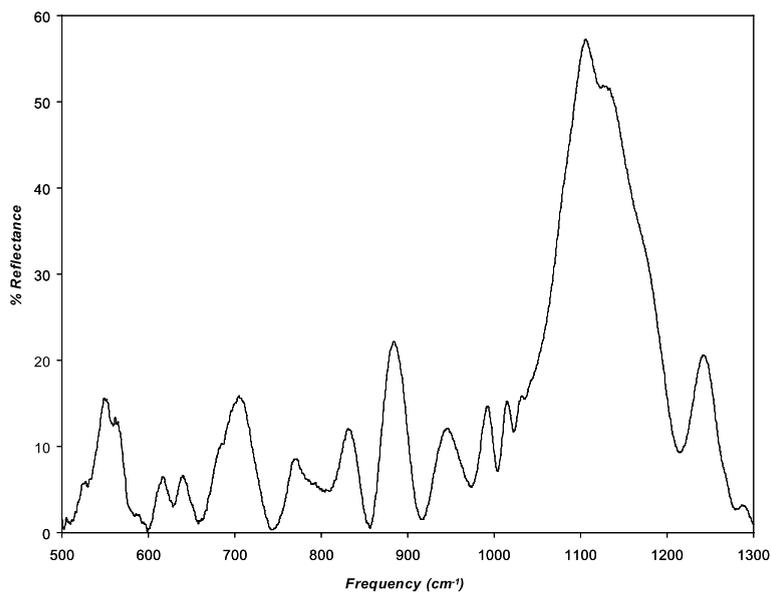


Fig. 6. Measured FTIR reflectance spectrum from an alumina-supported calcined zeolite MFI membrane in the IR-absorbing region.

Information describing dynamical processes in the membrane (such as structural changes induced by adsorption or calcination) can be obtained from the absorbing range of the IR spectrum, in particular by following changes in the frequencies, intensities, and widths of the IR absorption bands [9]. Fig. 6 shows the reflectance FTIR spectrum obtained from an MFI membrane in the absorbing frequency region. The spectra are quite complicated, representing both the IR absorption bands as well as the optical interference effects discussed in the present study. As a result, no reliable information on dynamical processes can be obtained without rigorous analysis of the reflectance data. The general theory for the reflectance of an IR-absorbing layered medium remains the same as presented in this study, but the refractive indices are now complex numbers. Previous studies have succeeded in fitting IR reflectance spectra from absorbing surfaces such as silica glasses and metals [9,21]. The generalization to layered media is a challenging aspect of research in this area. In the case of zeolite membranes, it can lead to more sophisticated methods of quantitatively probing membrane transport. Incorporation of the effects of crystal anisotropy can yield additional information, which can be extracted from FTIR measurements with polarized incident beams. Research along these lines is in progress in our laboratory.

5. Conclusions

A non-destructive method for extracting zeolite membrane characteristics from IR reflectance measurements has been introduced, based on the theory of optical reflection from a non-absorbing film. Parameters such as the membrane thickness, refractive index and surface roughness, have been extracted from IR reflectance spectra in the frequency range $1500\text{--}3000\text{ cm}^{-1}$ and the results compared with those of other characterization methods. In addition, the technique is shown to be sensitive to the presence of organic molecules adsorbed in the membrane.

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