Communications

Interferometric Study on the Adsorption-Dependent Refractive Index of Silicalite Thin Films Grown on Optical Fibers

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In the past two decades, various types of zeolite films have been coated on different electrical sensor devices to function primarily as semipermeable barriers or selective adsorbing overcoats for improving the detection sensitivity and selectivity.[1−8] Some pioneering research works have also revealed that the optical properties of zeolite crystals, for example, refractive index and Raman spectra, change dramatically upon loading and unloading guest molecules in the zeolitic pores.[9] In principle, such adsorption-induced changes in optical properties of zeolites can be used for chemical sensing with high sensitivity.

Recently, we have successfully fabricated a new type of optical chemical microsensors by directly growing dense MFI zeolite thin films (∼4 μm thick) on the cleaved endfaces of regular communication optical fibers.[10] Illuminated by a laser diode, the light power reflected from the zeolite-coated fiber was found to change monotonically and reversibly with the variation of 2-propanol concentrations in gas and liquid phases.[10,11] The sensor outputs exhibited clear correlations with the 2-propanol concentration appropriate for quantitative analysis. The zeolite-coated fiber chemical sensors offer the advantages of small size, immunity to electromagnetic interference, passivity and intrinsic safety, remote operation capability, and robustness for in situ monitoring in hostile environments.

However, the optimum design of the zeolite−fiber device requires in-depth knowledge of the adsorption-dependent refractive index of zeolite. Unfortunately, as a result of the polycrystalline nature of the films and current lack of suitable optical models, it is rather challenging to measure the refractive index of zeolite thin films. Striebel et al.[12] used a microcrystal prism method to measure the wavelength-dependent refractive index of A1PO4-5 zeolite single crystals in the UV/vis region. A large birefringence was observed when the zeolite was loaded with *p*-nitrodimethylaniline (PNDMA). Bjorklund et al.[13] reported adsorption-induced refractive index changes for silicalite thin films determined by spectroscopic ellipsometry in a wavelength range of 250−1000 nm. However, quantitative data of the refractive index was not reported because of the uncertainty about the optical model of the zeolite film. Nair et al.[14] measured the refractive index of MFI zeolite thin films coated on polished porous α-alumina substrates by analyzing the reflectance Fourier transform infrared spectra in the nonabsorbing region from 1500 to 3000 cm^{-1}. The authors found that adsorption of *p*-xylene caused a significant increase in the refractive index of the zeolite thin films.

So far, there have been no quantitative studies reported on the zeolite refractive index and its adsorption-dependency in the near-IR region (∼1550 nm). Information on the refractive index in the near-IR region is of great interest to the sensor community because a number of photonic devices, including light sources, detectors, and fiber devices, already exist in this wavelength range for developing in situ fiber optic chemical sensors.

In this study, dense silicalite thin films were grown on the cleaved optical fiber endface by in situ crystallization in a clear synthesis solution obtained by mixing 30 mL of H_2O, 5.65 mL (1 M) of tetrapropylammonium hydroxide (TPAOH), and 10.2 mL of tetraethyl orthosilicate. The optical fiber was single mode with a 125-μm-diameter cladding and a 9-μm-diameter core (Corning SMF28). Figure 1 shows the scanning electron microscopy (SEM) images of the dense silicalite film on the fiber tip. The thickness of the zeolite layer was ∼10 μm by SEM measurement. This zeolite−fiber integrated microdevice was used to study the change of the refractive index of the zeolite film when adsorbed with 2-propanol. The apparatus for optical experiments is shown schematically in Figure 2.

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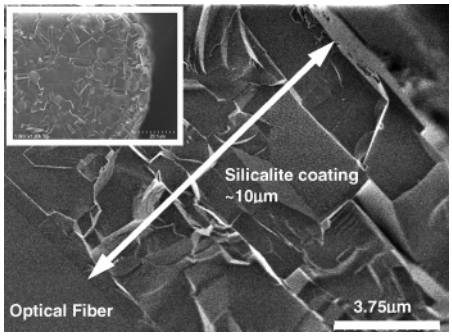

Figure 1. Cross section (fracture) SEM image of the zeolite-coated fiber. Inset: SEM image of zeolite-coated fiber endface.

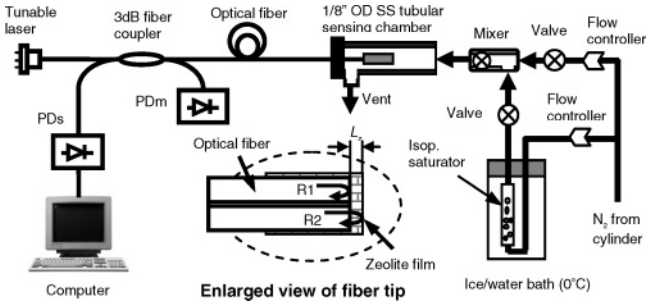

Figure 2. Schematic diagram of the experimental apparatus for optical refractive index measurements.

The zeolite-coated fiber was placed in a chamber made of a 1/8 in. o.d. stainless steel tube. The 2-propanol vapor carried by pure nitrogen gas flowed through the tube to contact the zeolite-coated fiber tip. The 2-propanol concentration (C_{ip}) in the gas flow was varied to study the adsorption dependence of the optical properties of the zeolite film. The optical reflections from the fiber/zeolite (R1) and zeolite/gas (R2) interfaces (enlarged view in Figure 2) interfered to generate the signal, which was detected by an optical power sensor (PDs). The interference spectra for the silicalite film were obtained by scanning the tunable laser in a wavelength range of 1520−1640 nm. An additional power sensor (PDm) was used to compensate for the power variation of the tun able laser during wavelength tuning in real time. All tests were conducted at 22 °C and atmospheric pressure (0.87 bar).

The spectral interferograms of the silicalite film in contact with gases of different 2-propanol concentrations are shown in Figure 3. The sinusoidal spectral interferograms indicated high quality interference signals generated by the silicalite film. The amplitude of the interferogram decreased as C_{ip} increased, indicating an increase in the refractive index of the silicalite film (n_z). The spectral positions of the interference maxima and minima shifted toward longer wavelengths when increasing C_{ip}, indicating an increase in the optical thickness ($L_z n_z$) of the silicalite film. The n_z value was calculated from the maximum (S_{max}) and minimum (S_{min}) intensities of the interferogram using the equation

$$n_z = \frac{2 - (\sqrt{S_{max}} + \sqrt{S_{min}})}{2 + (\sqrt{S_{max}} + \sqrt{S_{min}})} n_f \qquad (1)$$

where the refractive index of the fiber ($n_f = 1.4682$) was provided by the manufacturer. The refractive index of

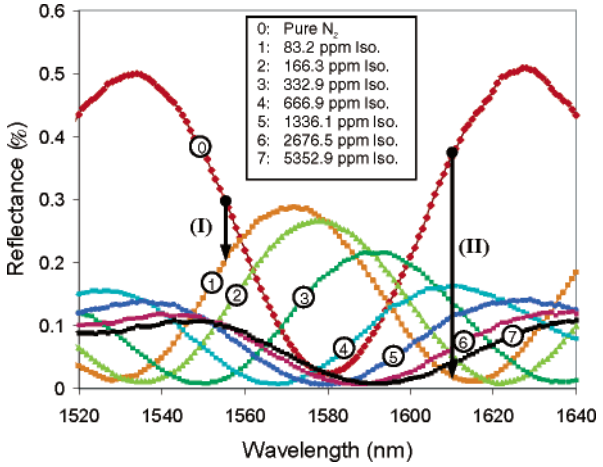

Figure 3. Spectral interferograms at various 2-propanol concentrations.

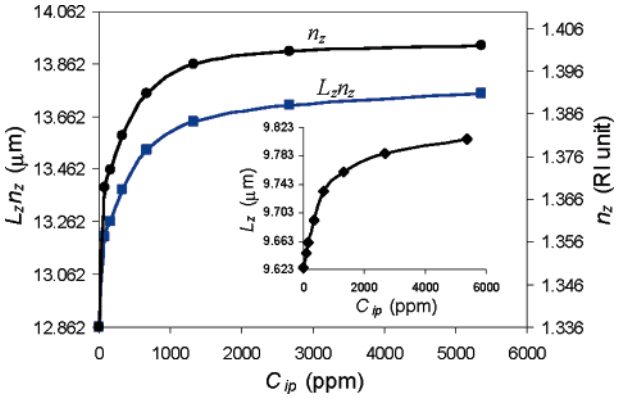

Figure 4. Optical thickness and refractive index as functions of 2-propanol concentration. Inset: effective physical thickness as a function of 2-propanol concentration.

silicalite film in pure N_2 was calculated to be 1.3361, which was in good agreement with the literature values.[14,15] The relationship between n_z and the 2-propanol concentration shown in Figure 4 is reminiscent of the type-I isotherm and suggests a deterministic dependence of n_z on the adsorption level.

The optical thickness of the zeolite film in pure N_2 ($L_{z,0}n_{z,0}$) was calculated to be 12.862 μm using the equation

$$L_{z,0}n_{z,0} = \frac{1}{4}\left(\frac{1}{1/\lambda_{max,0} - 1/\lambda_{min,0}}\right) \qquad (2)$$

where $\lambda_{max,0}$ and $\lambda_{min,0}$ are the spectral positions of the adjacent interference maximum and minimum, respectively.

The optical thickness ($L_{z,k}n_{z,k}$, $k = 0, 1, 2, ..., 7$) of the silicalite film at a specific $C_{ip,k}$ was calculated from the spectral shift of $\lambda_{min,k-1}$ to $\lambda_{min,k}$ using the following equation:

$$L_{z,k}n_{z,k} = \frac{\lambda_{min,k}}{\lambda_{min,k-1}} L_{z,k-1}n_{z,k-1} \qquad (3)$$

The optical thickness ($L_z n_z$) of the silicalite coating is also plotted in Figure 4 as a function of C_{ip}. The numerical values of Figure 4 are given in Supporting Information.

The inset of Figure 4 shows the physical thickness of the silicalite film ($L_z = (L_z n_z)/n_z$) as a function of C_{ip}. The

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calculated $L_{z,0}$ was 9.626 μm, which agreed well with the value estimated by SEM. The L_z increased with the 2-propanol sorption level in the zeolite as a result of the structure expansion upon adsorbing molecules. Expansion of the silicalite lattice structure upon sorption of 2-propanol was confirmed qualitatively by X-ray diffraction (XRD) examinations.

The adsorption dependence of the n_z and L_z of the silicalite film found in this study elaborates the principle of chemical sensing using the zeolite−fiber integrated microdevice in our previous work.[10,11] When interrogated with a fixed laser wavelength, the sensor signal (i.e., the reflected light power) depends on the initial film thickness ($L_{z,0}$) and the specific λ employed. For the zeolite−fiber device under study, the sensor response to a C_{ip} of 83.2 ppm was greater for the wavelength of 1610 nm (II) than that for 1555 nm (I) as indicated in Figure 3. Although the n_z and L_z changed monotonically with C_{ip}, monitoring the reflected power at a fixed wavelength did not provide monotonic correspondence between the reflected power and C_{ip} in the tested range. Therefore, quantitative measurement in a large concentration range may require monitoring n_z or ($L_z n_z$) of the silicalite film.

The results of this research not only enhance the fundamental understanding of the optical properties of zeolite thin films but also provide guidance to the development of zeolite−fiber microsensors for highly sensitive, in situ chemical detections. Such optical chemical sensors may find important applications in biochemical and energy processes, environmental management, and homeland security. With the knowledge of the quantitative relationship between the zeolite refractive index and the sorption level, the zeolite−fiber microdevice is also potentially useful for studying the molecular adsorption and diffusion behaviors in zeolites.

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Supporting Information Available: Material synthesis procedure, MFI lattice measurements by XRD, and optical interference model and calculations of optical length and refractive index. This material is available free of charge via the Internet at http://pubs.acs.org.

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