Selective Sensing of Alcohols in Water Influenced by Zeolite Coatings on Optical Fiber

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ABSTRACT

The application of a MFI type zeolite coating on the end of an optical fiber is presented. Zeolite coatings were directly grown on the freshly cleaved endface of optical fibers. It was found that the produced integrated zeolite-fiber sensors exhibit specific chemical sensitivity towards certain chemicals. The molecular adsorption induced change of zeolite refractive index was studied to understand the sensing mechanisms of the developed sensor system. This work can lead to a new class of portable zeolite thin film enabled miniaturized fiber optic sensors.

Keywords: Chemical Sensors, MFI type zeolite, thin films

1. INTRODUCTION

Low cost sensors, which are capable of rapid and sensitive response to trace chemicals have attracted much interest in recent years in applications such as environmental monitoring, biological analysis, industry process control, energy production and homeland security. Among them, optical fiber chemical sensors have shown the advantages of small size, immunity to electromagnetic interference, high sensitivity and fast response[1].

A promising strategy for adding chemical selectivity to optical fiber sensors is to coat a chemically selective optical material directly onto structured fiber surfaces. The coated functional material serves two purposes: to interact selectively with the ambient analyte that changes the material's optical properties, and to interact effectively with the light propagating inside the optical fiber to collect and transmit chemically induced optical responses[2, 3]. Zeolites are a class of aluminosilicate materials which have porosity, large surface area and sensitivity towards some chemicals. The effective pore sizes of zeolites vary from ~0.3 to 0.6 nm, depending on the crystal's structure. Thus zeolite materials are capable of discriminating low molecular weight chemicals by molecular sieving.

Therefore, there is promising progress in demonstrating the selectivity and performance of molecular selective materials such as zeolites for optical fiber chemical sensors. However, insight into how the material's optical property is altered by the uptake of chemical species is not well understood. In this paper, we provide some understanding of the link between material property upon the uptake of the well-studied species, ethanol and 2-propanol, to its optical property, which is subsequently used to detect these species. The well characterized material, MFI-type zeolite, was used as the chemically sensitive material.

2. EXPERIMENTAL METHODS

2.1 Membrane Synthesis

The zeolite was prepared at the end face of SMF-28 optical fiber (conventional Corning SMF-28, cladding diameter: 125.0 ± 0.7 μm, core diameter: 8.2 μm) under the hydrothermal reaction. Synthesis solution was: 5.65 mL of TPAOH

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(tetrapropyl ammonium hydroxide, 1.0M solution in water, Aldrich) as a directing agent to control and speed up the growth process, 10.2 mL of TEOS (tetraethyl orthosilicate, 98%, Sigma-Aldrich) and 30 mL of DDI water.

They were mixed together under constant stirring and heating at 50 ^{o}C for 3 hours. The optical fiber had its polymer coating removed several centimeters from the end using acetone and was cleaved by a diamond cutter perpendicular to its axis. The prepared optical fiber was guided into the correct orientation by fixing to a Teflon rod, and Teflon tape was wrapped over the remaining polymer coating to avoid contact with the solution. Each end face was orientated down or up to explore the orientation effect on growth. Growth was carried out at 180 ^{o}C for 4 to 17 hours, where increasing time leads to thicker coatings. Freshly coated sensors were washed with deionized water, dried at 80 ^{o}C for 2 hours then activated in air at 500 ^{o}C for 90 minutes to open the structure by removing the TPAOH growth template.

The coated optical fibers were dipped into different solutions of ethanol and iso-propanol. The concentrations were 10, 20,40,60,80 and 100% in DI water. Every measurement run for around 30 minutes and the intensity variation during time was recorded using Ando Optical Power Meter (Figure 3).

2.2 Membrane Characterization

SEM imaging

Scanning electron microscope (SEM) imaging was carried out using a JEOL JCM-5000 MXK37568 NeoScope Benchtop Scanning Electron Microscope at Victoria University.

XRD

XRD was carried out to measure the presence of the MFI structure on the end face of the optical fiber to confirm its material presence and function as a chemical sensor. This was done by a Panalytical X-Pert X-ray diffractometer at CSIRO.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images for the bare optical fiber and zeolite coated optical fibers, prepared at different orientation and growth times. As can be seen from the images there is a firm and homogenous coating at the end of optical fiber and there is no difference between the coatings obtained by downwards and upwards orientation.

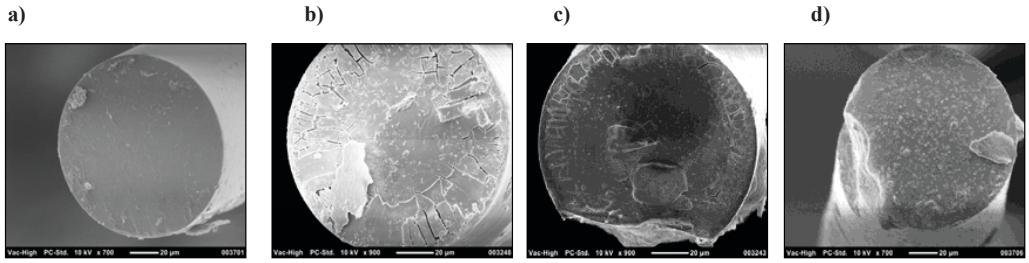

Figure 1. SEM imaging of optical fibers. a) Bare optical fiber. b) After 4 hours in upwards direction. c) After 4 hours in downwards direction. d) After 17 hours of hydrothermal condition in upwards direction.

Most coatings appeared successful, but the 4 hour grown fiber orientated downwards exhibited some cracking around the edges. Cracking of the MFI zeolite films is due to irregular stresses that arise from a difference in the thermal expansion between the support and the silicalite crystals and from removal of volatile materials from the zeolite framework. Therefore, the cracks are easily formed within the membrane during the treatment process (Figure 1b). These edge effects did not appear to reach the 8 μm diameter core of the optical fiber.

XRD results for the coated end face are shown in Figure 2. For comparison, the well characterized pattern of MFI is also presented. Here we see the most intense Bragg peaks at 7.9^{o} and 8.8^{o} 2-Theta (attributed to 101 and 200) that are

characteristics of the MFI structure. Therefore, we confirm the presence of a functional MFI zeolite coating on the optical fiber end face.

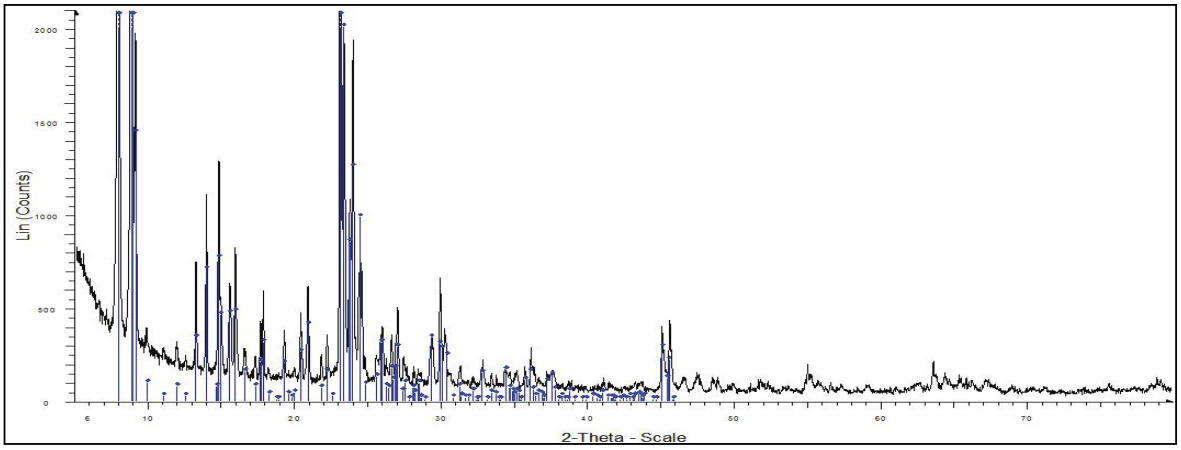

Figure 2: XRD result of the coating on the optical fiber end face. Typical pattern of MFI also shown (blue lines).

The performance of the three sensors is shown in Figure 3 as a function of increasing 2-propanol and ethanol concentrations in water. For the 4- and 17- hour grown zeolites, there is decreasing trend in intensity over increasing the 2-propanol concentration in water. This effect is strongest for the 4- hour grown zeolite. The 17- hour grown zeolite showed a very weak trend as 2-propanol concentration increases. There is no significant change in intensity for increasing ethanol concentration in water for the 4- hour grown zeolite.

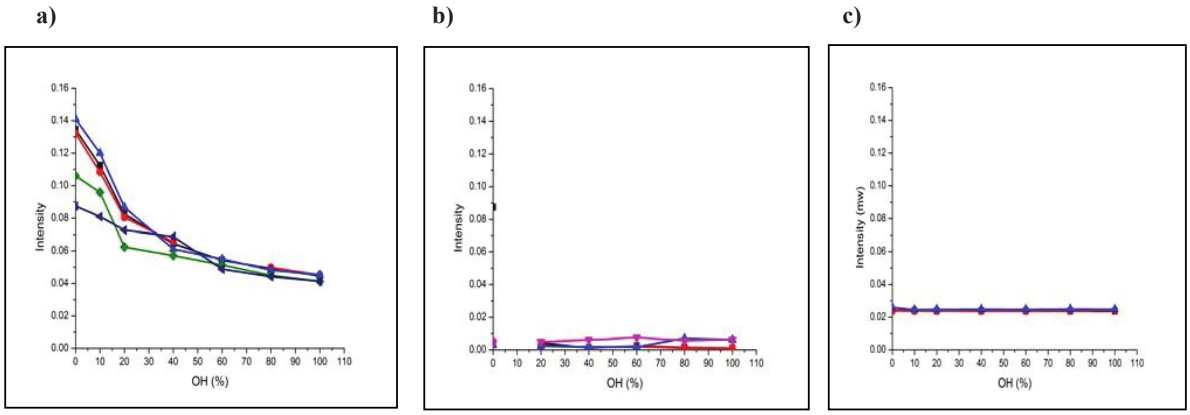

Figure 3: Performance of MFI zeolite coated optical fiber sensors: a) 4-hours sensor for 2-propanol, b) 4-hours sensor for ethanol, c) 17-hours sensor for 2-propanol

The result is interesting because there is no difference in RI between zeolites which grow over different times, because all are made of zeolite. However the thickness of the zeolite after 17 hours of hydrothermal reaction is the greatest and clearly reduces the effectiveness of the sensor despite being made of the same material. Therefore the effect of thickness on intensity overrides the effect of altered density (impacting intensity).

We understand that RI increases when the zeolite becomes loaded with 2-propanol. The filling of the empty zeolite pores, leads to a denser material that in turn reduces the intensity of the returned light[4, 5, 6] following the simple Fresnel reflection equation $R=(n_2 - n_1)^2/(n_2 + n_1)^2$. Assuming a constant physical thickness, for an increase in the alcohol concentration, the intensity of the reflected light decreases which is due to increasing the RI of the zeolite (guest

molecules from surrounding environment can enter the pores of zeolites). Upon absorbing these molecules, the density of zeolite will increase and as a result zeolite's RI will change and it will be detected by optical fiber.

The effect of organics within zeolites is well studied as continuously diffusing membrane films. Zeolite membranes have been extensively researched for many industrial separations via gas permeation and liquid pervaporation processes. General separation mechanisms in zeolite membranes include molecular sieving and competitive adsorption and diffusion. MFI zeolite has an effective intracrystal nanopore diameter of 0.51 nm which is smaller than the sizes of hydrates ions involved in current systems. As a result, complete rejection of hydrated ions can occur by using MFI zeolite membranes.

If the aluminum is not added during the synthesis process, the zeolite pore structure becomes completely hydrophobic, with an infinite Si/Al ratio. As a result, a significant pressure (> 40 MPa) is required to force water into the pores. Therefore, it is expected that water will only be adsorbed on the surface of these types of MFI zeolites (density of water inside the pores: 0.433 g/cm^3), and so an energy barrier exists which restricts water from entering into the zeolite pores.

Adsorption is another important parameter in permeation because molecules move through zeolite pores by surface diffusion. The organic molecules adsorb more strongly than water within pure silica MFI zeolite (silicalite). The heats of adsorption for the alcohols increase with the number of carbons due to increased van der waals interactions. This suggest that -ΔH of 2-propanol is greater than that of ethanol (-ΔH for ethanol: 70±10 kJ/mol and -ΔH for 2-propanol: 90±10 kJ/mol). And the separation factor for the alcohols increase with increasing -ΔH of the alcohols. Considering the observed higher selectivity of 2-propanol in water to ethanol in water, it seems the likely explanation that ethanol more strongly penetrated into the zeolite, yielding a more reduced intensity at the lowest concentration of 10%. Due to the inherent ability of MFI to resist 2-propanol compared to ethanol, we observed a weaker reduction in intensity, but was more sensitive to increasing concentration up to 100%.

4. CONCLUSION

An end face coated optical fiber sensor to detect trace organics in water has been presented. Results show that zeolite coated optical fiber had strongly responded to ethanol than 2-propanol and increasing growth time which lead to high membrane thickness had a negative effect on sensor response. Further work in this area will be coating the optical fiber by other types of functional materials and also by adding selectivity to zeolite coating to selectively detect other types of contaminants in drinking water for online quality monitoring.

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