MFI-type zeolite functional liquid phase sensor coated on the optical fiber end-face

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ABSTRACT

Optical fibers are a unique medium to coat with functional sensor materials that change in refractive index upon adsorption/interaction with specific compounds. In this work, we demonstrate a simple technique to coat the end face of an optical fiber with the microporous MFI-type zeolite. The exposure of the zeolite films from air to water or to aqueous solutions of ethanol and isopropanol causes a distinct change in the film's refractive index. This change was then detected using a simple fiber optic refractive index sensor by monitoring the signal intensity reflected back from the coated fiber endface and as the zeolite is transferred between air, water and solutions containing ethanol and isopropanol. The zeolite coating was developed using the in-situ templated growth technique to grow the zeolite crystals on the cleaved endface of an optical fiber. Effective coating was achieved when the fiber was oriented horizontally in the hydrothermal reactor. The zeolite coated end face reflected less energy in water, at 0.0201 μW, and exhibited almost no change (~2% increase) with increasing ethanol concentration, but exhibited a 135% increase in reflected energy, i.e. 0.048 μW, in 100% ethanol. The zeolite therefore gave the sensor alcohol selectivity. Further work is exploring applicability for liquid phase chemical and water quality analysis.

Keywords: Optical fiber, zeolite, chemical sensing, water quality sensing.

1. INTRODUCTION

1.1 The functional capacity of zeolites

The ability to measure chemicals and trace organic compounds in real-time is of significant interest for chemical and water industries. Of these, a priority area is the monitoring of toxic compounds in natural waterways and industry waste effluents. It is well known that zeolites can adsorb these compounds and thus can be used for remediation purposes, and researchers have adapted this capacity with the ability to catalytically react these compounds to make a dual function advanced material[1,2].

1.2 Adapting zeolitic frameworks for optical sensing

Zeolites are viable candidates for capturing small organic molecules because of their small cage size, which selectively adsorbs small organic species, whilst blocking molecules larger than 1nm. Upon the capture of certain organics, their properties change, including their refractive index. This enables the capacity to detect the adsorbed substance by measuring the optical properties before and after adsorption. So a zeolite coated at the interface of an optical fiber can therefore send a response to a detector to measure the change in zeolite's property.

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This concept has been demonstrated on the end face[3] and the more advanced long period fiber Bragg grating (LPFG) based sensing scheme [4] for the detection of organic vapors (isopropanol and toluene) in nitrogen gas or air. In this work, MFI-type zeolite structures were grown on the optical fibres as this framework is well known and easily produced in the laboratory. It also has a suitable structure to capture organic substances.

The concept of this sensor for the case of end-face coated optical fibers is shown in Figure 1. The sensitivity was estimated at ppb levels and thus validated the concept of the zeolite coated optical fiber sensor.

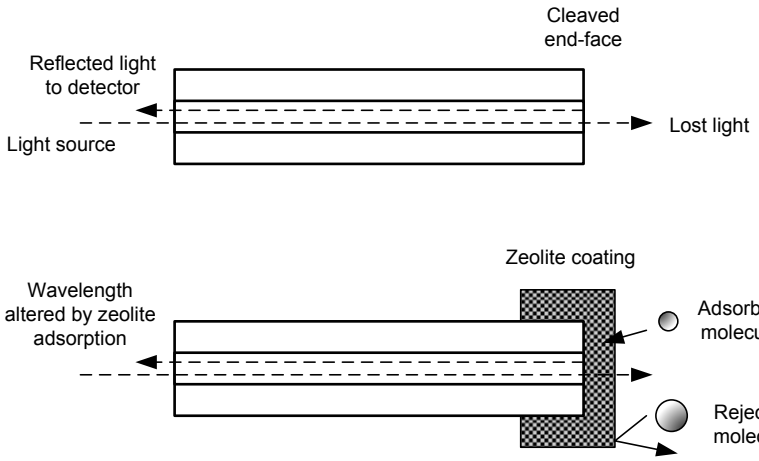

Figure 1. Concept of the end-face zeolite coated optical fiber. Top image shows the effect of light reflection at the end-face which is responsive to changes in refractive index at the surface. When the zeolite is coated at this interface, its change in refractive index upon selective adsorption of the desired compound is detected by change in wavelength.

1.3 Purpose of this work

Work to date has explored the operation of this type of sensor in the gas phase, but not the liquid phase, which has potential for chemical analysis and water quality monitoring. In this work, we present a low cost and simple optical method for detecting chemicals in liquid environments. It is based on the change of refractive index of zeolite thin films coated on the end face of optical fibers as they become exposed to water and to the presence of the model organics, ethanol and isopropanol.

2. METHODOLOGY

2.1 Zeolite formation method and coating procedure

The MFI-type zeolite coatings were prepared on the surface of SMF28 optical fiber using the in-situ growth method which uses an organic templating agent, tetrapropyl ammonium hydroxide (TPAOH) to control the growth of the zeolite under hydrothermal conditions. A similar procedure in literature was adopted to produce the zeolite synthesis solution, which was found to be effective in coating optical fibers [3]. In particular, this method does not use NaOH which we have found dissolved the glass fibers during hydrothermal conditions. In our method, we mixed together 5.65 mL of 1M TPAOH (Aldrich), 10.2mL of tetraethyl orthosilicate (TEOS - Aldrich) and 30mL of deionised water together under constant stirring and heated to 50°C for 3 hours.

To grow the zeolite on the fiber under hydrothermal condition, we used a 30cm glass autoclave to prevent the fiber from breaking under the hydrothermal conditions. A length of optical fiber was prepared with the protective polymer coating removed several cm from the end with the assistance of acetone. The fiber was then mechanically cleaved using a diamond cutting tool. Teflon tape was wrapped around the remaining plastic coating and the fiber length placed into the

reactor such that the end either faced horizontally or downwards to assess the effect of orientation on coating. Growth was carried out at 180°C for 4 hours, and the ends of the fibers were calcined at 500°C in air for 90 minutes.

2.2 SEM analysis

SEM imaging was carried out to visualize the coated optical fibers to assess the integrity of the zeolite layer and identify the presence of zeolite crystals. The SEM used was a JEOL JCM-5000 MXK37568 NeoScope Benchtop Scanning Electron Microscope. Samples were first sputter coated with gold using a JEOL MXK37652 Neocoater prior to the analysis.

2.3 Sensor measurement

Figure 2 illustrates a schematic representation of the optical characterization system that was deployed to test the sensing characteristics of the fiber sensor head. It consists of a simple 2x2 optical fiber coupler configuration where information about the sensor head is retrieved by monitoring the intensity levels of the back reflected signal from one of the ends of the fiber coupler. Light from a pigtailed erbium ESA source (1550 nm) is launched through one of the arms (ARM 1) of the fiber coupler and it splits into two equal parts. One of the receiving ends (ARM 3) is angled cleaved and subsequently immersed in index matching liquid to eliminate any possible back reflections interfering with the measuring signal. The other arm (ARM 4) is fusion spliced to the sensor head, while the coupler output (ARM 2) is connected to an optical power meter. A small portion of the transmitted light to the sensing arm will be reflected back from the zeolite coated fiber end towards the power meter. The intensity of the back reflected signal is dependent on the refractive index difference between the fiber core and its surrounding medium – in this case the zeolite layer. The fibre ends were tested for signal output in air, and also when immersed in solutions of with varying concentration of absolute ethanol and isopropanol in deionised water.

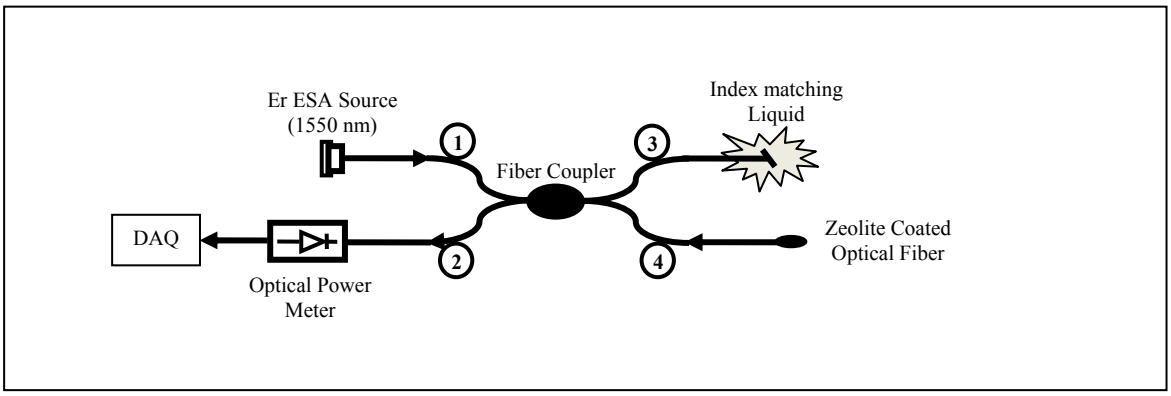

Figure 2. schematic representation of the optical characterization system.

3. RESULTS AND DISCUSSION

3.1 SEM analysis

Figure 3 shows the SEM images taken of the ends of the fiber facing downwards (left) and horizontally (right) in the autoclave. We see that for the downward facing sensor, that the surface was smooth and a small chip was present at the top. This is likely due to the diamond cleaving tool and thus we conclude that zeolite did not grow on the end face of this fiber. On the other hand, in horizontal orientation, we see that the end was covered by an intact coating of randomly orientated zeolite crystals. Both sensors were used in the analysis, but the downward facing sensor was considered to be uncoated.

Interestingly, Xiao and co-workers found that facing down in the autoclave was effective for making a zeolite coated optical fiber end face[3]. In their work, the SEM images showed a thinner zeolite coating to ours which is most likely due

to this orientation. Although we didn't observe any crystal growth on our downward facing fiber, our horizontal facing fiber may have collected precipitate falling downwards. So in our work, we conclude that our horizontal facing fiber had a thicker coating which contained zeolite crystals, but thinner coatings are achievable if the crystal nucleation and growth conditions as suitable to allow for growth when face is pointing downwards.

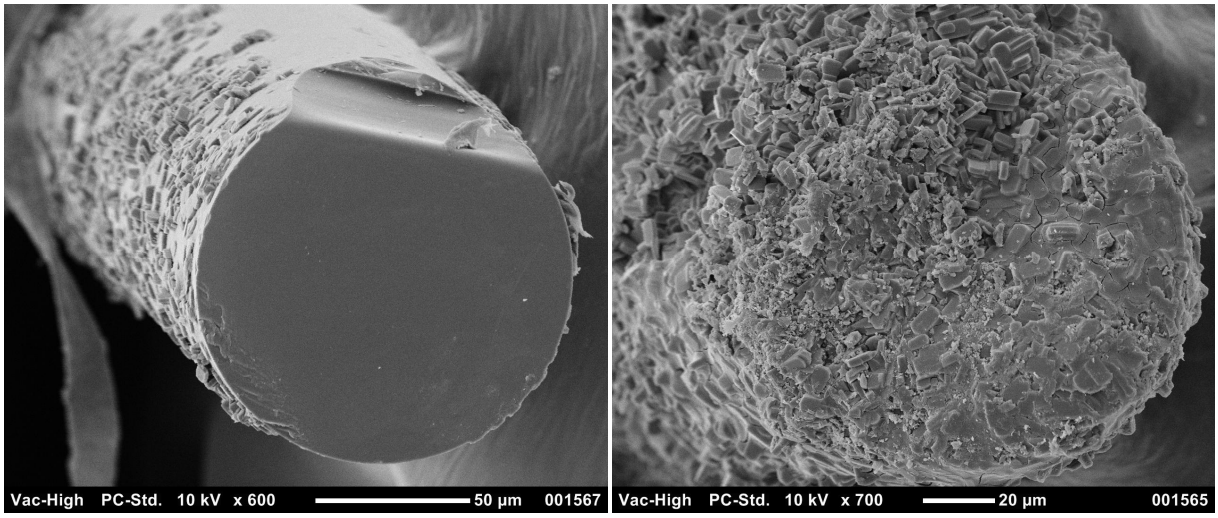

Figure 3. SEM images of the zeolite coated optical fiber end-faces for fibers facing down (left) and horizontal (right) in the autoclave.

3.2 Sensor performance

The performance of the two sensors is shown in Figure 4 for the fibers facing downwards (left) and horizontally (right) during hydrothermal growth. For the uncoated sensor (left), we see a similar trend in decreasing sensor output as a function of increasing alcohol concentration. This is attributed to the increasing refractive index of the solution with rising alcohol concentration. Differences were observed in the sensor signal especially when concentrations where larger than 5%. At 50%, ethanol adsorbed more light than isopropanol, but this appeared to reverse in pure alcohol. Despite these differences, we can say that ethanol had a stronger effect on sensor output than isopropanol, but both substances influenced the sensor output.

However in the case of the zeolite coated end-face (Figure 4, right), we see a very different trend. First, the sensor signal in pure water (alcohol concentration = 0%) was 2.6% of the value for the uncoated end face. Clearly, the zeolite had an effect in adsorbing more light than the uncoated end face. Then as alcohol concentration increased, we see that sensor signal was mostly independent of ethanol concentration (increased by 2.2% over full range). On the other hand, the sensor output responded strongly to increasing isopropanol concentration.

The increase in output was linear up to 10%. This trend did not continue, where sensor output rose to 0.048 µW at 100% isopropanol (136% increase over full range). Regardless, it appears that the zeolite coating gave the sensor an isopropanol selectivity over ethanol. Ethanol and isopropanol are commonly separated by MFI-type zeolite membranes by pervaporation, where water selectivity over the alcohols is preferred in order to dehydrate them[5,6,7]. In this work by Soydaş et al, and by Sano et al, ethanol is permeated in favor of water compared to isopropanol and water in MFI-type zeolite membrane[5,7]. In the presence of water, isopropanol competes with space in the zeolite, displacing the water and yielding preference to the alcohol. For ethanol, the same effect occurs, but to a much lesser extent than isopropanol[5]. So relating this to our findings, it seems a likely explanation that isopropanol entered the zeolite and displaced far more water than the case of ethanol and this lead to the change in refractive index. Interestingly, the effect for ethanol was so much lower that its effect to the zeolite was almost negligible.

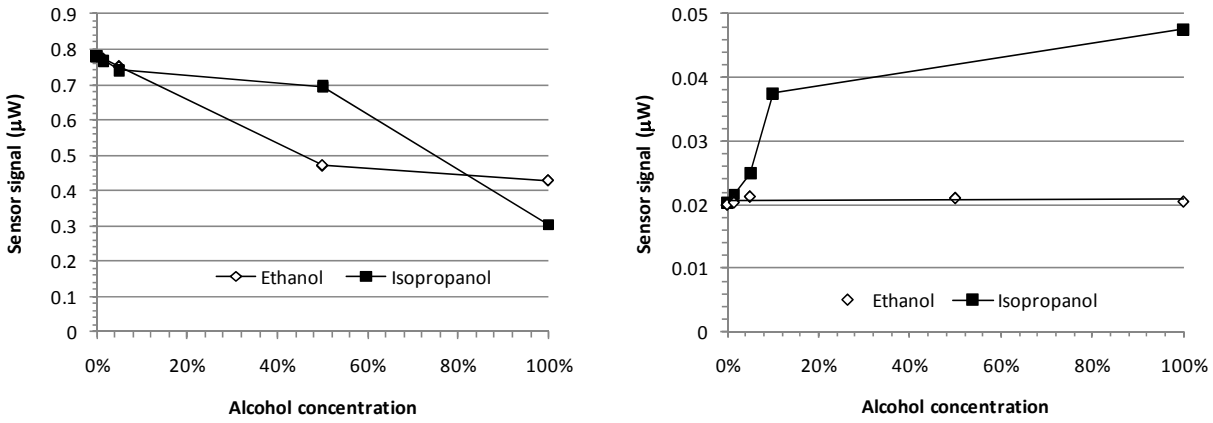

Figure 4. Sensor signal output for the optical fiber end face with varying alcohol content in solution with no coating (left) and MFI-type zeolite coating (right).

The dynamic trend of the zeolite coated sensor is shown in Figure 5. A stronger signal was detected in the presence of air compared to water, which corresponded to the decreasing refractive index of air over water. However upon the increase of isopropanol, we saw the sensor output rise, which might be due to its water displacing nature as mentioned above. This came about with a rise in the sensor output when returned to air, indicating a possibility that there was less water in the zeolite due to this, and also less alcohol as this is more volatile.

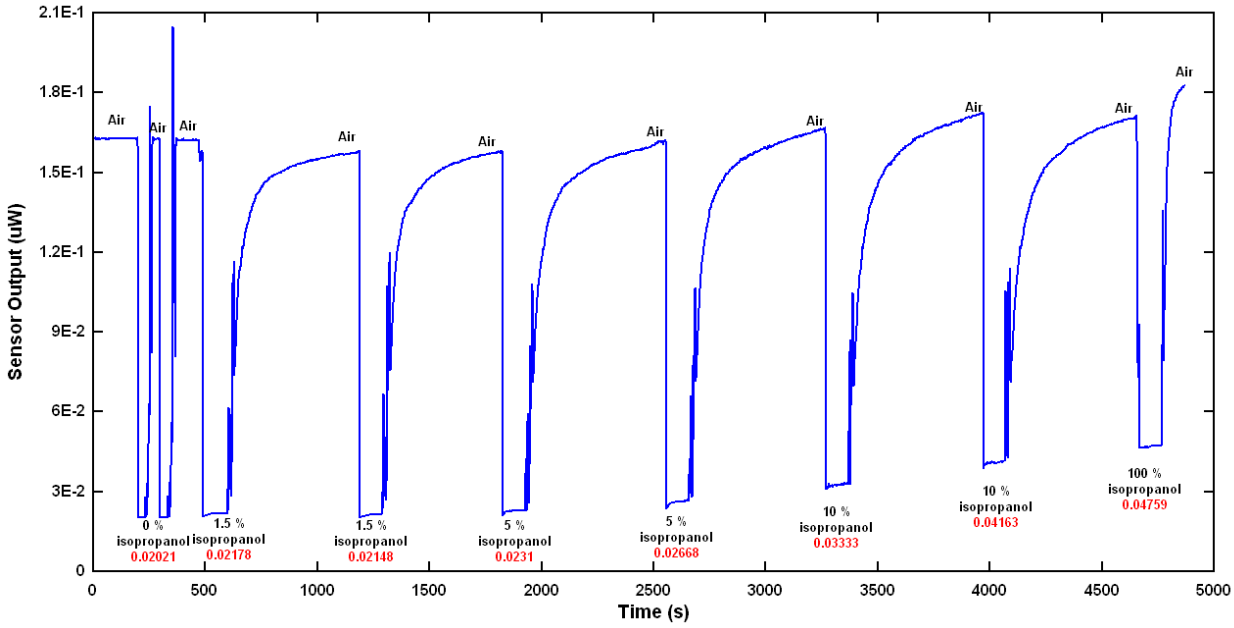

Figure 5. Dynamic trend of sensor output with repeated cycles of the sensor in air and immersion in liquid.

The results of the sensor outputs are summarized in Table 1. Here we see that no coating leads to much larger sensor outputs compared to when the zeolite is present, even in air, where although the zeolite is coated onto the fiber, it is likely to adsorb more energy due to its material, as well as the presence of adsorbed water.

Further work in this area is to continue to optimize the coating process to make uniform zeolite coatings on the end face of optical fibers, and even explore fiber grating based sensors for improved sensitivity. We also plan to expand the development of the materials, by modifying the material chemistry as a tool to improving features such as selectivity and sensitivity. Further, applications will be explored to monitor trace organic contaminants such as chlorinated hydrocarbons present in water supplies as a tool for online water quality monitoring. This work has thus formed the experimental platform to our further work in this area.

Table 1. Sensor output when exposed to air and immersed in either water or pure solutions of ethanol or isopropanol.

End face coating	Sensor output, air (μW)	Sensor output, water (μW)	Sensor output, ethanol (μW)	Sensor output, isopropanol (μW)
None	11.7	0.78	0.429	0.304
MFI-type zeolite	0.162	0.0201	0.0205	0.0476

4. CONCLUSIONS

In this work we demonstrated a simple means to prepare active zeolite coatings on the end-face of an optical fiber, and then test a unique liquid phase selectivity for sensing alcohols. Isopropanol was found to be selectively detected over ethanol, which aligned with well known alcohol separation performance of membrane made of the same materials. This has formed the basis for further work to explore key opportunities for liquid phase monitoring, for example in water quality applications.

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