

## Zeolite-Coated Optical Microfibers for Intrazeolite Photocatalysis Studied by in Situ Solid-State NMR

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The use of zeolites in photochemistry has attracted significant interest as they host a variety of organic transformations within their cavities and channels that often lead to product distributions considerably different from those in solution.<sup>1–4</sup> For example, Frei et al. used large-pore alkali or alkaline-earth zeolites to achieve the partial oxidation of small alkanes, olefins, and alkylbenzenes with unprecedented selectivity using visible light.<sup>5,6</sup> These reactions are conducted at ambient temperature and in the absence of solvent or photosensitizers. Important applications of hydrocarbon partial oxidation include the production of valuable products and the transformation of unwanted compounds into benign species.<sup>7,8</sup> Despite the high potential of the zeolites as a novel, solid reaction medium for photochemical transformations, there still remains a gap between our understanding of the mechanistic aspects of the zeolite-adsorbate photophysics and the remarkable specificity and selectivity observed.<sup>8</sup> Moreover, to scale-up the micromolar-quantity experiments, it is essential to improve upon the scattering of visible light by the zeolite matrix, the ability of reactants and products to diffuse through the catalyst bed, and the development of a continuous-flow reaction system.<sup>6</sup> Recently, we demonstrated<sup>9–11</sup> that in situ solid-state nuclear magnetic resonance (SSNMR) is useful to study the near-UV photooxidation reactions of organic molecules such as trichloroethylene (TCE) and ethanol and that it provides valuable information on the complex reaction chemistry at the surface of TiO<sub>2</sub> photocatalysts. SSNMR methods are advantageous as they allow an atom specific and quantitative examination of the reactions on the catalyst surface.<sup>12</sup> To overcome the inherent problem presented by light scattering and limitations due to the presence of dark regions within the interior of the material, we also reported the use of quartz optical microfibers as a TiO<sub>2</sub> photocatalyst support.<sup>13</sup> Although numerous literature is available on the deposition of zeolite crystallites on various substrates from a hydrothermal reaction gel, there are very few examples of three-dimensional objects that have been coated with films of pre-synthesized zeolites.<sup>14,15</sup> Among these is the approach reported by Bein et al.<sup>16,17</sup> in which silane-coupling agents are used to

coat various substrates such as gold electrodes or quartz crystals with zeolite–silica thin films. However, it remained a challenge to prepare a zeolite-coated substrate system that could decrease light scattering and would be robust enough to tolerate sample spinning at 3000 Hz during the SSNMR experiments. We report a new approach to the study of intrazeolite photochemistry which uses the combination of a novel zeolite-coated optical microfiber catalyst and in situ SSNMR. We demonstrate that the use of zeolite composite catalysts results in increased photoefficiency for selective oxidation reactions of chlorinated hydrocarbons such as TCE and methylene chloride.

Zeolite crystals were coated onto optical microfibers from a tetraethyl orthosilicate (TEOS) solution via the sol–gel process. An alcohol solution of TEOS was subjected to acid-catalyzed hydrolysis of the alkoxide groups into hydroxyl groups followed by a condensation reaction of these groups to form –Si–O–Si– linkages. In a typical procedure, the stock solution of the silica sol was prepared by adding 5 mL of TEOS and 5 mL of ethanol. A small amount of acid (about 0.5 mL of 0.04 M HCl) was added to the silica sol as a silicate oligomerization catalyst. Additional experiments were also carried out using 0.04 M HNO<sub>3</sub> (about 0.5 mL) and 5 M NH<sub>4</sub>OH (about 1.0 mL) as a base catalyst. The dip-coated zeolite–silica composite was prepared by adding 0.4 g of the cleaned and cut microfibers<sup>18</sup> (1.5 cm length) to a suspension of 0.5 g of BaY<sup>19</sup> zeolite in 1.0 mL of silica sol, which was then diluted with 15 mL of ethanol, and stirred for 1 h at 298 K. The coated fibers were then drained and dried in a vacuum oven at 343 K for 4 h to remove the solvent. The resulting silicate films converted to a gel by calcining at 753 K for 8 h in the presence of flowing air and locked into the particular configuration of zeolite crystals. The covalent bond between the native oxide surface of the optical fibers and the organosilicon compounds makes these films particularly robust.<sup>20</sup> The amount and nature of the composite zeolite–silica coating was controlled by varying the silica sol content, ethanol concentration, pH, and the zeolite content in the reactant gel. Figure 1 shows scanning electron micrograph (SEM) images of the quartz optical microfibers before (Figure 1a) and after (Figure 1b and c) coating with BaY zeolite.

In situ SSNMR experiments were performed on a 300 MHz Varian Unity Plus NMR spectrometer with a home-built double resonance magic angle spinning (MAS) probe. In a typical experiment, 60 mg of BaY zeolite-coated optical fibers were packed into a 5 mm glass NMR tube (Norell), which was then attached to a glass manifold. The catalyst sample was evacuated to  $2 \times 10^{-5}$  Torr at 403 K and then cooled to 298 K. Typically, 30  $\mu$ mol of <sup>13</sup>C-labeled TCE or CH<sub>2</sub>Cl<sub>2</sub> (Cambridge Isotope Laboratories) and 90  $\mu$ mol O<sub>2</sub> were introduced onto the zeolite sample using a liquid nitrogen trap. The NMR tube was then sealed above the catalyst sample. Light produced by a 300 W Xe arc lamp (ILC Technology) was filtered by a dichroic mirror (Oriol Corporation, 420–630 nm) and was delivered evenly over the spinning sample via a liquid light guide.<sup>10</sup>

<sup>13</sup>C MAS NMR results for the in situ photocatalytic oxidation of TCE and CH<sub>2</sub>Cl<sub>2</sub> are presented in Figure 2. The narrow line widths of the peaks indicate that TCE (Figure 2a) and the photooxidized products (Figure 2b) are quite mobile. The spectra indicate 78% degradation of TCE after 100 min and the

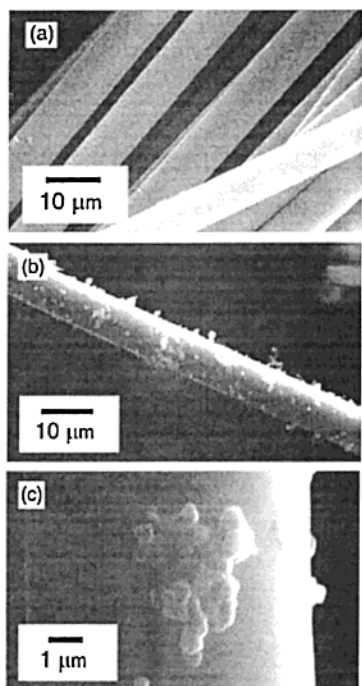
\* Corresponding author.

- (1) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219.
- (2) Ramamurthy, V.; Lakshminarasimhan, P.; Grey, C. P.; Johnston, L. J. *Chem. Commun.* **1998**, 2412.
- (3) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321.
- (4) Xiang, Y.; Larsen, S. C.; Grassian, V. H. *J. Am. Chem. Soc.* **1999**, *121*, 5063.
- (5) Blatter, F.; Vasenkov, S.; Frei, H. *Catal. Today* **1998**, *41*, 297.
- (6) Frei, H.; Blatter, F.; Sun, H. *CHEMTECH* **1996**, *24*.
- (7) Sheldon, R. A., van Santen, R. A., Eds. In *Catalytic Oxidation, Principle and Applications*; World Scientific Publishing: Singapore, 1995.
- (8) Centi, G.; Misono, M. *Catal. Today* **1998**, *41*, 287.
- (9) Hwang, S.-J.; Petucci, C.; Raftery, D. *J. Am. Chem. Soc.* **1997**, *119*, 7877.
- (10) Hwang, S.-J.; Petucci, C.; Raftery, D. *J. Am. Chem. Soc.* **1998**, *120*, 4388.
- (11) Hwang, S.-J.; Raftery, D. *Catal. Today* **1999**, 1579.
- (12) See, for example, Haw, J. F.; Xu, T. *Adv. Catal.* **1998**, *42*, 115 and references therein.
- (13) Rice, C. V.; Raftery, D. *Chem Commun.* **1999**, 895.
- (14) Bein, T. *Chem. Mater.* **1996**, *8*, 1636 and references therein.
- (15) Jansen, J. C. et al. *Microporous Mesoporous Mater.* **1998**, *21*, 213.
- (16) Bein, T.; Brown, K. J. *Am. Chem. Soc.* **1989**, *111*, 7640.
- (17) Kurth, D. G.; Bein, T. *J. Phys. Chem.* **1992**, *96*, 6707.

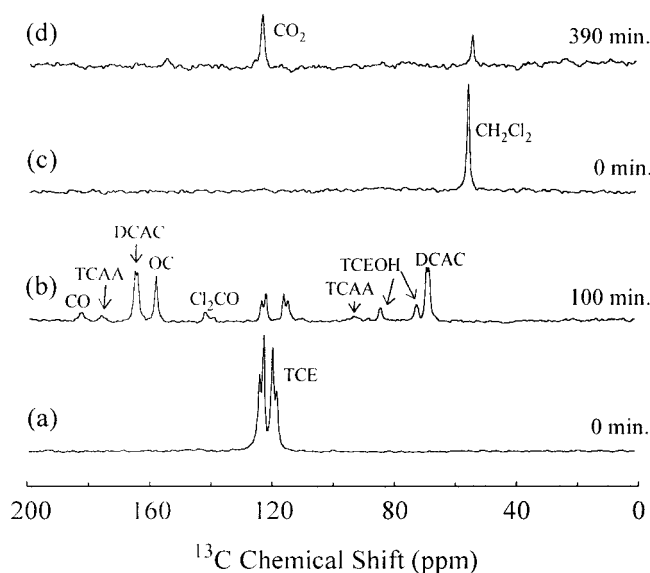
(18) The polyimide cladding present on the quartz microfibers (Quartzel Fibers; 9  $\mu$ m diameter) was removed first by calcination at 753 K for 8 h in the presence of flowing oxygen and by treatment with piranha solution (7:3 concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub>) at 363 K for 1 h.

(19) Zeolite BaY was prepared from NaY zeolite (Zeolyst International, CBV-100, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.1) by ion-exchange using a 0.5 N BaCl<sub>2</sub> solution (Alfa Aesar).

(20) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Ashley, C. S. *J. Non-Cryst. Solids* **1982**, *48*, 47.



**Figure 1.** SEM images of (a) bare quartz optical microfibers, (b) BaY zeolite-coated optical fibers, and (c) a magnified image of (b). The BET surface area of this composite catalyst was determined to be 140 m<sup>2</sup>/g.



**Figure 2.** Proton-decoupled <sup>13</sup>C MAS NMR spectra. (a) TCE and O<sub>2</sub> adsorbed on BaY-coated optical fibers before irradiation and (b) after irradiation with visible light for 100 min; (c) CH<sub>2</sub>Cl<sub>2</sub> and O<sub>2</sub> adsorbed on BaY-coated optical fibers and (d) after irradiation with visible light for 390 min.

formation of dichloroacetyl chloride (Cl<sub>2</sub>CHCOCl, DCAC, doublets at δ 69.3 and 164.5) and oxalyl chloride (ClCOCOCl, OC, δ 158.3) as major products. Additionally, minor products 1,1,2-trichloroethan-2-ol (Cl<sub>2</sub>CHCHClOH, TCEOH, doublets at δ 72.7 and 84.7), phosgene (CCl<sub>2</sub>O, adsorbed δ 142.4 and gas-phase δ 139.2), trichloroacetaldehyde (CCl<sub>3</sub>CHO, TCAA, doublet at δ 93.0 and 176.0), and carbon monoxide (CO, δ 182.6) were also formed. The reaction intermediate TCEOH was observed to be very unstable and was converted into TCAA during storage. The products observed over BaY-coated optical fibers in the presence of visible light is similar to that observed over semiconductor photocatalysts, such as TiO<sub>2</sub>, in the presence of UV irradiation.<sup>9,10</sup>

However, the significant concentration of oxalyl chloride suggests that the reaction mechanism may involve the formation of a hydroperoxide intermediate as proposed by Frei et al.<sup>6</sup> When the photocatalytic experiment was repeated using 40 mg BaY zeolite powder alone (i.e., without optical fibers) as the catalyst, a similar product distribution was observed; however, in situ irradiation with visible light resulted in only 34% degradation of TCE even after 533 min. The difference in the activity demonstrates the superior photocatalytic performance of the coated optical fibers versus the powder catalyst; moreover, the performance is even more significant, considering that the BaY zeolite constitutes less than 50% of the composite catalyst. After the reaction, the zeolite composite catalyst was regenerated,<sup>21</sup> and the catalytic activity was tested again. It was found that the catalyst could degrade 69% of TCE during the experiment. The restoration of catalytic activity (compared to 78% over the fresh catalyst) indicates that there is no significant loss of zeolite particles from the optical fibers while spinning during the SSNMR experiments or during the regeneration process. The robust nature of this catalyst will be important for future development of a continuous flow reactor system.

The intrazeolite photooxidation of CH<sub>2</sub>Cl<sub>2</sub> was also examined. The results in Figure 2c and d indicate 51% degradation of CH<sub>2</sub>Cl<sub>2</sub> (δ 54.8) after 390 min. CO<sub>2</sub> (δ 124.4) is observed as the major product of the photocatalysis. Control experiments using BaY zeolite powder as the catalyst (i.e., without optical fibers) showed that the initial rate of CH<sub>2</sub>Cl<sub>2</sub> degradation was roughly 20 times slower than that observed using the zeolite-coated optical fibers. This finding is significant as it suggests that compounds previously dismissed as unreactive with powder zeolites may react with coated optical fiber composite catalysts. Higher performance of the fiber catalyst can be attributed to a decrease in the light scattering due to the presence of a monolayer of zeolite particles supported on the transparent optical fibers. Moreover, loose packing of the optical fibers facilitates easy transport of reactants to the active sites and desorption of products, which significantly increases the activity of the catalyst system. In contrast to the zeolite-coated optical microfiber catalysts, the photooxidation of CH<sub>2</sub>Cl<sub>2</sub> using TiO<sub>2</sub> is less inefficient and requires high energy UV irradiation. Separate experiments were performed to measure the catalytic activity using acid (HNO<sub>3</sub>) and base (NH<sub>4</sub>OH) silicate oligomerization catalysts during the preparation of the zeolite fibers. These experiments showed that the catalytic activity of these optical fibers is comparable (within a factor of 2) to the HCl-prepared fiber catalysts. Further detailed experiments are planned to study the reaction kinetics and the possible effects of the acid or base used in the reaction gel on the photocatalytic activity of the composite catalysts.

In summary, we have demonstrated that pre-synthesized and ion-exchanged zeolites such as BaY can be coated on optical microfibers via a sol-gel process from TEOS. The use of zeolite-coated optical fibers reduces light scattering by the zeolite matrix, facilitates free transport of reactant and product molecules, and creates the possibility of transferring light photons to the active sites via optical fibers. It also significantly increases photocatalytic efficiency compared to bulk powders. Moreover, the use of zeolite-coated optical microfibers provides an efficient methodology to study zeolite photochemistry with SSNMR, which will be useful for a wide range of fundamental investigations.

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(21) After the reaction, the sealed NMR tube was broken open, and the zeolite composite catalyst was regenerated in the presence of O<sub>2</sub> at 753 K for 8 h. The fibers were repacked in the NMR tube, and the catalytic activity was tested following the procedure presented earlier.