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Photocatalytic oxidation of trichloroethylene using TiO_2 coated optical microfibers

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TiO_2 particles have been attached to optical microfibers to allow the irradiation of the interior of a powdered photocatalyst, and the UV initiated photocatalytic oxidation of trichloroethylene was followed using ^{13}C solid-state NMR.

The photocatalytic activity and surface chemistry of TiO_2 is currently of significant interest owing to its use in light harvesting[1] and pollutant remediation applications.[2] Much is known about TiO_2 photocatalysis at the liquid/solid interface whereas the gas/solid interface is less well understood.[3] A variety of experimental techniques have been applied to study the surface photochemistry of TiO_2, including GC–MS,[4] IR[5] and XPS.[6] We have shown that solid-state nuclear magnetic resonance (SSNMR) spectroscopy can provide information about the identity and nature of surface-bound and gas-phase species during *in situ* photocatalytic reactions.[7] Owing to the light scattering characteristics of TiO_2, it is best to disperse the catalyst as a thin film to expose the particles in a homogeneous fashion. However, the outer portions of TiO_2 powders packed inside the SSNMR rotor will either scatter or absorb most of the incoming photons and create dark regions within the interior of the sample. Reactants in these dark regions will not participate in the photochemical reaction, producing long-lived species and complicating the interpretation of results. Our laboratory has previously circumvented this problem by supporting monolayer TiO_2 films on porous Vycor glass. This reduces scattering and can be successfully used to follow the photoreactions with SSNMR.[7] Here, we report a different approach which allows UV light to penetrate the interior of a powdered sample and creates an opportunity to use SSNMR to study the photocatalytic surface chemistry on TiO_2 powders.

TiO_2 powders can be supported on glass plates,[8] rods,[9] beads,[10] meshes[11] and large diameter optical fibers.[12] However, these supports are impractical for use in SSNMR experiments. Thus, we utilized microscopic quartz optical fibers to deliver the UV photons to the interior of the sample. The optical microfibers can be tightly packed inside the SSNMR rotor and the incident photons can be directed towards either the ends of the fibers or perpendicular to their long axis. The photochemical behavior of the coated fibers was evaluated by monitoring the conversion of trichloroethylene (TCE), an important environmental contaminant, into several intermediates and final products.

The quartz microfibers (Quartzel Fiber®, 9 μm diameter, Quartz Products Company) were supplied as a roving with each strand composed of 4800 individual fibers. Approximately 20 sections of the roving (each 15 cm long) were placed in a test tube (2.5 cm OD, 30 cm long) and calcined at 400 °C to remove the polyimide cladding. The fibers were allowed to cool, bound together at one end with copper wire and dipped into an aqueous suspension of TiO_2 similar to that used by Nazeeruddin *et al.*[13] The suspension was prepared by adding 4 ml of water to 10 g of TiO_2 powder (Degussa P-25, surface area 55 $m^2 g^{-1}$, 70% anatase) in a ceramic mortar. A thick paste was formed by grinding the mixture and adding 800 μl of pentane-2,4-dione to promote dispersion of the particles. The paste was diluted by the slow addition of 16 ml of water while grinding. To allow the suspension to cover the fibers evenly, 200 μl of a detergent (Triton X-100, Aldrich) was added.

After dipping the fibers, they were heated at 500 °C for 30 min, cooled to room temperature and rinsed under flowing water to remove excess TiO_2. The dipcoating, heating, and rinsing procedure was repeated 2 additional times. It was found that the surface area of the coated fibers could be increased further by allowing the coated fibers to dry, then dipping them into a 20% solution of titanium isopropyl alcohol (Aldrich) in anhydrous isopropyl alcohol (Aldrich) and calcining at 500 °C for 3 h. After cooling, the fibers were rinsed a final time and dried. Assuming even coverage of the fibers, gravimetric analysis indicated that the TiO_2 layer is *ca.* 0.5 μm thick.

In a typical experiment, *ca.* 40 000 coated microfibers (estimated by weight) were gathered into a bundle and inserted into a Teflon tube (4.5 mm ID, Small Products Company). A 1 cm section of the fiber-filled tube was cut, held at the opening of a standard 5 mm NMR tube (Norell) and a glass rod used to push the fiber bundle into the bottom of the NMR tube. After attachment to a vacuum manifold, the fibers were calcined at 400 °C to remove any remaining organic material, cooled to room temperature and exposed to humid air for 12 h to rehydrate the surface. The NMR tube was reattached to the manifold and heated at 150 °C under vacuum (10^{-4} Torr) for 2 h to remove excess water. The tube was then cooled to 77 K for the addition of per-^{13}C trichloroethylene (Cambridge Isotopes) and oxygen. The sample was isolated from the manifold by flame sealing. The gas pressure of the reagents in the tube at room temperature is estimated to be 1–2 atm.

NMR analysis was performed on a 300 MHz Varian Unity Plus NMR spectrometer with a home built, double resonance optical magic angle spinning (MAS) probe which has been described previously.[7] A 300 W Xe arc lamp (ILC Technology) was used as the light source and a dichroic mirror (Oriel Corp.) was used to limit the light to 350–450 nm. Irradiation of the sample in the end-on configuration was performed outside the magnet while the side irradiation experiments were performed *in situ* as described previously.[7]

The proton decoupled ^{13}C MAS NMR spectra collected during the photocatalysis of 48 μmol of TCE in the presence of 96 μmol of O_2 are shown in Fig. 1. The sample was irradiated in the end-on configuration. Each spectrum represents an average of 256 transients obtained with a recycle time of 4 s. Spectra taken after various irradiation times show the formation and decomposition of reaction intermediates which have been identified by comparison with reported ^{13}C chemical shift data. As can be seen in the Fig. 1, dichloroacetyl chloride (DCAC, $Cl_2CHCOCl$, doublets at δ 70 and 167), dichloroacetic acid (Cl_2CHCO_2H, doublets at δ 63 and 167) oxalyl chloride (ClCOCOCl, δ 159), phosgene (CCl_2O, adsorbed, δ 143 and gas phase, δ 139), trichloroacetaldehyde (CCl_3CHO, doublets at δ 93 and 177) and carbon dioxide (δ 123) are formed during the reaction. The major products are phosgene and CO_2 with small quantities dichloroacetic acid and trichloroacetaldehyde remaining at the end of the reaction.

Although these results demonstrate the photocatalytic behavior of the coated optical fibers, the question as to whether the

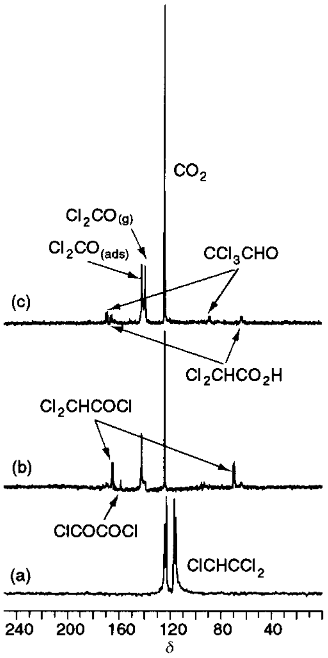

Fig. 1 Proton-decoupled ^{13}C MAS NMR spectra obtained during the photooxidation of 48 μmol of TCE and 96 μmol of O_2 on the TiO_2 coated optical fibers irradiated in the end-on configuration for (a) 0, (b) 30 and (c) 150 min. The spinning rate was 3 kHz.

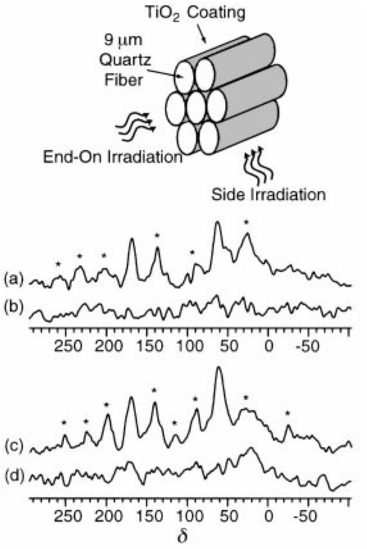

Fig. 2 ^{13}C proton-decoupled CP MAS spectra of chemisorbed dichloroacetate collected with ^1H–^{13}C cross polarization (contact time = 3 ms): (a) before end-on irradiation; (b) after end-on irradiation for 120 min; (c) before side irradiation; (d) after side irradiation for 150 min. The spinning rate was 3.0 kHz and asterisks denote spinning sidebands.

light is penetrating to the interior of the sample remained. This issue was explored by monitoring the formation and degradation of DCAC, which is known to chemisorb to the TiO_2 surface by reaction with hydroxyl groups to form dichloroacetate. The degradation of dichloroacetate requires additional UV photons, and thus its persistance under continued irradiation indicates the presence of dark regions within the sample.[7] In the case of the TiO_2-coated optical fibers, the concentration of dichloroacetate was maximized by stopping the photocatalysis of TCE after 30 min (when the DCAC concentration was highest) and storing the sample in the dark for several days to allow the DCAC to react with the surface hydroxyl groups. The sample was then broken open and evacuated to remove all non-surface bound species. Oxygen was reintroduced and the sample flame sealed. Fig. 2 shows the ^{13}C NMR spectrum taken using cross polarization (CP) and MAS conditions. Surface bound dichloroacetate has two isotropic peaks (δ 64 and 177) as well as a number of spinning sidebands. Subsequent irradiation of this sample in the end-on configuration shows the loss of the acetate signal [Fig. 2(b)] indicating that light is indeed reaching the interior of the sample. The experiment was repeated with the light directed towards the side of the sample and the degradation of the acetate [Fig. 2(c), (d)] was also observed, although the rate was slower. At this time, the mechanism for light transmission to the interior of the sample is not known. It is likely that the photons propagate down the microfibers, and that side irradiation is successful because the TiO_2 layer is not thick enough to absorb all of the photons.[14] Alternatively, it may be that the coated microfibers are able to create void spaces within the powder allowing the light to propagate between the particles which may also explain the success of side irradiation. Future experiments are planned to explore this issue further.

In summary, we have demonstrated that supporting TiO_2 powders on optical microfibers decreases light scattering, permitting study of the surface photochemistry with SSNMR. Efforts are currently underway to expand this methodology to other photochemical systems where light scattering is problematic, such as zeolite photochemistry.[15]

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Notes and references

1 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583; J. Hagen, W. Schaffrath, P. Otschik, R. Fink, A. Bacher, H. W. Schmidt and D. Haarer, *Synth. Met.*, 1997, **89**, 215; B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737.

2 D. F. Ollis, E. Pelizzeti and N. Serpone, *Photocatalysis Fundamentals and Applications*, John Wiley and Sons, New York, 1989.

3 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341; A. L. Linsebigler, G. Lu and J. T. Yates Jr., *Chem. Rev.*, 1995, **95**, 735; A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49; M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.

4 M. R. Nimlos, W. A. Jacoby, D. M. Blake and T. A. Milne, *Environ. Sci. Technol.*, 1993, **27**, 732; Y. Luo and D. F. Ollis, *J. Catal.*, 1996, **163**, 1.

5 J. Fan and J. T. Yates Jr., *J. Am. Chem. Soc.*, 1996, **118**, 4686; M. D. Driessen, A. L. Goodman, T. M. Miller, G. A. Zaharias and V. H. Grassian, *J. Phys. Chem. B.*, 1998, **102**, 549.

6 S. A. Larson and J. L. Falconer, *Appl. Catal. B: Environ.*, 1994, **4**, 325.

7 S.-J. Hwang, C. Petucci and D. Raftery, *J. Am. Chem. Soc.*, 1997, **119**, 7877; 1998, **120**, 4388; S.-J. Hwang and D. Raftery, *Catal. Today*, 1999, **49**, 353.

8 H. Tada and M. Tanaka, *Langmuir*, 1997, **13**, 360; P. Wyness, J. F. Klausner, D. Y. Goswami and K. S. Schanze, *J. Sol. Energy Eng.*, 1994, **116**, 2.

9 K. Hofstadler, R. Bauer, S. Novalic and G. Heisler, *Environ. Sci. Technol.*, 1994, **28**, 670.

10 H. Al-Ekabi and N. Serpone, *J. Phys. Chem.*, 1988, **92**, 5726.

11 C. Shifu, Z. Mengyue and T. Yaowu, *Microchem. J.*, 1996, **54**, 54; V. Brezova, A. Blazkova, L. Karpinsky, J. Groskova, B. Havlinova, V. Jorik and M. Ceppan, *J. Photochem. Photobiol. A*, 1997, **109**, 177.

12 N. J. Peill and M. R. Hoffmann, *Environ. Sci. Technol.*, 1995, **29**, 2974; N. J. Peill and M. R. Hoffmann, *Environ. Sci. Technol.*, 1996, **30**, 2806; N. J. Peill and M. R. Hoffman, *J. Sol. Energy Eng.* 1997, **119**, 229.

13 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Gratzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.

14 H. Tada and H. Honda, *J. Electrochem. Soc.*, 1995, **142**, 3438.

15 N. J. Turro, A. L. Buchachenko and V. F. Tarasov, *Acc. Chem. Res.*, 1995, **28**, 69.

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