In Situ Solid-State NMR Observations of Photocatalytic Surface Chemistry: Degradation of Trichloroethylene

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Environmental catalysts that can efficiently degrade hazardous chemicals are of growing importance. Among these, TiO_2 photocatalysts show high potential for effective degradation of harmful species, particularly chlorine containing compounds, which are chemically persistent.[1−3] TiO_2 photocatalysts can display efficiencies (degradation rate/unit energy) that are 1−2 orders of magnitude higher than thermal catalysts, particularly for the low chlorocarbon concentrations often encountered.[4] Gas-surface experiments[5−10] show that reactions occur both in the gas phase and/or on the surface of TiO_2 catalysts and can involve the following radical initiators: O_2^-, OH, and Cl. Although a number of studies have been carried out by means of GC,[7−9] MS,[6,8] and FT-IR,[5−8,10] a detailed understanding of the reaction mechanisms remains elusive. In the present work, we report a new approach to the study of photocatalysis, namely *in situ* solid-state nuclear magnetic resonance (SSNMR) spectroscopy.[11−13] SSNMR methods are advantageous because they allow a quantitative examination of the reactions on the catalyst surface as well as in the gas phase. We have characterized the reaction of trichloroethylene (TCE) over two types of TiO_2 photocatalysts and have identified new intermediates in the complex surface chemistry.

Figure 1 shows proton-decoupled ^{13}C magic angle spinning (MAS) NMR spectra obtained from photooxidation of TCE in the presence of O_2 and Degussa P-25 TiO_2 powder.[14] The NMR spectra show the degradation of TCE, the formation of dichloroacetyl chloride ($Cl_2CHCOCl$, DCAC), CO, phosgene (CCl_2O), and pentachloroethane (C_2HCl_5), and their conversion to the final product CO_2. The narrow line widths of the peaks indicate that these species are very mobile and most likely exchange rapidly between the surface and the gas phase. Assignment of these intermediates are confirmed by comparing ^{13}C NMR shifts for liquid samples reported in the literature[15] or prepared in our lab and from proton coupled spectra during the photoreactions. Most of the intermediates identified above are in good agreement with previous reports.[8,10] There was no indication of the formation of mono- or dichloroacetaldehyde observed in previous liquid-phase[16] or gas-phase[7] reaction studies.

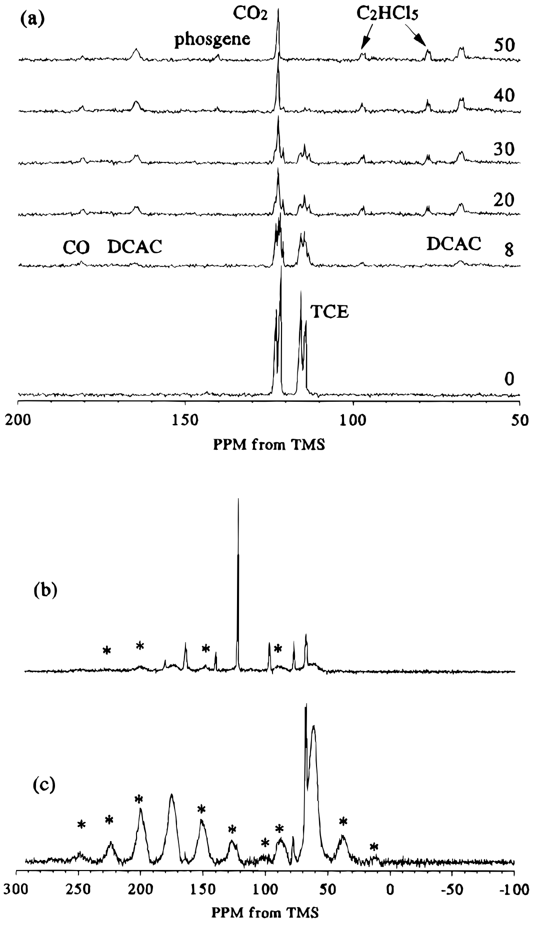

Figure 1. Proton-decoupled ^{13}C MAS NMR spectra obtained during the photocatalytic oxidation of TCE on 170 mg of Degussa P-25 TiO_2. Closed reaction cells were prepared by sealing off 5 mm NMR tubes after doubly ^{13}C labeled TCE and O_2 were introduced onto previously calcined and evacuated (both at 773 K for 5 hours) TiO_2 catalysts. Approximately 5 mW of near UV light (350−450 nm) is delivered evenly over the surface of the spinning sample via a liquid light guide terminated by a 50 mm quartz rod. Spectra were obtained in a Varian Unity Plus 300 spectrometer operating at 75.4 MHz for ^{13}C and using a homebuilt in situ MAS probe. (a) Reaction of 48 μmol of TCE with 60 μmol of O_2 (48 scans each, delay 4 s). The UV irradiation time is indicated in minutes. Assignments: TCE (116.7 and 124 ppm with $^{13}C-^{13}C$ coupling, $J = 103$ Hz), DCAC (70 and 167 ppm), C_2HCl_5 (79.5 and 100 ppm), CO_2 (124 ppm), phosgene (144.5 ppm), and CO (184 ppm). (b) Spectrum (2000 scans, 20 s recycle time) recorded after UV light was turned off. (c) A spectrum obtained with $^1H-^{13}C$ cross polarization. The asterisks indicate spinning sidebands of surface bound dichloroacetate (center bands: 64 and 177.3 ppm).

A carbon balance obtained from the peak areas of the aforementioned six species, however, indicates a significant loss of signal (up to 50%) from the original TCE concentration. A spectrum acquired using an extended accumulation time (Figure 1b) exhibits additional broad peaks which account for the apparent loss in signal. The observed line widths result from adsorption site heterogeneity. A separate spectrum obtained with cross polarization (CP) is displayed in Figure 1(c) and gives further proof of the strong adsorption of this species, which we identify as dichloroacetate (DCAc). DCAc presumably forms

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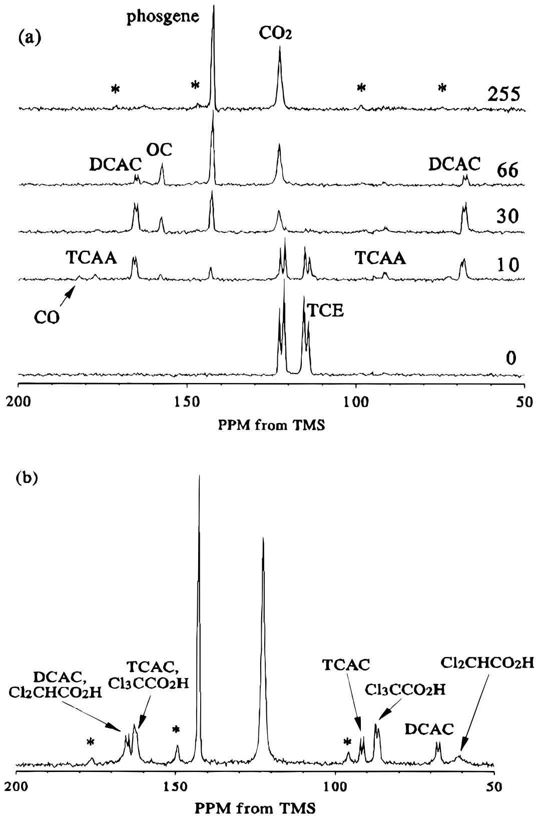

Figure 2. ^{13}C MAS NMR spectra obtained during TCE photooxidation on the PVG supported TiO_2 catalyst. The catalyst was prepared from a gas phase reaction of $TiCl_4$ (48 μmol) on a degassed and calcined PVG rod followed by hydration and recalcination. The NMR samples were prepared with the same procedure used for the powdered catalyst. (a) Spectra acquired during UV irradiation. Assignment: Cl_2CHCO_2H (63 and 167.5 ppm), Cl_3CCO_2H (88 and 164 ppm), TCAA (93 and 177 ppm), TCAC (94 and 164 ppm), and OC (159 ppm). (b) A spectrum obtained with extended accumulation after the lamp was turned off. The asterisks indicate spinning sidebands of strongly surface adsorbed CO_2.

from the reaction of DCAC with surface hydroxyl groups. Continued UV irradiation did not break up DCAc, while other, more mobile species were converted into CO_2. These results indicate that some reaction intermediates such as DCAC migrate to the nonirradiated, central portion of the catalyst and react to form stable, strongly surface-bound species.

A second TiO_2 photocatalyst consisting of highly dispersed TiO_2 (roughly 25% of a monolayer) on the surface of transparent porous Vycor[17] glass (PVG) was employed[18] in order to minimize the UV light scattering problem of the powdered catalyst. ^{13}C MAS NMR spectra (Figure 2a) show that TCE quickly breaks down to form a number of reaction intermediates and final products phosgene and CO_2 in samples prepared under dry conditions. Among these species, trichloroacetaldehyde (Cl_3CCHO, TCAA), DCAC, CO, and phosgene were observed as for the powdered catalyst and/or other previous reports.[6,8,10] Three new intermediates, oxalyl chloride (ClCOCOCl, OC), trichloroacetyl chloride (Cl_3CCOCl, TCAC), and trichloroacetic acid (Cl_3CCO_2H) were identified. The small size of the spinning sidebands evident in the spectra indicate that only a small fraction of the CO_2 is bound to the surface. Photocatalytic reactions in the presence of H_2O as a coreactant resulted in the observation of similar intermediates; however, TCAA and OC were not observed, and phosgene was rapidly and almost completely converted to CO_2. DCAC was found to react with H_2O to form dichloroacetic acid (Cl_2CHCO_2H). No surface-bound species were observed from the photocatalytic degradation of TCE on the TiO_2-anchored PVG catalyst in contrast to the powdered catalyst.

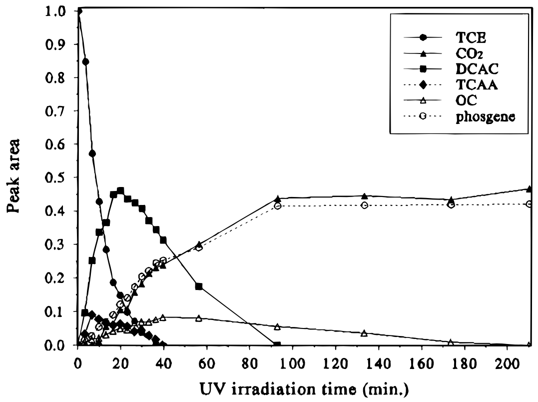

Figure 3. Reaction kinetic plot from the TCE reaction on the TiO_2/PVG photocatalyst.

TCAC and Cl_3CCO_2H species are more evident in Figure 2(b), in which a separate UV irradiation was carried out with the addition of a small amount of water and with an extended signal accumulation after the UV lamp was turned off. The spectrum shows DCAC, Cl_2CHCO_2H, TCAC, and Cl_3CCO_2H as well as phosgene and CO_2. A dark reaction takes place which transforms DCAC and TCAC to their corresponding acids on a time scale of several hours. It is clear from these experiments that the unstable intermediates DCAC and TCAC are first formed from TCE photodegradation and later form acids via reaction with surface water molecules. However, they remain as mobile species and do not form acetates in the presence of light. Upon further UV irradiation they convert to CO_2.

Quantitative information on the fate of each species can be acquired from the direct integration of peak areas in the ^{13}C MAS NMR spectra. Figure 3 shows such a kinetic plot from the experimental results of Figure 2(a). Kinetic studies showed that the fastest rates of catalysis were observed under conditions of excess oxygen and low concentrations of water. However, the addition of water was useful in decreasing the lifetime of potentially harmful intermediates such as phosgene and OC. There was no observed reaction of TCE without added O_2. Detailed kinetic analysis of the photooxidation is still under investigation and will be published separately.

In light of the intermediates and kinetics observed in these experiments, our NMR studies strongly support the position that molecular oxygen is the primary initiating species in TiO_2 photocatalysis. Additional ^1H NMR investigations indicated that there was no significant loss of surface hydroxyl groups, further suggesting that a mechanism involving surface-bound H_2O or OH groups[5,7] as the initiating species in TCE degradation is not suitable. However, the formation of chlorine radicals would explain the formation of C_2HCl_5 and TCAC. The formation of surface-bound chloroacetates may play a role in the observed deactivation of titania catalysis.[9,19] The use of supported catalysts also had a significant effect on the observed reactions, and such systems may be useful in tuning the chemistry to favor certain species. *In situ* SSNMR methods will be advantageous to investigate these and other issues relevant to photocatalytic surface chemistry.

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