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Sarah Pilkenton
Framingham State University

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Daniel Raftery
University of Washington Seattle

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Ethanol Photocatalysis on TiO₂-Coated Optical Microfiber, Supported Monolayer, and Powdered Catalysts: An in Situ NMR Study

Sarah Pilkenton, Son-Jong Hwang,[†] and Daniel Raftery*

H. C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

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In situ solid-state NMR methodologies have been employed to investigate the photocatalytic oxidation of ethanol (C_2H_5OH) over a TiO₂-coated optical microfiber catalyst and two other TiO₂-based catalysts. Adsorption of ethanol on the surface of the TiO₂/optical microfiber catalyst formed a strongly hydrogen-bonded species and a Ti ethoxide species. In situ UV irradiation experiments under ^{13}C magic angle spinning (MAS) conditions reveal the formation of two main reaction intermediates, 1,1-diethoxyethane ($CH_3CH(OC_2H_5)_2$) and acetic acid, under dry conditions. The catalyst was shown to be highly effective for the degradation of ethanol as complete photooxidation of ethanol was observed to form acetic acid and CO_2. These results were compared to those using a monolayer catalyst supported on porous Vycor glass and powdered TiO₂. Solid-state NMR investigations on TiO₂ powder modeled after temperature-programmed desorption experiments confirm the identities of the hydrogen-bonded and Ti ethoxide species and show that the strongly bound ethoxide species has a number of adsorption sites. Kinetic experiments indicate this latter species reacts much more rapidly. Studies of the effect of surface hydration show that the presence of water decreases the rate of ethanol photodegradation. Water and ethanol compete for the same adsorption sites on the surface of the TiO₂ catalysts.

I. Introduction

Heterogeneous semiconductor photocatalysis represents an emerging area of environmental catalysis with significant potential to detoxify noxious organic pollutants in an effective manner. A variety of semiconductor materials have been investigated due to the growing interest in the development of inexpensive and efficient methodologies to reduce environmental problems.[1,2] TiO₂ is the most frequently investigated semiconductor photocatalyst due to its stability, nontoxicity, availability, and cost-effectiveness, as well as its ability to degrade a variety of harmful organic pollutants including halogenated and nonhalogenated compounds. A number of authors have reviewed the important features of TiO₂ surface chemistry at both the liquid–surface and gas–surface interfaces.[3–6]

Because of the complexity inherent in the numerous photocatalytic surface processes and photooxidation reaction mechanisms, significant research efforts using a variety of experimental and analytical methods are underway to improve our fundamental understanding of this surface chemistry and to provide greater utilization of the technology. A new approach we have introduced to the study of photocatalytic surface chemistry is the use of in situ solid-state nuclear magnetic resonance (SSNMR) spectroscopy.[7–10] The utility of SSNMR for the study of a variety of environmental chemistry related topics is increasingly apparent.[11–16] Due to NMR's atomic specificity, high resolution, and quantitative capabilities, in situ SSNMR observations during near-UV light driven photocatalysis yield very valuable information regarding the complex reaction chemistry of organic molecules on the catalyst surface and in the gas phase. In this paper, we report further detailed in situ

SSNMR investigations of the photocatalytic oxidation of ethanol using a new type of photocatalytic system, as well as studies of the adsorption of ethanol on the catalyst surface under both hydrated and dehydrated conditions. Ethanol was chosen for study because it is a relatively simple molecule and can be used along with other alphatic alcohols as a probe of the surface properties of TiO₂. Ethanol is also a common solvent in spraying and coating applications and a major component of bakery and brewery emissions.

The photocatalytic oxidation of ethanol on TiO₂ catalysts has been studied at the liquid–solid[17,18] and gas–solid[9,19–26] interfaces using a variety of methods. The reaction intermediates identified to date at the gas–solid interface include acetaldehyde, acetic acid, formaldehyde, and formic acid.[21,22,24–26] As described in these studies, the formation of acetaldehyde is the first step in the oxidation of ethanol, but the further oxidation steps that convert acetaldehyde to CO_2 are not agreed upon. Nimlos et al.[21] proposed a sequential reaction mechanism where acetaldehyde is oxidized to acetic acid, while Sauer et al.[22] and Muggli et al.[24–26] proposed that acetaldehyde is oxidized by parallel reaction channels. The primary difference in these reaction mechanisms is whether acetic acid is an intermediate in the formation of formaldehyde. The presence of two adsorption sites is believed to be responsible for the different reaction channels.[21,24–26] In a previously published in situ SSNMR investigation using a monolayer catalyst supported on porous Vycor glass and TiO₂ powdered catalysts, we observed two ethanol adsorption sites and identified them as a strongly hydrogen-bonded species and a surface bound Ti ethoxide species. The formation of acetaldehyde, acetic acid, acetate, formic acid, and carbon dioxide was observed during the photocatalytic oxidation of one and two monolayers of ethanol, and the surface bound ethoxide species was determined to be the photocatalytically active surface ethanol species. Also, in our studies of the photocatalytic oxidation of multiple mono-

* To whom correspondence should be sent. FAX: (765) 494-0239. E-mail: raftery@purdue.edu.
† Present address: Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

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layers of ethanol on TiO_2 powder, we observed the formation of a new reactive intermediate that could not be identified.[9] In the present work, in situ SSNMR methods are used to identify this intermediate and to study the adsorption and surface reactions during the photocatalytic oxidation process under dry and hydrated conditions. Photocatalytic oxidation reactions were carried out on three different types of catalysts: (1) TiO_2 particles supported on optical microfibers, (2) a monolayer film catalyst, and (3) TiO_2 powder (Degussa P-25).

The local coordination environments at the binding sites on the TiO_2 surface have been investigated widely using adsorption and thermal desorption and/or decomposition of ethanol.[27−34] The presence of two adsorption patterns, hydrogen bonding of ethanol to surface hydroxyl groups and the dissociation of ethanol at coordinatively unsaturated Ti atoms to form surface bound Ti ethoxide species ($CH_3CH_2O^-$), has been observed by both infrared and temperature-programmed desorption (TPD) experiments.[28−34] TPD studies also show that two types of ethoxide species exist on the TiO_2 surface. In these studies, the first ethoxide species recombines with a surface hydroxyl group and desorbs as ethanol at approximately 400 K, and the second ethoxide species undergoes dehydration, dehydrogenation, and hydrogenation reactions and desorbs as a number of products including diethyl ether, acetaldehyde, and ethylene at approximately 600 K.[30−32,34] The surface bound species have been identified as a monodentate ethoxide species and a bidentate ethoxide species in which the oxygen is bridge-bonded to two subsurface metal cations.[32,34] TPD and infrared spectroscopy studies of ethanol adsorption on TiO_2 surfaces predosed with water show that ethanol and water compete for the same coordinatively unsaturated Ti adsorption sites on the catalyst.[28,32,34] Additional SSNMR studies designed to model temperature-programmed desorption experiments were carried out to study the adsorption of ethanol on the catalyst surface. We have also used SSNMR methods to study the effect of surface hydration on the formation of surface bound species on two TiO_2-based catalysts: TiO_2 powder and a monolayer TiO_2 catalyst dispersed on porous Vycor glass.

II. Experimental Section

A. Catalyst Preparation. *1. Coated Optical Microfibers.* Approximately 20, 15 cm long sections of roving consisting of 4800 individual quartz microfibers per strand (Quartzel Fiber, 9 μm diameter, Quartz Products Co.) were placed in a test tube and calcined at 773 K for 10 h to remove the polyimide cladding. Once the fibers cooled to room temperature, they were placed in a mixture of 30% hydrogen peroxide and concentrated sulfuric acid (7:3) and heated to 363 K for 1 h to further clean the surface of the fibers. The fibers were then removed from the H_2O_2/H_2SO_4 mixture, rinsed with deionized water, and dried under vacuum at 413 K for 1.5 h.

After the fibers cooled to room temperature, they were bound together at one end with a copper wire and dipped into an aqueous suspension of TiO_2 similar to that used by Nazeeruddin et al.[35] The suspension was prepared by adding 4 mL of water to 10 g of TiO_2 powder (Degussa P-25, specific surface area 55 m^2 g^{-1}, 70% anatase) in a ceramic mortar to form a thick paste. An 800 μL aliquot of pentane-2,4-dione (Aldrich) was added to the paste to promote dispersion of the particles. The paste was then diluted by the slow addition of 16 mL of water while grinding. Finally, 200 μL of Triton X-100 (Aldrich) was added to allow the suspension to coat the fibers evenly. After dipping the fibers in the TiO_2 dispersion, the fibers were heated to 773 K for 30 min, cooled to room temperature, and rinsed
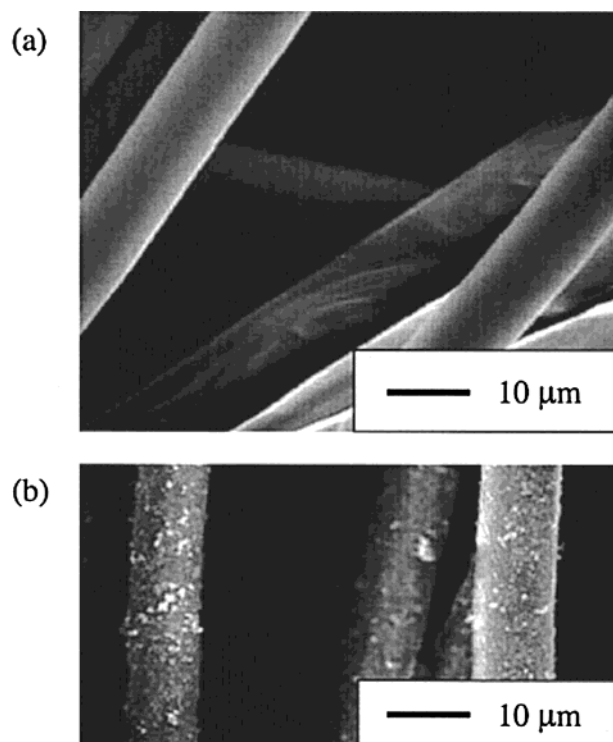

Figure 1. SEM micrographs of (a) uncoated and (b) TiO_2-coated optical microfibers.

under flowing water to remove any excess TiO_2. This process was repeated two more times. To further increase the surface area of the TiO_2-coated catalysts, the fibers were dipped into a 20% solution of titanium isopropoxide in anhydrous isopropyl alcohol and calcined at 773 K for 3 h. After cooling, the TiO_2 coated fibers were rinsed with deionized water one final time and dried. BET isotherm analysis of the TiO_2-coated optical fibers yielded a final specific surface area of 7.4 ± 0.1 m^2 g^{-1}.

A comparison of the microfibers before and after coating with TiO_2 is shown in Figure 1. Images of the TiO_2-coated fibers (Figure 1b) obtained using scanning electron microscopy (SEM) show a relatively uniform layer of TiO_2 coating on the fibers as compared to the uncoated fibers (Figure 1a).

2. TiO_2 Powder Catalyst. To make the dehydrated TiO_2 powder catalyst, 180 mg of TiO_2 powder was packed into a 5 mm glass NMR tube (Norell), attached to a gas manifold, placed in a ceramic heater, evacuated at 773 K for 4 h to remove weakly and strongly adsorbed water molecules as well as the majority of surface hydroxyl groups, and then calcined at 773 K under 1 atm of O_2 for an additional 4 h. Typically, the O_2 was pumped out and replaced with fresh O_2 during the calcination process. The sample was then evacuated to a pressure of 5.0×10^{-5} Torr and allowed to cool to room temperature inside the ceramic heater. A hydrated TiO_2 catalyst was first prepared using the above method, then exposed to water vapor overnight, attached to the gas manifold, and evacuated at room temperature for 2 h.

3. TiO_2/PVG Catalyst. A third TiO_2 catalyst was prepared by dispersing one monolayer of TiO_2 on the surface of transparent porous Vycor glass (PVG). The preparation of supported monolayer TiO_2 catalysts using the gas-phase hydrolysis of $TiCl_4$ with OH groups at the PVG surface has been established by Anpo et al.[36−38] A PVG rod (Corning 7930, BET surface area ~150 m^2 g^{-1}, pore diameter 40 Å) that was 3.6 mm in diameter and 12 mm long, weighing 180 mg, was

degassed and calcined at 773 K for 4 h each. The saturated vapor pressure of $TiCl_4$ (11 Torr) corresponds to 88 μmol of $TiCl_4$ (Aldrich) on our gas rack. To ensure the complete reaction of all surface hydroxy groups with $TiCl_4$, the pretreated PVG rod underwent a series of four, 88 μmol reaction cycles with $TiCl_4$ at room temperature. After each reaction cycle, the HCl gas produced was completely evacuated. After the $TiCl_4$ was anchored to the PVG support, the catalyst was hydrated, degassed, and calcined under O_2 at 773 K to produce a dehydrated TiO_2/PVG catalyst. A hydrated TiO_2/PVG catalyst was prepared by soaking the pretreated TiO_2/PVG catalyst in deionized water for 24 h to hydrate the surface, and the catalyst was then placed on a gas manifold and evacuated to a pressure of 1.0×10^{-3} Torr. The catalyst changed from its normal transparent appearance to a milky white color while the catalyst was being evacuated.

B. Sample Preparation. Photocatalytic oxidation reactions were carried out in sealed 5 mm glass NMR tubes (Norell) at room temperature. All samples were prepared by loading the catalyst in the NMR tube and pretreating the catalyst by evacuation at 773 K for 4 h to remove water molecules as well as the majority of surface hydroxyl groups. The catalysts were then calcined at 773 K in a ceramic heater under 1 atm of O_2 gas for another 4 h, evacuated to a pressure of 5.0×10^{-5} Torr, and then cooled to room temperature inside the heater. After loading with reagents, the NMR tube was sealed 10−12 mm above the catalyst.

The TiO_2-coated microfibers were loaded into the NMR sample tubes by first inserting them into a Teflon tube. A 12 mm long section of the Teflon tube containing the fiber bundle was cut and held at the opening of an NMR tube, and the fiber bundle was pushed to the bottom of the NMR tube using a glass rod. The mass used for a typical fiber bundle sample was approximately 100 mg. The TiO_2-coated fiber bundle catalyst was attached to a gas manifold, pretreated, and once the catalyst had cooled to room temperature, 24 μmol of 1,2-^{13}C-labeled ethanol (Cambridge Isotope Laboratories) and 96 μmol of O_2 were loaded onto the TiO_2 coated fiber bundle using a liquid nitrogen trap. The sample was then sealed.

A second TiO_2 catalyst was prepared by packing 180 mg of TiO_2 powder in an NMR tube, followed by pretreatment, and cooled to room temperature. The pretreated TiO_2 catalyst was then loaded with 48 μmol of 1,2-^{13}C-labeled ethanol using a liquid nitrogen trap. The sample was sealed using a stopcock valve and left for 1 h in order to allow ethanol vapor to diffuse evenly over the TiO_2 powder. Four samples were prepared by heating the ethanol loaded TiO_2 powder to 423, 473, 523, and 623 K for 1 h while evacuating. Once the sample had cooled to room temperature, 96 μmol of O_2 was loaded onto the sample, and the NMR tube was sealed. One sample was prepared at room temperature as well. For additional experiments, dehydrated and hydrated TiO_2 powder catalysts prepared as described above in section A.2 were loaded with 48 μmol of 1,2-^{13}C-ethanol and 96 μmol of O_2 using a liquid nitrogen trap, and the NMR tubes were then sealed.

The third type of catalyst used was the TiO_2/PVG catalyst. Inside a glovebox, plastic endcaps whose outer diameter fit snugly into the NMR tube were placed on each end of the PVG supported catalysts for MAS experiments. Once the endcaps were placed on the catalyst, both the hydrated and dehydrated catalysts described in section A.3 were placed in NMR tubes, removed from the glovebox, evacuated, and then loaded with 48 μmol of 1,2-^{13}C-ethanol and 96 μmol of O_2 before the NMR tubes were sealed.
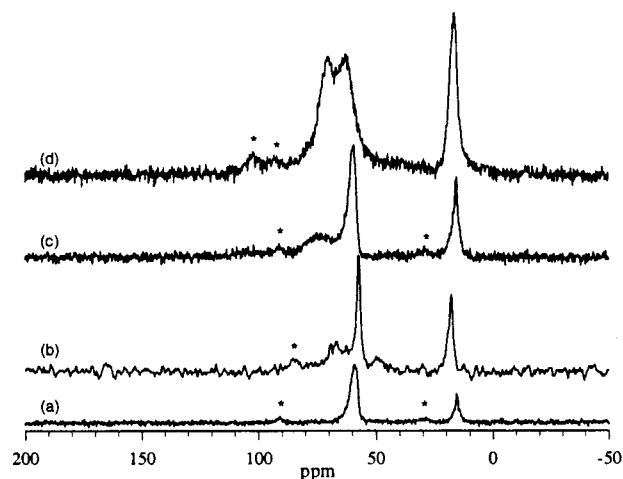

Figure 2. Proton-decoupled ^{13}C CP/MAS NMR spectra of ethanol adsorbed on different surfaces: (a) porous Vycor glass (PVG); (b) TiO_2/optical microfibers; (c)TiO_2/PVG; (d) TiO_2 powder. Samples (a), (c), and (d) contain 48 μmol of ethanol, while sample (b) contains 24 μmol. Note: asterisks indicate spinning sidebands.

C. NMR Methods. In situ NMR experiments were performed using a home-built optical/magic angle spinning (MAS) probe and light delivery system. The UV light source is a 300 W xenon arc lamp (ILC Technology) from which near-UV light (350 < λ < 550 nm) was delivered to the sample using a dichroic mirror and a liquid-filled optical light guide (Oriel Corp.). A 70 mm long quartz rod light pipe was attached to the end of the liquid light guide, and the near-UV light was brought to the sample through a 10 mm gap in the RF coil. The probe is doubly tuned for ^{1}H and ^{13}C observation at frequencies of 300 and 75.4 MHz, respectively, using a Varian Unity Plus spectrometer. The probe is capable of spinning the sealed NMR samples at speeds as high as 2.7 kHz. The near-UV light power reaching the sample was measured to be 5 mW by standard ferrioxalate actinometry.[39]

III. Results and Discussion

A. Adsorption of Ethanol on the Catalyst Surface. The adsorption of ethanol on the TiO_2/optical microfiber catalyst was examined using ^{13}C Bloch decay and cross-polarization (CP) experiments. Chemisorbed molecules are easily distinguished from physisorbed or gaseous molecules using CP/MAS experiments because the CP/MAS spectrum is influenced significantly by the mobility of molecules due to its effect on the ^{1}H−^{13}C dipolar coupling. Figure 2 shows a comparison of the proton decoupled ^{13}C CP/MAS NMR spectra of ethanol loaded onto (a) pure Vycor, (b) TiO_2/optical microfibers, (c) TiO_2/PVG, and (d) TiO_2 powder catalysts. The CP/MAS spectra were obtained with short cross-polarization contact times (0.050 ms) in order to detect only the strongly bound molecules. As seen in Figure 2, there are at least two distinct adsorption sites of ethanol on the TiO_2/PVG and TiO_2 powder catalysts whereas there is only one adsorption site on the pure PVG sample. Also, at least two different ethanol adsorption sites are present on the TiO_2/optical microfiber catalyst. The observed chemical shifts are 57.4 and 67 ppm for the methylene carbon. The binding sites on the TiO_2 polycrystalline surface and TiO_2 single crystals have been studied extensively using temperature-programmed desorption of ethanol. These studies show that there are two adsorption patterns that produce a hydrogen-bonded molecular ethanol species and surface bound Ti ethoxide ($CH_3CH_2O^-$) species that occurs at coordinatively unsaturated

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TABLE 1: Chemical Shifts of the Methylene Carbon of Adsorbed Ethanols on Different Catalysts

catalyst	ethanol species	chemical shift (ppm)[a]
PVG	hydrogen bonded	58.0
TiO₂/PVG	hydrogen bonded	59.4
	Ti ethoxide	73
TiO₂ powder	hydrogen bonded	62.2
	Ti ethoxide	69.9
TiO₂/optical microfibers	hydrogen bonded	57.4
	Ti ethoxide	67
none	liquid[40]	57.7

[a] The error bars for the chemical shifts are ±1.0 ppm for the surface bound species.

Ti atoms.[28−32,34] In our previous study of ethanol on TiO_2 powder and TiO_2/PVG catalysts, we observed two methylene carbon resonances at 62.2 and 59.4 ppm which we assigned to hydrogen-bonded ethanol on the TiO_2 powder and TiO_2/PVG catalysts, respectively, and further downfield resonances at 69.9 and ~73 ppm, which we assigned to the ethoxide species on these catalysts.[9] Similarly, for the coated fiber catalyst, the peak at 57.4 ppm is assigned to the strongly hydrogen-bonded ethanol molecule, and the surface bound ethoxide is observed as a broad peak at 67 ppm. Table 1 gives the chemical shift values observed for the methylene carbon of the surface bound ethanol species on the four catalysts used in this study.

The amount of ethanol loaded onto the TiO_2/optical microfiber catalyst (24 μmol) corresponds to 19.6 molecules/nm², which is roughly 6 times the saturation coverage (3.0−3.2 molecules/ nm²)[30,31] of the TiO_2 anatase surface. As shown previously, multiple monolayers of ethanol do not result in a change in the CP/MAS NMR line shape,[9] and therefore, the CP/MAS spectrum of ethanol on the TiO_2/optical microfibers catalyst can be compared to those for the TiO_2 powder and TiO_2/PVG catalysts. As can be seen in Figure 2, the number of adsorption sites for ethoxide formation on the TiO_2/optical microfiber catalyst is significantly less than that observed for the TiO_2 powder catalyst and to some extent the TiO_2/PVG catalyst as well. In all cases, the hydrogen-bonded ethanol species outnumber the ethoxide species. In addition to the difference in the amount of ethoxide species formed, the difference in the chemical shift values for the ethoxide species on the TiO_2 powder, TiO_2/PVG, and TiO_2/optical microfiber catalysts (Table 1) indicates that the ethoxide species are positioned in somewhat different electronic environments on the catalysts. The chemical shift of the ethoxide species on the optical microfiber catalyst is more similar to that of the TiO_2 powder than the TiO_2/PVG catalyst, which is not surprising since the fibers are coated with a dispersion of Degussa P-25 TiO_2 powder.

B. Photocatalytic Oxidation of Ethanol on the TiO₂/ Optical Microfiber Catalyst. The photocatalytic oxidation of 24 μmol of ethanol (approximately 6 monolayers) and 96 μmol of oxygen using the TiO_2/optical microfiber catalyst resulted in the immediate formation of an intermediate with resonances at 14.5, 22.5, 61.6, and 93.8 ppm, which we identified as 1,1-diethoxyethane (acetal, $CH_3CH(OC_2H_5)_2$).[40] In comparison to other gas-phase studies of the photocatalytic oxidation of ethanol using TiO_2 catalysts, the formation of acetal is unique to studies performed with multiple monolayer coverages of ethanol, while the formation of intermediates, acetaldehyde (CH_3CHO, 198.7 and 28.8 ppm), acetate (CH_3COO^-, 179.0 and 21.85 ppm), formic acid (HCOOH, 161.2 ppm), and formaldehyde (CH_2O), which were observed in low ethanol coverage experiments on TiO_2 powder and TiO_2/PVG catalysts,[9] were not observed here. Studies of the liquid-phase photocatalytic oxidation of ethanol using TiO_2 in the form of a TiO_2/ethanol suspension have shown
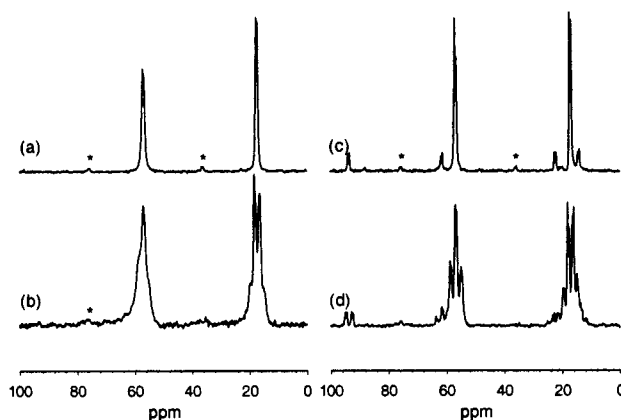

Figure 3. ¹³C MAS NMR Bloch decay spectra of ethanol on TiO_2/ optical microfibers before UV irradiation: (a) proton-decoupled and (b) proton-coupled. After 50 min of UV irradiation: (c) proton-decoupled and (d) proton-coupled.

TABLE 2: Chemical Shifts of Species Observed over the TiO₂/Optical Microfiber Catalyst

species	chemical formula	chemical shifts (ppm) and J-couplings[a]
ethanol	CH_3CH_2OH	17.0, 56.9 (J_{C-C} = 37 Hz, J_{H-C} = 125, 139 Hz)
1,1-diethoxyethane	$CH_3CH(OC_2H_5)_2$	14.5, 22.5, 61.6, 93.8 (J_{C-C} = 37, 44 Hz)
acetic acid	CH_3COOH	19.6, 176.2
carbon dioxide	CO_2	124.5

[a] The error bars for the chemical shifts are ±0.5 ppm for the mobile species, and the error bars for the J-couplings are ±5 Hz.

that the reaction of one acetaldehyde molecule and two ethanol molecules results in the formation of the reaction intermediate, 1,1-diethoxyethane.[17,18] The identity of this same intermediate, 1,1-diethoxyethane, in our experiments was confirmed by performing a proton-coupled ¹³C MAS NMR experiment on a sample prepared with 40 μmol of ethanol and 112 μmol of O_2 loaded on to 100 mg of the TiO_2/optical microfiber catalyst that was irradiated for 50 min (Figure 3). In addition to the proton-coupled ¹³C MAS NMR experiment, integration of the acetal resonances collected during the in situ UV irradiation of ethanol on the TiO_2/optical microfiber catalyst (not shown) shows a 2:1 ratio between the ethoxy resonances (14.5, 61.6 ppm) and the ethane resonances (22.5, 93.8 ppm). The observed carbon−carbon J-couplings are 37 Hz for the ethoxy carbons and 44 Hz for the ethane carbons of 1,1-diethoxyethane. Table 2 gives the chemical shifts and J-couplings of the species observed in the photooxidation of ethanol on the TiO_2/optical microfiber catalyst. Immediately after irradiation, a reduction in the line widths of the ethanol resonances (17.0 and 56.9 ppm) was also detected. This indicates that surface bound ethoxide and ethanol molecules are actively involved in the photooxidation process when the surface is illuminated.

Parts a and b of Figure 4 show the proton-decoupled ¹³C MAS NMR spectra of the photocatalytic oxidation reaction of 24 μmol of ethanol and 96 μmol of oxygen on approximately 100 mg of TiO_2/optical microfibers before and after 187 min of UV irradiation, respectively. As shown in Figure 4a,b, further irradiation resulted in the conversion of the acetal intermediate to acetic acid. Parts c and d of Figure 4 are the corresponding ¹³C CP/MAS NMR spectra before and after UV irradiation, respectively. The spectrum taken before irradiation shows the presence of the surface bound ethanol species, and the spectrum taken after irradiation shows only the presence of acetic acid
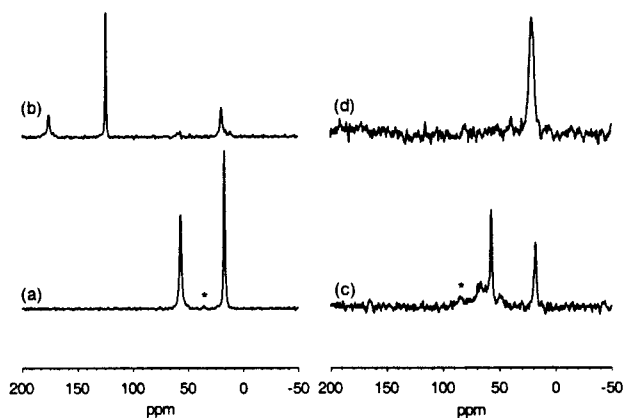
Figure 4. Proton-decoupled ^{13}C MAS NMR spectra of ethanol on TiO_2/optical microfibers. Bloch decay: (a) before UV irradiation and (b) after 187 min of UV irradiation; (c) and (d) are the corresponding CP/MAS spectra.

on the surface of the catalyst. There is no carbonyl resonance signal at short contact times. These data indicate that all of the surface bound ethanol species are photooxidized in the presence of oxygen. The photocatalytic oxidation of ethanol was also examined without oxygen as a reagent on the TiO_2/optical microfiber catalyst as a control experiment. No degradation of ethanol was observed after approximately 1 h of UV irradiation.

Using these data and information from previous experiments, a reaction mechanism for the photooxidation of multiple monolayer coverages of ethanol on TiO_2 can be proposed. The first step is the oxidation of ethanol to acetaldehyde.[9,21-26] We previously observed acetaldehyde formation under conditions of low ethanol coverage on the TiO_2/PVG and TiO_2 powder catalysts.[9] Even though acetaldehyde is not observed directly using the TiO_2/optical microfiber catalyst, acetaldehyde is a precursor for the formation of acetal,[17,18] and therefore, we assume that acetaldehyde quickly reacts with surrounding ethanol molecules through an undetected hemiacetal intermediate, $CH_3CH(OH)(OC_2H_5)$, to produce the acetal intermediate. Acetal is then photooxidized to acetic acid. A similar transformation was observed in photooxidation reaction of silica-supported niobium oxide suspended in liquid ethanol.[41] Acetic acid is then further oxidized to formaldehyde, formic acid, and ultimately CO_2.[21,22,24-26] Scheme 1 shows the proposed mechanism for ethanol oxidation on the TiO_2/optical microfiber catalyst.

Studies of the photooxidation of multiple monolayers of ethanol on the TiO_2 powder and TiO_2/PVG catalysts (not shown) also show the formation of 1,1-diethoxyethane immediately after UV irradiation while the formation of acetaldehyde is not observed. After 100 min of irradiation, acetaldehyde is detected. We can conclude that in the beginning of the photooxidation reaction acetaldehyde is produced, but it reacts immediately with surrounding ethanol molecules to form the acetal intermediate. As the concentration of ethanol decreases, acetaldehyde is observed. Since there are fewer ethanol molecules surrounding the acetaldehyde molecule, acetal is no longer produced. Therefore, acetaldehyde is further oxidized to CO_2 as shown in previous experiments, without going through the acetal intermediate.[9,21,22,24-26]

In addition to the new intermediate detected in the photocatalytic oxidation of ethanol using the TiO_2/optical microfiber catalyst, the catalyst is more efficient than the TiO_2 packed powder and TiO_2/PVG catalysts. Complete oxidation of ethanol was never observed using in situ SSNMR experiments on either the TiO_2 powder or the TiO_2/PVG catalysts.[9] The

increased efficiency of the TiO_2/optical microfiber catalyst is due to the ability to illuminate the center of the sample that is impossible to do using the TiO_2 powder catalyst, as well as the increased activity of the P-25 active sites as compared to the monolayer TiO_2 sites. In addition, the rate of photocatalytic activity is also enhanced by fast chemical exchange of ethanol molecules on the surface when multiple monolayers of ethanol are present as previously observed in studies on the TiO_2 powder catalyst.[9]

C. Investigation of the Ethanol Surface Bound Species on TiO_2 Powder. To investigate the binding strength and nature of the ethoxide species, a series of samples were prepared at different temperatures using TiO_2 powder. Figure 5 shows proton-decoupled ^{13}C CP/MAS NMR spectra of ethanol after it was first loaded onto the catalyst at 298 K and then evacuated from the surface of the catalyst at various temperatures. Figure 5a shows that both the hydrogen-bonded (62.2 ppm) and ethoxide (69.9 ppm) species are present at room temperature. As the evacuation temperature is increased, the peak corresponding to the hydrogen-bonded species decreases and eventually disappears by 473 K. This is in good agreement with a previous TPD study of ethanol adsorption on polycrystalline anatase powders.[31] The ethoxide species is stable up to temperatures as high as 500 K. In fact, there appear to be a number of ethoxide species present, as indicated by changes in chemical shift values observed for multiple ethoxide peaks in Figure 5a–c. Among the ethoxides, due to the heterogeneity of the surface, multiple adsorption sites, and/or the presence of different TiO_2 surfaces (anatase and rutile), their resonances are dispersed between ~66 and ~80 ppm. For the ethanol sample evacuated at 423 K, the NMR spectrum indicates the presence of two different ethoxide species (Figure 5b). As the evacuation temperature is increased up to 473 K, only one broad peak remains with a chemical shift (74.6 ppm) that is somewhat between that of the two peaks shown in Figure 5b. These NMR results show more detailed information regarding the adsorption sites than TPD studies, although we are currently unable to assign unambiguously the identities of the ethoxide species. Studies by Gamble et al.[34] on rutile single crystals and Lusvardi et al.[31,32] on polycrystalline anatase and rutile powders have identified the ethoxide that desorbs at 380 K as a monodentate ethoxide (bonded to a single metal cation) and the ethoxide that desorbs above 500 K (~600 K on anatase powder) as a bidentate ethoxide (bridge-bonded to two metal cations). At this time, the peak at 69.9 ppm in Figure 5a is thought to correspond to an ethoxide species that desorbs by reaction with a hydroxide group to form ethanol at 390 K, and the peak at 74.3 ppm in Figure 5c,d is the ethoxide species that desorbs at 600 K as ethylene, diethyl ether, and water. The two ethoxide species present in Figure 5b have no assignment at this time. Such a large number of observed ethoxide species could be due to the observation of both ethoxide species on both anatase and rutile forms of TiO_2 present in Degussa P-25 TiO_2. In addition to the presence of both anatase and rutile forms of TiO_2, these spectra are also complicated by the possibility of readsorption and reaction of products as they diffuse through the packed powder sample and the presence of defect sites (edges, steps, etc.) on the powder surface as well.[32] TPD studies by Lusvardi et al. on anatase and rutile powders show that the first ethoxide species desorbs at different temperatures on the anatase (380 K) and rutile (415 K) powders while the second ethoxide species desorbs in approximately the same temperature range (600–630 K due to the large number of desorption species) from both surfaces.[31] The presence of an ethoxide peak was not detected

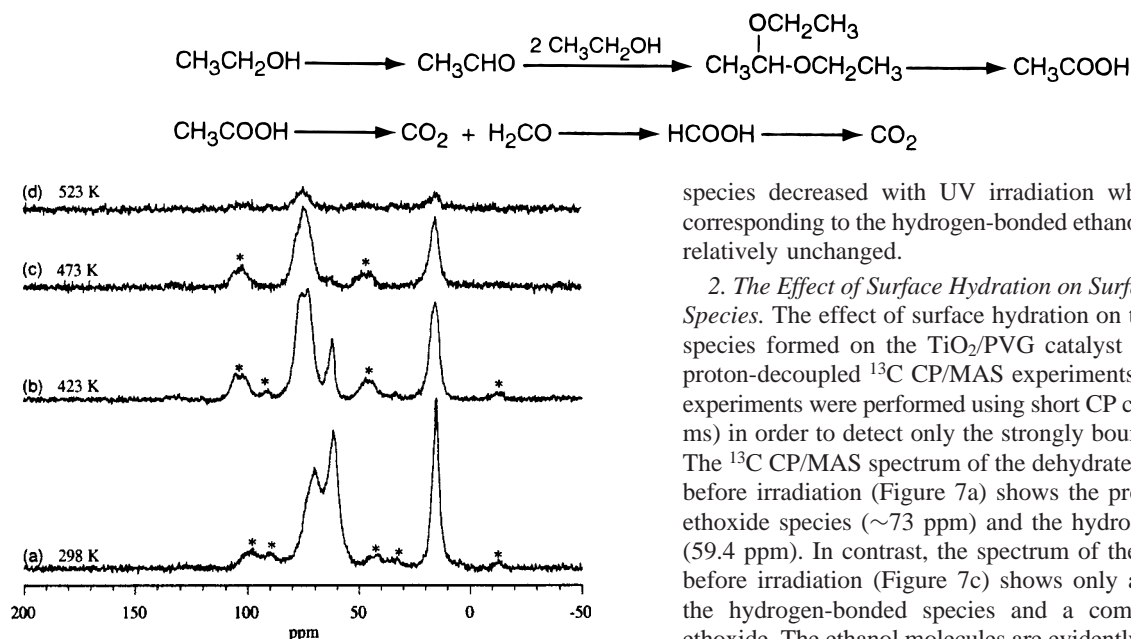Ethanol Photocatalysis

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SCHEME 1

$$CH_3CH_2OH \longrightarrow CH_3CHO \xrightarrow{2\ CH_3CH_2OH} \underset{\displaystyle CH_3CH\text{-}OCH_2CH_3}{\overset{\displaystyle OCH_2CH_3}{|}} \longrightarrow CH_3COOH$$

$$CH_3COOH \longrightarrow CO_2 + H_2CO \longrightarrow HCOOH \longrightarrow CO_2$$

Figure 5. Proton-decoupled ^{13}C CP/MAS spectra of adsorbed ethanol (48 μmol) loaded onto the TiO$_2$ powder catalyst and then evacuated from the surface at (a) 298 , (b) 423, (c) 473, and (d) 523 K.

in the sample we prepared by heating to 623 K, in agreement with previous TPD work.[30,31]

D. Surface Reactivity and Hydration Studies. A final set of experiments was designed to study the reactivity of surface ethanol species on the TiO$_2$/PVG catalyst under dry conditions and the effect of surface hydration on the formation and reactivity of surface ethanols. Similar in situ SSNMR studies on the TiO$_2$ powder catalyst were also performed.

1. Reaction of Surface Bound Species on Dehydrated TiO$_2$/PVG. The reactivity of the surface ethanol species formed on the TiO$_2$/PVG catalyst was studied using the pulse sequence shown in Figure 6a. A shutter (Uniblitz Electronic) was attached to the UV light source, and the ^{13}C CP/MAS pulse sequence was modified to control the opening and closing of the shutter. The shutter was opened for 1.0 s, exposing the sample to UV irradiation, and then closed for 0.4 s while the ^{13}C CP/MAS spectrum was acquired. Figure 6b shows the in situ ^{13}C CP/MAS NMR spectra obtained as a function of irradiation time during the photocatalytic oxidation of ethanol on a dehydrated TiO$_2$/PVG catalyst. The intensity of the ethoxide resonance ($\sim$73 ppm) clearly decreased with time while the resonance corresponding to the hydrogen-bonded ethanol species (59.4 ppm) remained relatively unchanged. The methyl resonance contains contributions from both species, and it therefore also decreases markedly. Figure 6c shows the intensity of the resonances corresponding to ethoxide and hydrogen-bonded ethanol species plotted as a function of the amount of time the sample was irradiated. Since the intensity of the ethoxide resonance decreased while the intensity of the resonance corresponding to the hydrogen-bonded ethanol species decreased only slightly, it can be concluded that the ethoxide species is the photochemically active surface ethanol species. The coordinatively unsaturated Ti sites are the photochemically active sites on the TiO$_2$/PVG catalyst, and their presence is critical for the effective photocatalytic oxidation of ethanol. Similar experiments performed on the TiO$_2$ powdered catalyst (not shown) also show that the intensity of the resonance corresponding to the ethoxide

species decreased with UV irradiation while the resonance corresponding to the hydrogen-bonded ethanol species remained relatively unchanged.

2. The Effect of Surface Hydration on Surface Bound Ethanol Species. The effect of surface hydration on the surface ethanol species formed on the TiO$_2$/PVG catalyst was studied using proton-decoupled ^{13}C CP/MAS experiments (Figure 7). These experiments were performed using short CP contact times (0.050 ms) in order to detect only the strongly bound surface species. The ^{13}C CP/MAS spectrum of the dehydrated catalyst obtained before irradiation (Figure 7a) shows the presence of both the ethoxide species ($\sim$73 ppm) and the hydrogen bound species (59.4 ppm). In contrast, the spectrum of the hydrated catalyst before irradiation (Figure 7c) shows only a small amount of the hydrogen-bonded species and a complete lack of the ethoxide. The ethanol molecules are evidently quite mobile over the surface of the catalyst in the presence of H$_2$O. The lack of the ethoxide peak indicates that water occupies the coordinatively unsaturated Ti sites on the catalyst surface, and thus these sites are unavailable for ethoxide formation. This finding is in good agreement with the TPD experiments by Gamble et al., who observed that in the presence of predosed water there is an increase of molecularly adsorbed ethanol that desorbs at temperatures below 160 K (ethanol hydrogen bonded to water on the surface of the catalyst) and a decrease in the amount of ethanol desorbing in the temperature range from 250 to 400 K which represents the ethoxide species.[34] As demonstrated in Figure 7a,b, the ethoxide species is consumed in the photooxidation reaction on the dehydrated catalyst, while little change is observed in the resonance representing the hydrogen-bonded species. The ^{13}C CP/MAS NMR spectrum of the hydrated catalyst prior to UV irradiation shows only a very small presence of the hydrogen-bonded species; therefore, a decrease in photocatalytic activity is expected for the hydrated catalyst. Additional evidence of the stronger binding capabilities of water with respect to ethanol on a TiO$_2$ surface is provided in Figure 8. ^{13}C CP/MAS spectra show a decrease in the amount of ethoxide species present as surface hydration is increased for the TiO$_2$ P-25 powdered catalyst.

After UV irradiation, the CP/MAS spectrum of the hydrated catalyst (Figure 7d) shows an increased concentration of the hydrogen bound species that is due to either photodesorption of water from the surface of the catalyst or UV-enhanced exchange between water and ethanol. Gamble et al.[34] observed isotopic exchange between ethanol and water in TPD studies, and Muggli et al.[42] have observed an increase in the exchange rate of water and O$_2$ on TiO$_2$ upon UV irradiation; therefore, exchange between water and ethanol is also likely to occur. To determine whether UV enhanced exchange was taking place between ethanol and water, ethanol and O$_2$ were loaded onto the hydrated TiO$_2$/PVG catalyst, and the CP/MAS NMR spectrum was taken before and after the sample was heated at 373 K for 100 min. In contrast to the spectra taken during UV irradiation, little difference was observed in the two spectra after this thermal treatment; therefore, we believe UV enhanced exchange between ethanol and oxygen is occurring on the catalyst surface.
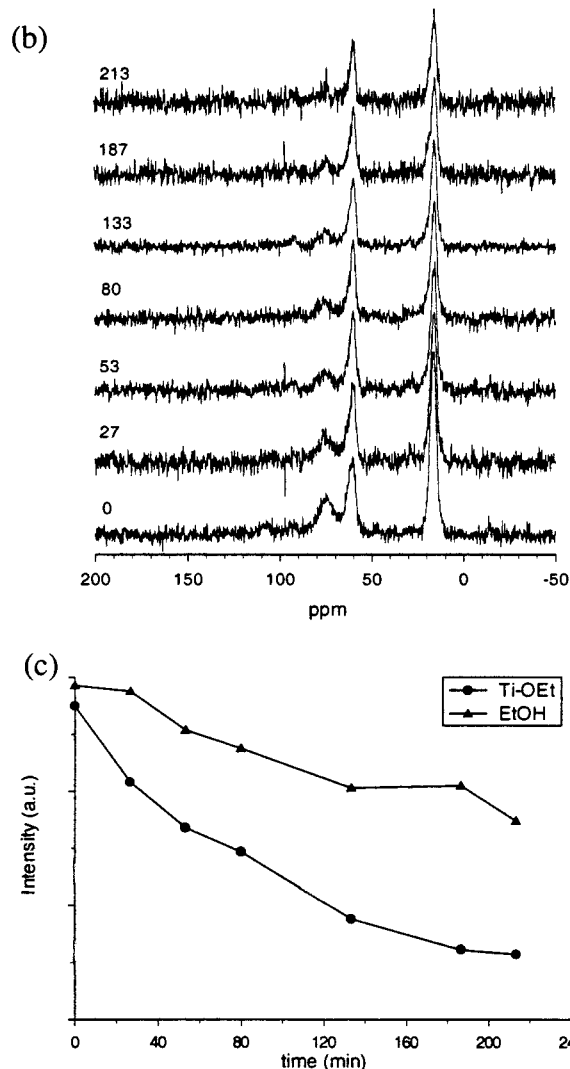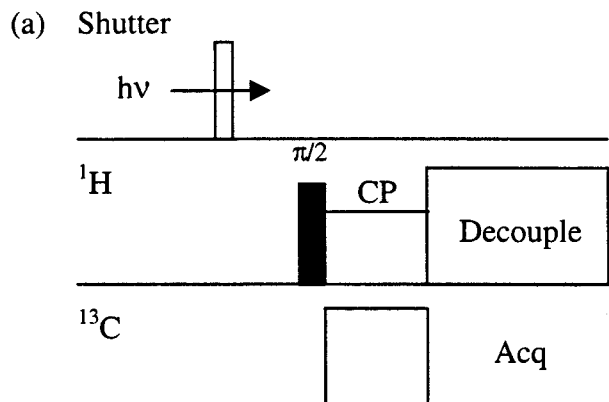
(a) Shutter

(b)

(c)

Figure 6. (a) ^{13}C CP/MAS pulse sequence incorporating a shutter to interrupt UV irradiation. (b) In situ ^{13}C CP/MAS NMR spectra obtained during the photocatalytic oxidation of ethanol (96 μmol) on the TiO$_2$/PVG catalyst. The UV irradiation time is indicated in minutes. (c) Plot of ethoxide and hydrogen-bonded ethanol peak intensities versus UV irradiation time.

3. In Situ SSNMR Study of the Effect of Surface Hydration. The photocatalytic activities of the dehydrated and hydrated TiO$_2$/PVG catalysts were compared using ^{13}C Bloch decay spectra obtained during in situ UV irradiation experiments (Figure 9). Eighty-three min of irradiation of the dehydrated catalyst (Figure 9b) resulted in the formation of the acetaldehyde intermediate (29.6 and 205.0 ppm) and the final product, carbon
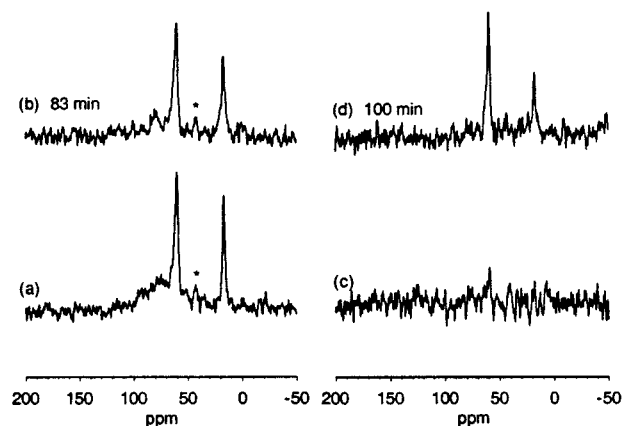
Figure 7. Proton-decoupled ^{13}C CP/MAS NMR spectra of 48 μmol of ethanol and 96 μmol of O$_2$ loaded onto the dehydrated TiO$_2$/PVG catalyst (a) before and (b) after continuous UV irradiation and loaded onto the hydrated TiO$_2$/PVG catalyst (c) before and (d) after continuous UV irradiation.
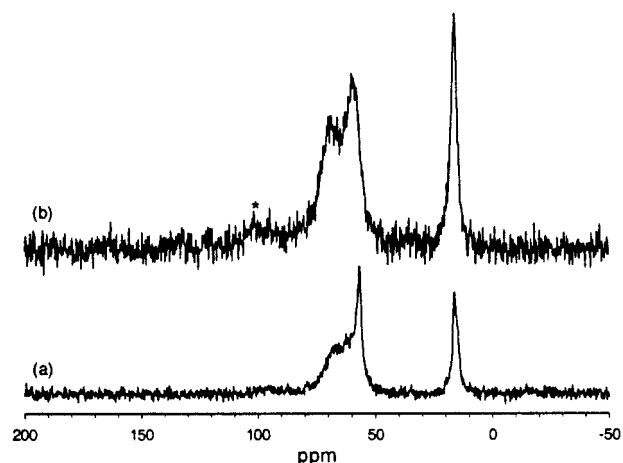
Figure 8. Proton-decoupled ^{13}C CP/MAS NMR spectra of 48 μmol of ethanol and 96 μmol of O$_2$ loaded onto (a) hydrated and (b) dehydrated TiO$_2$ powder catalysts.
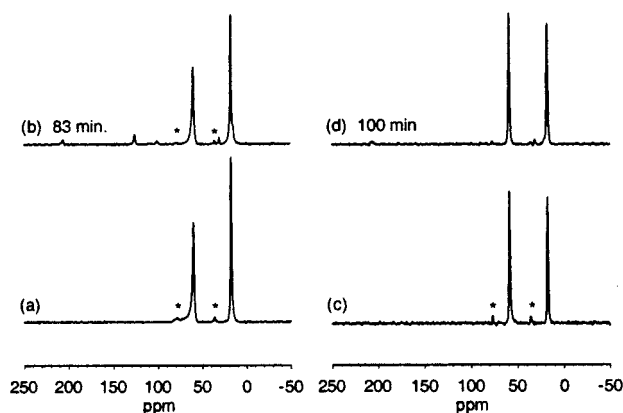
Figure 9. Proton-decoupled ^{13}C MAS NMR Bloch decay spectra of 48 μmol of ethanol and 96 μmol of O$_2$ loaded onto TiO$_2$/PVG catalysts. Dehydrated catalyst (a) before and (b) after continuous UV irradiation. Hydrated catalyst (c) before and (d) after continuous UV irradiation.

dioxide (124.5 ppm), whereas 100 min of irradiation of the hydrated catalyst resulted in the formation of only a small amount of acetaldehyde (Figure 9d). Clearly, the presence of water on the surface of the TiO$_2$/PVG catalyst retards the photooxidation of ethanol to carbon dioxide due to interference

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of water with the active sites. Anpo et al.[43] have also observed that the presence of water on the surface of the catalyst decreases the rate of photocatalytic activity of TiO_2 in experiments on the photocatalytic oxidation of isobutylene and propylene. They attributed this observation to a decrease in valence and conduction band bending caused by the formation of positively charged species on the surface. As a result, the electrons and holes formed when the semiconductor is irradiated recombine more easily than when water is absent.

In addition to information regarding how surface hydration of the TiO_2 catalyst affects the rate of the photooxidation reaction of ethanol, the ^{13}C MAS NMR spectra (Figure 9) provide insight as to how ethanol interacts with the surface of the catalyst. As shown previously, the methylene peak on the dehydrated catalyst consists of a broad component corresponding to the ethoxide and hydrogen-bonded species and a narrow component corresponding to the mobile ethanol species. Because of this broad component, the intensity of the methylene peak is much smaller than the intensity of the methyl peak (Figure 9a). The ^{13}C MAS NMR spectrum of ethanol loaded on the hydrated TiO_2/PVG catalyst prior to irradiation shows methylene and methyl peaks of similar intensity (Figure 9c). In fact, this spectrum is very similar to ^{13}C NMR spectra of liquid ethanol. From this information, it can be concluded that the ethanol has a relatively weak association with the surface and experiences a homogeneous environment on the hydrated catalyst compared to the inhomogeneous environment of the dehydrated catalyst consisting of coordinatively unsaturated and saturated Ti sites. A combination of the lack of ethoxide formation as well as changes in the surface electronic environment may be responsible for the reduction in reactivity.

IV. Conclusions

In situ SSNMR is useful for investigating the photocatalytic oxidation of ethanol as well as other organic compounds on the TiO_2 surface due to its ability to identify mobile and immobile reaction intermediates, its atomic specificity, and its quantitative capabilities. ^{13}CP/MAS NMR provides a broad range of useful information regarding the adsorption sites of ethanol and other reactive intermediates on the surface of a variety of TiO_2 photocatalysts. The following conclusions can be drawn from this work:

1. The photocatalytic oxidation of multiple monolayers of ethanol on TiO_2 powdered catalysts results in the formation of an intermediate, 1,1-diethoxyethane, which is not observed in experiments with low ethanol coverage. The ability to irradiate the interior of the sample using optical microfibers results in the complete conversion of ethanol to acetic acid and carbon dioxide with a rate that is fast compared to those for packed powder and supported monolayer TiO_2 catalysts.

2. Two distinct adsorption sites of ethanol were observed on TiO_2 powder, supported TiO_2 monolayer, and TiO_2/optical microfiber catalysts. Resonances corresponding to the hydrogen-bonded ethanol species and the surface bound ethoxide species were unambiguously assigned. The formation of the fast reacting ethoxide species is critical to efficient photocatalysis. Using experiments designed to model temperature-programmed desorption, we were also able to observe a number of ethoxide species on the TiO_2 powder catalyst.

3. Using CP/MAS NMR experiments, we determined that water and ethanol compete for the same surface sites, with water being the more strongly bound species. UV irradiation enhances exchange between water and ethanol adsorbed on the

TiO_2 surface. The presence of water on the TiO_2 surface has also been shown to retard the rate of photocatalytic oxidation of ethanol because water occupies the coordinatively unsaturated Ti sites that have been shown to be photocatalytically active.

SSNMR experiments will be useful to explore further fundamental issues relevant to photocatalytic surface chemistry, and a broad range of studies on TiO_2 and other photocatalysts are currently underway.

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