ELSEVIER

Catalysis Today 49 (1999) 353–361

CATALYSIS TODAY

In situ solid-state NMR studies of ethanol photocatalysis: characterization of surface sites and their reactivities

Son-Jong Hwang, Daniel Raftery*

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

Abstract

In situ solid-state NMR methodologies have been employed to investigate the photocatalytic oxidation of ethanol (C_2H_5OH) over two TiO_2-based catalysts, Degussa P-25 powder and a monolayer TiO_2 catalyst dispersed on porous Vycor glass. Two adsorption sites were observed for ethanol, a chemisorbed species identified as an ethoxide species, and a hydrogen-bonded species. The Ti-bound ethoxide was found to be the more photocatalytically reactive species. ^{13}C magic-angle spinning (MAS) experiments revealed that long-lived intermediates, including acetaldehyde (CH_3CHO), acetic acid, formic acid, and acetate were observed under dry conditions and in the presence of molecular oxygen. Similar reaction intermediates form on the surfaces of both catalysts. ^{13}C cross-polarization MAS experiments allowed us to identify and follow the evolution of surface-bound species during UV irradiation. Acetate, which forms from mobile acetic acid, appears to be bound to the non-irradiated surfaces of the powdered TiO_2 catalyst, and was also observed on the surface of TiO_2/PVG catalyst, and further degradation was not possible. The presence of molecular oxygen was found to be essential for photooxidation to proceed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Solid-state NMR; Photocatalysis; Magic angle spinning; Titanium-based catalysts; Organic pollutants; Surface processes; Surface chemistry

1. Introduction

Heterogeneous photocatalytic oxidation has been widely investigated because of its potential for efficient detoxification of noxious organic pollutants. A growing interest has developed for efficient and inexpensive methodologies to reduce environmental problems caused by toxic chemicals [1,2], which has spurred the intensive study of photocatalytic processes using a variety of semiconductor materials. Due to its stability and non-toxicity, TiO_2 has been most frequently investigated for the degradation of a variety of environmentally harmful organic molecules including halogenated and non-halogenated compounds. A number of researchers have reviewed the important features of TiO_2 surface chemistry at both the liquid-surface and gas-surface interfaces [3–6].

To date, photocatalytic surface processes are not completely understood, and in particular, photooxidation mechanisms remain elusive for many important organic molecules. Effective use of this technology for waste destruction, therefore, requires further fundamental studies of the relevant surface chemistry. Recently, with an attempt to understand the complex

---

*Corresponding author. Fax: +1-765-494-0239; e-mail: raftery@chem.purdue.edu

PII: S0920-5861(98)00449-0

surface chemistry and to provide complementary information on the mechanisms, we introduced a new approach to the study of photocatalytic oxidation reactions, namely in situ solid-state nuclear magnetic resonance (SSNMR) spectroscopy [7,8]. As described in our previous work, in situ SSNMR observations during near-UV light driven photocatalysis are very valuable for exploring the complex reaction chemistry of organic molecules such as trichloroethylene both in the gas-phase and on the catalyst surface, particularly due to NMR's atomic specificity, high resolution and quantitative capabilities. In this paper, we report on our in situ SSNMR investigation of the photocatalytic oxidation of ethanol on TiO_2 under several different reaction conditions. Ethanol was used in this study because it represents a relatively simple molecule and, along with other aliphatic alcohols, it can be used as a probe of the surface properties of TiO_2. The adsorption and thermal decomposition of ethanol with TiO_2 has been widely used in exploring local coordination environments at the binding sites on TiO_2 surfaces [9–15]. In addition, it is a common solvent in spraying and coating applications and a major component of bakery and brewery emissions.

The photocatalytic oxidation of ethanol using TiO_2 catalysts has been studied previously at the gas–solid interface using a variety of methods [16–22]. The reaction intermediates identified to date include acetaldehyde, acetic acid, formaldehyde, and formic acid [18,19,21,22]. While it is generally agreed that the formation of acetaldehyde is a result of the first oxidation step, the subsequent oxidation to form CO_2 remains controversial. Nimlos et al. [18] proposed a single sequential reaction pathway whereas Sauer et al. [19] and Muggli et al. [21,22] suggested that acetaldehyde is oxidized via parallel reaction channels. The main difference between these kinetic models is whether or not the acetic acid appears as an intermediate on the way to form formaldehyde. Two reaction sites on TiO_2 were postulated to accommodate different reaction intermediates in the two pathways [18,21,22]. Different reactivity of the two ethanol carbons were also proposed by Muggli et al. [21,22]. In these studies, however, no direct spectroscopic evidence regarding the adsorbed species and their reactivities on the near-UV illuminated TiO_2 surface was presented. In the present work, we utilize in situ SSNMR to identify the reaction intermediates, their adsorption, and surface reaction during the photocatalytic oxidation of ethanol. We have used two TiO_2-based catalysts, commercially available Degussa P-25 powder[1] and a monolayer TiO_2 catalyst dispersed on porous Vycor glass (PVG)[2] which we synthesized by vapor deposition [7,8]. In particular, we have focused on the formation and evolution of the surface-bound species on the TiO_2 surface. With careful studies of the structure of our observed reaction intermediates involved during the ethanol photodegradation, we have obtained additional information on the reaction mechanisms.

2. Experimental

2.1. Sample preparation

Photocatalytic oxidation reactions were carried out in sealed glass NMR tubes at room temperature. The experimental procedures for catalyst sample preparation for TiO_2 powder and the supported TiO_2 catalyst are described in detail elsewhere [8]. 180 mg of TiO_2 powder were packed into 5 mm glass NMR tubes (Norell), which were first evacuated at 773 K for 4 h to remove water molecules as well as the majority of surface hydroxyl groups, and then calcined at 773 K in a ceramic heater under 1 atm of O_2 gas for another 4 h. Evacuation down to 2×10^{-5} Torr was followed by cooling the powdered sample to room temperature in the heater. 1,2-^{13}C labeled ethanol (Cambridge Isotope Laboratories) was then loaded onto the pretreated TiO_2 catalyst. Three NMR samples were prepared with ethanol loadings of 16, 48, and 96 μmol (denoted as samples I, II, and III, respectively) and 60 μmol of O_2 each. The NMR tubes were sealed off 10–12 mm above the catalyst sample.

A second TiO_2 catalyst [8] was prepared by dispersing TiO_2 (with coverage of a monolayer) on the surface of a transparent PVG substrate which was 3.6 mm in diameter, 12 mm long, and weighed 180 mg. The TiO_2/PVG was first degassed and then calcined under O_2 at 773 K for 4 h each before loading

---

[1] TiO_2 P-25 powdered catalyst is a gift from Degussa Corp.

[2] Vycor 7930 silicate glass is obtained from Corning, BET surface area ~150 m^2/g, pore diameter 40 Å.

ethanol and O_2. Three NMR samples were prepared with ethanol loadings of 8, 24, and 48 μmol while the O_2 loading was 96 μmol for all the TiO_2/PVG samples.

2.2. NMR methods

A home-built optical/magic angle spinning (MAS) NMR probe [8] and light delivery system were used for the in situ NMR experiments. A 300 W Xe arc lamp (ILC Technology) was used as the UV light source from which near-UV light ($350 < \lambda < 550$ nm) was delivered to the sample using a dichroic mirror (Oriel Corp.) filter and a liquid-filled optical light guide (Oriel Corp.). This liquid light guide was terminated with a 70 mm long quartz rod light pipe, 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 ^1H and ^{13}C observation at frequencies of 300 and 75.4 MHz, respectively, and is capable of spinning the sealed NMR samples at speeds as high as 2.7 kHz. The near-UV light power that reaches the sample was measured to be 5 mW by standard ferrioxalate actinometry [23].

3. Results and discussion

3.1. Adsorption of ethanol on catalyst surfaces

The adsorption of ethanol on the different catalysts was primarily examined by observing ^{13}C NMR signals. Bloch decay and cross polarization (CP) experiments were employed to explore the adsorptivity of bound molecules at the surface. With this approach, chemisorbed molecules can be easily distinguished from either physisorbed or gaseous molecules because a CP/MAS spectrum will be significantly influenced by molecular mobility. Fig. 1 shows proton-decoupled ^{13}C MAS NMR spectra (Fig. 1(a)–(c)) and corresponding proton-decoupled ^{13}C CP/MAS NMR (Fig. 1(e)–(g)) for 48 μmol of ethanol loaded onto catalysts consisting of pure Vycor, TiO_2/PVG, and TiO_2 powder, respectively. A sample with a higher loading of ethanol (96 μmol) on TiO_2 powder was also examined and the resulting spectra are shown in Fig. 1(d) and (h) for ^{13}C MAS and ^{13}C CP/MAS NMR spectra, respectively. Note that CP/MAS spectra were obtained with a short cross-polarization contact time (0.05 ms) in order to detect only the strongly

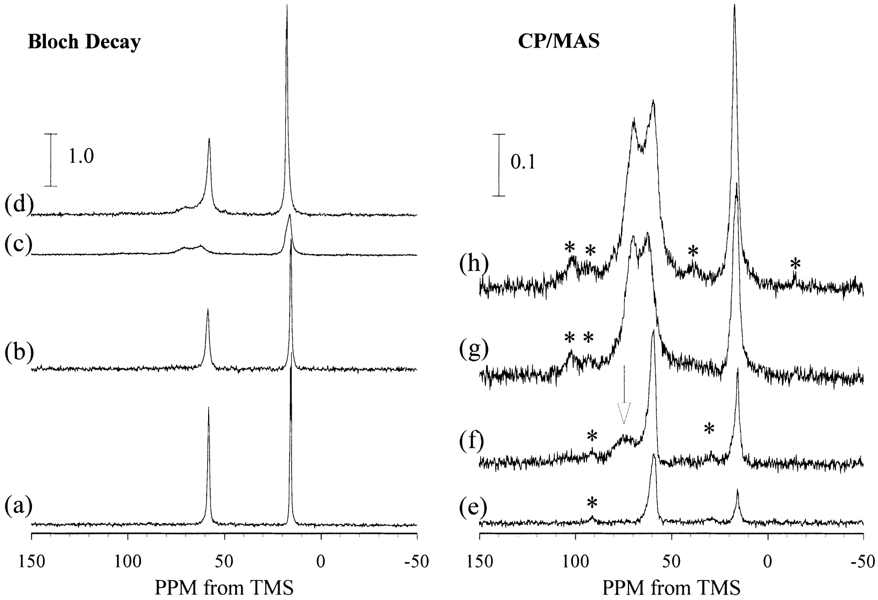

Fig. 1. Proton-decoupled ^{13}C MAS NMR spectra of ethanol on different surface environments. Bloch decay: (a) porous Vycor glass (PVG); (b) TiO_2/PVG; (c) TiO_2 powder with an ethanol loading of 48 μmol; (d) TiO_2 powder with 96 μmol; (e)–(h) CP/MAS with same samples as (a)–(d). The asterisks indicate spinning sidebands of strongly adsorbed species.

bound molecules. In the Bloch decay spectrum, resonances of the methyl (CH_3–) and methylene (–CH_2–) carbons of ethanol on the PVG surface are observed at 15.5 and 58.0 ppm, respectively (see Fig. 1(a)). Their linewidths are ~70 Hz, which indicates that most of the ethanol is either very mobile on the surface or exchanges rapidly between the gas-phase and the surface. The signals observed by CP/MAS NMR (see Fig. 1(e)) represent only a small portion of the ethanol which interacts relatively strongly with hydroxyl groups on the SiO_2 surface. The hydrogen-bonded ethanol species on pure SiO_2 has a methylene carbon resonance at 58.9 ppm. The NMR shifts and linewidths of both ethanol carbons depend considerably on the adsorption site. As shown in Fig. 1(c) and (g), ethanol is immobilized at a minimum of two different sites on the TiO_2 powder with the observed chemical shifts occurring around 62 and 70 ppm for the methylene carbon. The peak areas in the Bloch decay spectrum (Fig. 1(c)) were measured to be approximately the same for the both resonances. The amount of loaded ethanol (48 μmol) corresponds to 3.2 molecules/nm^2, which is roughly the same amount reported for the saturation coverage (2.98–3.3 molecules/nm^2) on the TiO_2 anatase surface [12,13,22]. Binding sites on polycrystalline TiO_2 have been investigated extensively via temperature-programmed desorption studies of ethanol [10–15]. From these studies the existence of two ethanol species are generally agreed upon: (1) a hydrogen-bonded ethanol species, and (2) a surface-bound Ti-ethoxide (CH_3CH_2O-Ti) [12–15], which occurs at coordinatively unsaturated Ti atoms. Two adsorption sites were also discussed by Nimlos et al. [18] who estimated the relative number of sites using GC methods to be roughly 50% dissociation sites and 50% hydrogen bonding sites. Based on evidence presented below, we assign the peaks at 62 and 70 ppm to strongly hydrogen-bonded ethanol and surface-bound ethoxide species, respectively. The peak intensities for each site observed in our studies are in good agreement with the results of Nimlos et al. [18]. When the ethanol concentration was doubled (2 monolayer coverage) on the TiO_2 powder, significant changes in the Bloch decay spectrum (see Fig. 1(d)) were observed while there was no evident change in the line shape of the CP/MAS spectrum (see Fig. 1(h)). Narrow lines in Fig. 1(d) indicate that the additional ethanol molecules that compose the second monolayer are very mobile. Broad peaks underneath these narrow lines remains unaffected, verifying that the surface-bound ethoxides and hydrogen-bonded ethanol molecules are not involved in fast exchange with molecules in the second monolayer. A slight increase in the intensities of both carbons peaks in CP/MAS spectrum (Fig. 1(h)) was observed and a new peak at 59.4 ppm appeared at this high loading, which overshadows the original peak at 62 ppm reducing it to small but repeatedly observed shoulder. ^{13}C MAS NMR spectra (Fig. 1(b) and (f)) reveal how the SiO_2 surface of porous Vycor is modified when a TiO_2 monolayer is dispersed. The presence of two adsorption sites for ethanol is clearly indicated by the two peaks in CP/MAS spectrum (Fig. 1(f)). The broad peak at around 73 ppm marked with an arrow is most likely attributed to the formation of surface-bound Ti ethoxide while the narrower peak at 59.4 ppm can be assigned to hydrogen-bonded ethanol molecules. Ethoxide formation was not observed on the pure PVG surface as indicated in Fig. 1(e). In comparison with this spectrum, the larger intensity of the 59.4 ppm peak and the methyl carbon peak shown in Fig. 1(f) indicate that hydroxyl groups on TiO_2 surface seem to produce more hydrogen-bonded ethanol molecules than the pure PVG surface. The surface area of TiO_2/PVG (~150 m^2/g) is roughly three time higher than TiO_2 powder (~50 m^2/g) samples used in this study. However, as clearly shown in CP/MAS NMR spectra (Fig. 1(f) and (g)), the number of adsorption sites for the ethoxide formation on TiO_2/PVG surface is significantly less than that observed on TiO_2 powder. In addition, the difference in the observed chemical shift of the ethoxide species between the two surfaces (70 and 73 ppm for TiO_2 powder and TiO_2/PVG, respectively) also indicates that ethoxides are located in different electronic environments on the catalysts. Reactivities of the two surface-bound ethanol species were examined and are discussed in the following section.

3.2. Photocatalytic oxidation of ethanol on TiO_2 powder

Photocatalytic oxidation reactions of ethanol on TiO_2 powder were examined as a function of the ethanol loadings. Samples I, II, and III were prepared by loading 16, 48, and 96 μmol of ethanol on 180 mg

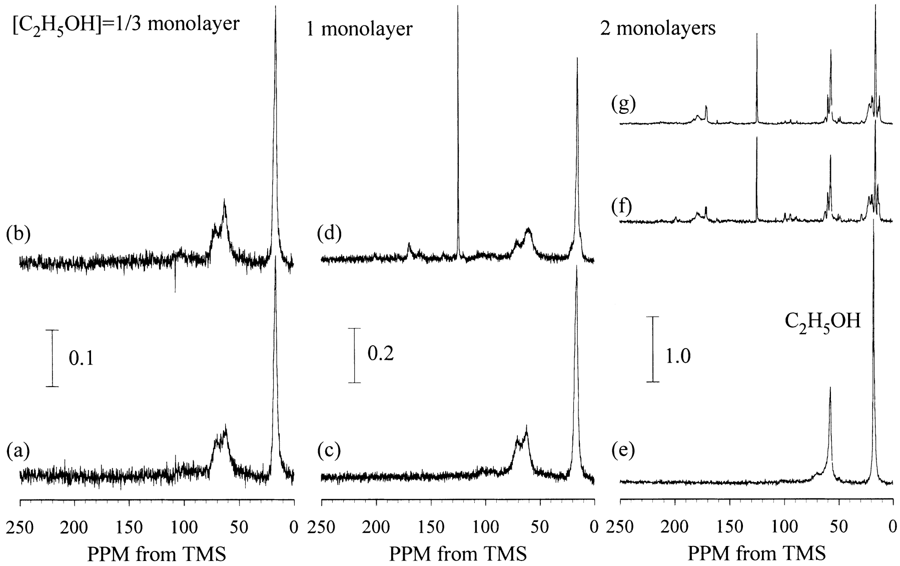

Fig. 2. ^{13}C MAS NMR spectra obtained during photocatalytic oxidation of ethanol on the TiO_2 powdered catalyst. Sample I: 16 μmol ethanol, UV irradiation time (a) 0 min; (b) 140 min. Sample II: 48 μmol ethanol, UV irradiation time (c) 0 min, (d) 115 min. Sample III: 96 μmol ethanol, UV irradiation time (e) 0 min, (f) 210 min, (g) 290 min.

of TiO_2 powder that had been packed in 5 mm NMR tubes. The ethanol concentrations correspond to about 1/3, 1, and 2 monolayer coverages on the powdered catalyst and their ^{13}C MAS NMR spectra are shown in Fig. 2(a), (c), and (e), respectively. ^{13}C MAS NMR spectra were obtained in 14 min intervals (repetition time 4.0 s and 200 accumulations) during continuous UV irradiation, and some of the resulting spectra were displayed in Fig. 2 for the three samples (see Fig. 2(b), (d), (f) and (g)). No reaction occurred in Sample I, while the formation of CO_2 and other reaction intermediates was observed in Sample II and Sample III. Among these intermediates, acetaldehyde (CH_3CHO, 198.7 and 28.8 ppm), acetic acid (CH_3COOH, 171.2 and 19.2 ppm), acetate (CH_3COO^-, 179.0 and 21.9 ppm) and formic acid (HCOOH, 161.2 ppm) were identified and their formation are in good agreement with other studies [16,18,19,21,22], while there was no indication of the formation of formaldehyde (CH_2O). The formation of these intermediates was very low in concentration for Sample II. Most of these intermediates, with the exception of acetate, appear to be mobile on the surface. However, production of CO_2 was observed immediately after UV irradiation. As shown in Fig. 2(c) and (d), a decrease in the ethoxide concentration is more pronounced than that for the hydrogen-bonded ethanol molecules, indicating that the ethoxide species is more reactive. No additional production of CO_2 was observed after about 100 min of UV irradiation. At an ethanol loading of 2 monolayers (Sample III), the broad components in the NMR spectrum were markedly reduced after 20 min of irradiation, and the growth of a new narrow peak around 60 ppm was observed. This result indicates that the surface-bound ethoxide and ethanol molecules are actively involved in the photooxidation process when the surface is illuminated. As shown in Fig. 2(f) and (g), the NMR spectra become very crowded as a result of the formation of several other reaction intermediates, particularly around 90–100 ppm, 59–63 ppm, 45–54 ppm, and 11–14 ppm. These NMR lines have not yet been assigned unambiguously, and complete identification of these species will be published in the future. Unsaturated hydrocarbons such as ethylene or ether compounds are considered to be responsible for those lines, and observation of these intermediates was previously reported [16,21]. Muggli et al. [21,22] proposed that acetaldehyde, formed from the photooxidation of ethanol, adsorbs on two different sites and one of them selectively oxidizes the methylene carbon faster than the methyl carbon. The quantity of acetaldehyde formed from our experiments was very low, and it appeared to be a mobile species so that its adsorption to the surface could not be characterized. The only strongly bound species observed after UV irradiation was acetate, and multiple adsorption sites for the acetate could not be resolved. No further degradation of ethanol or other intermediates was observed after about 150 min of UV illumination. Continuous irradiation up to 290 min brought about the appearance of an intense blue color to the powder, which is an indication of complete O_2 consumption and subsequent accumulation of electrons in the TiO_2 conduction band as the result of efficient hole scavenging by ethanol [24].

Fig. 3(a)–(c) show ^{13}C CP/MAS NMR spectra that correspond to the Bloch decay spectra shown in Fig. 2(e)–(g). The changes in the broad peaks observed at 62 and 70 ppm are highlighted here. It is evident from the significant changes in the spectra that surface-bound species were considerably affected by the photooxidation reaction. This result is in contrast to the expected immobility of ethoxide and hydrogen-bonded ethanol molecules on the TiO_2 powder as discussed in Section 3.1. This result is particularly interesting because of the packed powder conditions used in our experiments in which only TiO_2 particles on the outside wall of the NMR tube are exposed to UV light. Strongly bound molecules residing at non-irradiated regions are expected to remain unaffected during the UV irradiation. This speculation seems to be quite reasonable because no reaction occurred in Sample I (see Fig. 2(a) and (b)) and only a small amount of adsorbed ethanol was oxidized in Sample II. Similar experimental results were observed by us previously in the case of dichloroacetate formation on the TiO_2 powdered catalyst [7,8]. One explanation for this experimental finding is that slow exchange between the first and second adsorbed layers might be at least partly responsible. Water formed as a result of ethanol oxidation could replace hydrogen-bonded ethanol at the surface, but this explanation may not be applicable to the Ti-ethoxide (70 ppm) species [10,12,13,15]. An accumulation of acetate on the surface could accelerate the desorption of ethoxides, and we do observe the formation of acetate. Nimlos et al. [18] proposed in their kinetic model that competition of adsorption sites between ethanol and acetic acid take place. In this case, the formation of acetate (CH_3COO-Ti) is expected since acetic acid is produced as a reaction intermediate. It is also possible that long-lived radical species might cause the destruction of these strongly bound ethoxides. Nevertheless, it is evident that the surface-bound species can be easily removed from the surface when the ethanol loading is higher than a monolayer coverage.

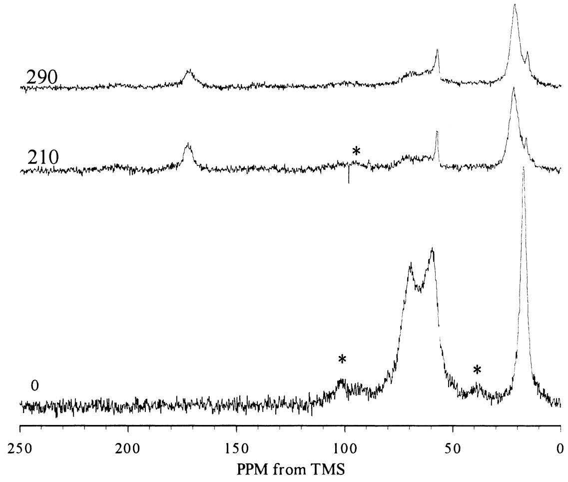

Fig. 3. ^{13}C CP/MAS NMR spectra obtained from Sample III after UV irradiation of (a) 0 min, (b) 210 min, (c) 290 min.

3.3. *Photocatalytic oxidation of ethanol on TiO_2/PVG*

Photocatalytic oxidation of ethanol without oxygen on TiO_2/PVG was first examined as a control experiment. No degradation of ethanol was observed even after 200 min of UV irradiation, while an intense blue color again appeared. It is evident that O_2 is necessary for the photocatalytic oxidation of ethanol to proceed as was emphasized in the case of trichloroethylene [8]. The appearance of the blue color indicates an accumulation of electrons in the conduction band [24]. This result strongly supports the statement that our TiO_2/PVG catalysts exhibit a very similar photocatalytic process to that observed in the powdered catalysts. By comparison, we note that neither a color change nor ethanol photooxidation was observed on

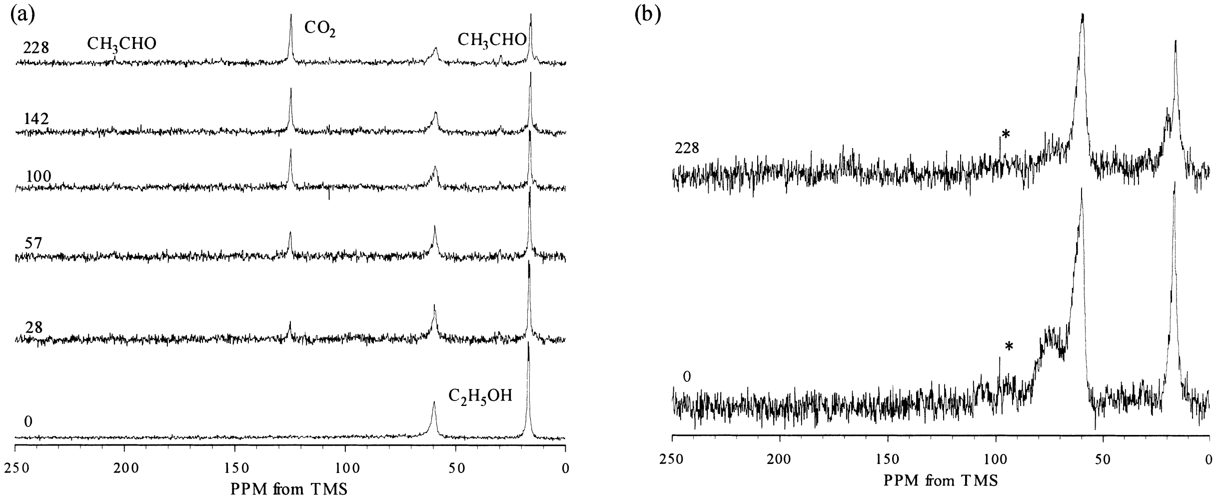

Fig. 4. Proton-decoupled ^{13}C MAS NMR spectra during the photocatalytic oxidation of ethanol on the TiO_2/PVG catalyst (a) and CP/MAS spectra (b). Initial concentration of ethanol is 24 μmol and that of O_2 is 96 μmol. The UV irradiation time in minutes is indicated to the left of each spectrum.

the PVG surface which did not contain TiO_2. Fig. 4(a) shows the in situ NMR observation during the photocatalytic reaction of 24 μmol of ethanol in the presence of 96 μmol of O_2. The production of CO_2 is indicated in the ^{13}C MAS NMR spectra soon after the UV irradiation starts. A reaction intermediate, acetaldehyde, is also present in very low concentration, as indicated by the peaks appearing at 29.6 and 205.0 ppm. No further significant degradation of ethanol occurred after 200 min of irradiation. ^{13}C CP/MAS spectra (see Fig. 4(b)) obtained before and after the UV reaction reveal the photocatalytic acitivities of the ethoxides and the hydrogen-bonded ethanol surface species. Most of the ethoxide species appears to have been destroyed while destruction of the hydrogen-bonded ethanol molecules was negligible. This observation suggests that the adsorption sites for the ethoxides are preferentially active. In addition, Bloch decay spectra shown in Fig. 4(a) reveal that the narrow component of the ethanol lines decreased markedly, whereas the broad component remains unaffected. This evolution of the NMR line shapes indicates that once ethoxides are oxidized and CO_2 is formed mobile ethanol can occupy the sites and can proceed to further catalytic oxidation cycles. On the other hand, hydrogen-bonded ethanol molecules can not compete for the active sites due to their low mobility. Nimlos et al. [18] pointed out that the reaction appeared limited by adsorption of the ethanol when low concentration of ethanol is used. This result implies that oxidation of hydrogen-bonded ethanol is the rate-determining step for completion of the ethanol photooxidation. In fact, complete mineralization of ethanol was not observed even using a very small loading of ethanol (8 μmol) with excess O_2 (96 μmol) and UV irradiation for 300 min.

4. Photocatalytic reactivities of surface-bound species

In order to further examine the reactivity of surface-bound species, we performed the following experiments. 48 μmol of ethanol ($^{12}CH_3$ $^{13}CH_2OH$) and 96 μmol of oxygen were first reacted for about 11 hours until there was no more degradation of ethanol observed due to O_2 deficiency. The resulting CP/MAS spectrum (contact time 3.0 ms) is shown in Fig. 5(a) which reveals the formation of reaction intermediates including acetaldehyde, acetic acid, formic acid as well as the final product CO_2 and unreacted ethanol. Note that the peak intensity of CO_2 appears to be low in the CP/MAS spectrum since only surface adsorbed molecules are detected in this case. The NMR sample

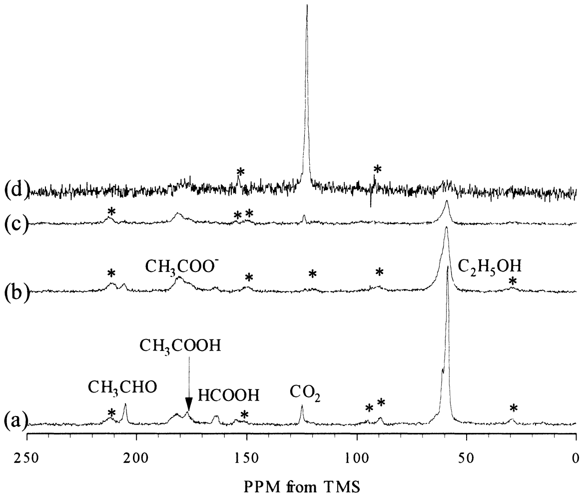

Fig. 5. ^{13}C CP/MAS NMR spectra of ethanol photooxidation on TiO_2/PVG (a) after 11 h of UV irradiation of 48 μmol ethanol with 96 μmol O_2; (b) after the catalyst was evacuated at room temperature and resealed with 96 μmol O_2; (c) after 510 min of UV irradiation; (d) Bloch decay under the same condition as in (c). The asterisks indicate spinning sidebands of the strongly adsorbed species.

was then broken and the catalyst was transferred to a fresh NMR tube, and evacuated to a pressure 2×10^{-5} Torr. Ninety-six μmol of O_2 was re-introduced and the sample was again sealed. The CP/MAS spectrum acquired at this stage of the experiment is shown in Fig. 5(b). The spectrum clearly shows the removal of ethanol and other intermediates in the gas phase after evacuation. The remaining species are assumed to be strongly bound to the surface via hydrogen bonding or coordination to Ti sites. Note that the existence of ethoxide (73 ppm) is not observed in the spectrum as it had been entirely converted. In situ NMR observation was then made after UV irradiation of the sample for 510 min, and the NMR measurements are shown in Fig. 5(c) (CP/MAS) and Fig. 5(d) (Bloch decay). Degradation of surface-bound ethanol, acetaldehyde, acetic acid, formic acid and the formation of CO_2 are clearly revealed in the spectra. Some of the surface-bound ethanol remains unreacted while there was no significant loss in the signal intensity of acetate. This result indicates that hydrogen-bonded ethanol reacts very slowly and acetate is very resistive to further destruction. Assuming the acetate is bound to Ti sites, its degradation mechanism is considered to be different from that of ethoxides (see Section 3.3). In this case, the resistivity of the acetate for photocatalytic oxidation may cause the slow reaction rate of ethanol by blocking the photocatalytic active sites. However, it is also possible that acetate formation takes place on inactive sites such as Si sites on the catalyst surface which could be present in small numbers due to incomplete coverage of the TiO_2. In a previous study, we were able to differentiate between Ti-bound dichloroacetate and Si-bound dichloroacetate [8]. However, in this case, starting with ethanol we do not form acetate on the pure PVG surface and therefore comparison is not possible. We note that the reactivity of acetate on the powdered TiO_2 catalyst could not be examined since acetate resides at the dark regions.

5. Conclusions

1. In situ SSNMR is useful for investigating the photo-initiated surface reactions because of its ability to precisely identify reaction intermediates both in the gas-phase and on the catalyst surface, and to directly quantify these species. Using these methods, the photocatalytic oxidation of ethanol over titania-based catalysts has been studied. CP/MAS NMR was used to investigate the photocatalytic reactivities of individual adsorption sites of ethanol both on the powdered and the supported catalysts.
2. Two different adsorption sites were observed in the spectra when ethanol is loaded on either the powdered TiO_2 catalyst or the supported TiO_2 catalyst. On the supported catalysts the dissociation site, where Ti-ethoxide species are formed, shows photocatalytic reactivity while the reactivity of the hydrogen-bonded ethanol site was negligible.
3. Photocatalytic oxidation of ethanol produces CO_2 as a final product. However complete oxidation of ethanol was never observed due to the slow reaction rate of hydrogen-bonded ethanol. When the O_2 concentration is low, the formation of stable reaction intermediates including acetaldehyde, acetic acid, formic acid, and other unidentified species is observed.
4. Formation of acetate on the surface was observed and it was found to be very difficult to oxidize on the supported catalyst.

5. We believe the SSNMR methods will be very useful to characterize further the surface chemistry of ethanol photooxidation. Currently studies are underway to investigate catalyst deactivation and reactivation processes and will be published at a later date.

Acknowledgements

Partial support for this research from the National Science Foundation (CHE 94-22235 and CHE 97-33188), the Donors of the Petroleum Research Foundation administered by the American Chemical Society, and from the AT&T and Lucent Technologies Industrial Ecology Program is gratefully acknowledged. D.R. is a Cottrell Scholar of the Research Corporation.

References

[1] M. Schiavello, in: M. Schiavello (Ed.), Photocatalysis and Environment: Trends and Applications, vol. 237, NATO ASI Series C, Boston, 1987, 351.
[2] A. Mills, R.H. Davies, D. Worsley, Chem. Soc. Rev. 22 (1993) 417.
[3] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[5] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.
[6] A. Hagfeldt, M. Gratzel, Chem. Rev. 95 (1995) 49.
[7] S.-J. Hwang, C. Petucci, D. Raftery, J. Am. Chem. Soc. 119 (1997) 7877.
[8] S.-J. Hwang, C. Petucci, D. Raftery, J. Am. Chem. Soc. 120 (1998) 4388.
[9] A.V. Kiselev, A.V. Uvarov, Surface Sci. 6 (1967) 399.
[10] I. Carrizosa, G. Munuera, J. Catal. 49 (1977) 174.
[11] I. Carrizosa, G. Munuera, J. Catal. 49 (1977) 189.
[12] K.S. Kim, M.A. Barteau, W.E. Farneth, Langmuir 4 (1988) 533.
[13] V.S. Lusvardi, M.A. Barteau, W.E. Farneth, J. Catal. 153 (1995) 41.
[14] V.S. Lusvardi, M.A. Barteau, W.R. Dolinger, W.E. Farneth, J. Phys. Chem. 100 (1996) 18183.
[15] Y. Suda, T. Morimoto, M. Nagao, Langmuir 3 (1987) 99.
[16] J. Cunningham, E. Finn, N. Samman, Faraday Discuss. Chem. Soc. 58 (1974) 160.
[17] J. Cunningham, D.J. Morrissey, E.L. Goold, J. Catal. 53 (1978) 68.
[18] M.R. Nimlos, E.J. Wolfrum, M.L. Brewer, J.A. Fennell, G. Bintner, Environ. Sci. Technol. 30 (1996) 3102.
[19] M.L. Sauer, D.F. Ollis, J. Catal. 158 (1996) 570.
[20] A.V. Vorontsov, G.B. Barannik, O.I. Snegurenko, E.N. Savinov, V.N. Parmon, Kinetics and Catal. 38 (1997) 84.
[21] D.S. Muggli, S.A. Larson, J.L. Falconer, J. Phys. Chem. 100 (1996) 15886.
[22] D.S. Muggli, J.T. McCue, J.L. Falconer, J. Catal. 173 (1998) 470.
[23] C.G. Hatchard, C.A. Parker, Proc. Royal Soc. London, Ser. A 235 (1956) 518.
[24] R.F. Howe, M. Grätzel, J. Phys. Chem. 89 (1985) 4495.