

Characteristics of Water Adsorbed on TiO₂ Photocatalytic Systems with Increasing Temperature as Studied by Solid-State ¹H NMR Spectroscopy

Atsuko Y. Nosaka,^{*,†} Toshimichi Fujiwara,[‡] Hiromasa Yagi,[‡] Hideo Akutsu,[‡] and Yoshio Nosaka^{*,†}

Department of Chemistry, Nagaoka University of Technology, Nagaoka, 940-2188 Japan, and Institute for Protein Research, Osaka University, Suita, 565-0871 Japan

Received: October 31, 2003; In Final Form: April 27, 2004

The time profiles of the intensities, line widths, and chemical shifts of ¹H NMR signals of adsorbed water at 358 K were investigated for six different TiO₂ photocatalysts with different properties by solid-state ¹H NMR spectroscopy. The apparent single water peak was found to comprise the signals with different line widths and chemical shifts, which correspond to those of the water molecules with different structures and mobility. The adsorbed water region observed with NMR is characterized by three layers: (I) the innermost layer with rigid water molecules with highly restricted mobility and/or hydroxyl groups on the solid surface; (II) the intermediate layer with relatively mobile water molecules; and (III) the outermost layer with highly mobile water molecules. The thickness of the water layer is almost the same for the six photocatalysts. The ratio of the number of the water molecules contained in each layer could be roughly estimated to be 3(I):2(II):5(III). The surface properties of the individual photocatalysts are distinctly reflected in the water molecules in layer I but not in those in layer III.

Introduction

The TiO₂ photocatalyst has been extensively investigated because of practical functions such as strong oxidation power, chemical inertness, and detoxification.^{1,2} The functions are mainly caused by the exertion of the active species produced through the reactions of photogenerated electrons and holes with adsorbed water or titanol on TiO₂. For a better understanding of the various functions of TiO₂, the structures and behaviors of adsorbed water have been intensively investigated with various spectroscopic techniques.^{3–29} Previously, we measured the ¹H NMR spectra of several TiO₂ photocatalysts with different properties in powder form at 295 K by solid-state NMR spectroscopy. The signal intensities were well correlated with their primary particle size and the surface area of the particles, and the peak was attributed to the relatively mobile physisorbed water.²¹ Furthermore, for Degussa P25 we found that the line width of the water peak became broader with a decrease in the intensity by 40% on increasing temperature up to 358 K and that the signal intensity recovered completely in 17 h when the sample was kept at room temperature.²² In the present study, we investigated the more detailed characteristics of the water molecules adsorbed on TiO₂ by observing the behavior of ¹H NMR signals at a high temperature of 358 K for six different TiO₂ photocatalysts in powder form including Degussa P25.

Experimental Section

Six different commercially available TiO₂ powders—Degussa P25 (Japan Aerosil), Hombikat UV-100 (Sachtleben Chemie), ST-01 (Ishihara Techno), F4 (Showa Titanium), AMT-100, and

TABLE 1: Relative Intensities of ¹H NMR Signals and Physical Properties of TiO₂ Photocatalysts²⁴

TiO ₂	NMR intensity	anatase component %	primary particle size nm	BET surface area m ² g ⁻¹	peak intensity/surface area
P25	1.0	80	32	49	7.0
F4	1.2	90	28	56	7.3
AMT-600	1.2	100	30	50	8.1
AMT-100	6.3	100	6	260	8.4
ST-01	7.0	100	7	320	7.5
UV-100	8.7	100	10	270	11.0

AMT-600 (Tayca)—were used as received. All TiO₂ powders were generous gifts from the corresponding manufacturers.

¹H NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz. The spectra were obtained after the Fourier transformation of the FID signals following single-pulse excitation with a pulse duration of 3.0 μs and a 5-s relaxation delay. The FID was multiplied by an exponential apodization function, equivalent to a Lorentzian line broadening of 50 Hz. TiO₂ powder was packed into a 4-mm o.d. ZrO₂ NMR sample tube in contact with the air through a small hole, and the samples were rotated at the magic angle at a rate of 12.6 kHz. To eliminate the background signal of the NMR probe, the spectrum measured with an empty NMR sample tube was subtracted from all of the spectra. All NMR spectra were recorded from samples heated under dry, flowing air. Chemical shifts were measured relative to DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an external reference.

Results and Discussion

¹H NMR spectra of six TiO₂ photocatalysts in powder form measured with magic angle spinning (MAS) presented a single NMR peak with a line width of 300–700 Hz at a half peak height at 295 K. As shown in Table 1, the peak area increases with the decrease in the primary particle size and the increase

* Corresponding author. E-mail: nosaka@nagaokaut.ac.jp. Fax: +81-258-47-9315.

[†] Nagaoka University of Technology.

[‡] Osaka University.

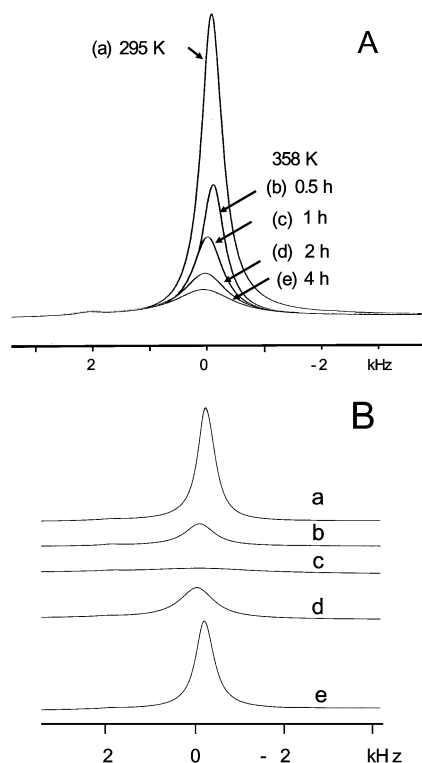


Figure 1. (A) ^1H MAS NMR spectra of TiO_2 powder (ST-01) measured at (a) 295 K and (b) 0.5 h, (c) 1 h, (d) 2 h, and (e) 4 h after the temperature was raised to 358 K. (B) ^1H MAS NMR spectra of TiO_2 powder (ST-01) measured at (a) 295 K, (b) 358 K (2 h after the temperature was raised to 358 K), (c) 295 K (just after the temperature was decreased back to 295 K), and (d and e) 295 K (after the sample was kept at room temperature for 20 h and 1 month, respectively).

in the surface area, as reported previously.²¹ The amount of adsorbed water observed by NMR per unit surface area was estimated by dividing the peak area by the BET surface area, which is almost the same for the six photocatalysts as shown in Table 1 although for UV-100 the value is slightly higher. Therefore, the thickness of the overall adsorbed water layer observed by NMR is considered to be almost the same for the six photocatalysts.

Figure 1A shows the change in the ^1H NMR signal of ST-01 with time when increasing the temperature up to 358 K. The temperature could not be raised above 358 K because of the instrumental limitation. When the sample was kept at 358 K, the signal intensity gradually decreased with increasing line width, and the signal shifted slightly downfield. After 4 h, the peak area decreased by 70% as compared with that at 295 K. When decreasing the temperature back to 295 K, the peak became 3 times broader than that before the temperature increase, as shown in Figure 1B. This broad signal can be ascribed to very rigid water molecules with restricted mobility near the solid surface region or surface OH groups, which remained in the photocatalytic system after the vaporization of volatile water molecules with narrow line widths. This result indicates that sharp and broad water signals cannot be discriminated at 295 K before the temperature increase because of the signal overlap. With increasing temperature and with the vaporization of the mobile water, the rigid water components remaining in the system would become dominant to contribute to the broader signal. When the sample was kept at 295 K, water in the air readsorbed gradually on the surface of the photocatalyst to form mobile water layers. The signal intensity was found to recover completely after 1 month to that before the temperature increase, but in the case of P25, it recovered completely

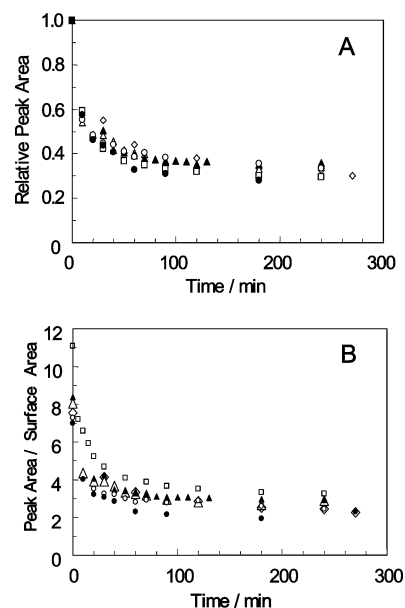


Figure 2. (A) Time profiles of the relative peak area (the ratio of peak area to that measured at 295 K) of ^1H NMR signals of TiO_2 powders measured at 358 K. (\square UV-100, \diamond ST-01, \blacktriangle AMT-100, \triangle AMT-600, \circ F4, and \bullet P25). (B) Time profiles of the peak area per unit surface area (peak area/surface area) of ^1H NMR signals of TiO_2 powders measured at 358 K. (\square UV-100, \diamond ST-01, \blacktriangle AMT-100, \triangle AMT-600, \circ F4, and \bullet P25).

in 20 h.²² Thus, a single peak observed at 295 K comprises the signals with different line widths and chemical shifts, corresponding to the water molecules with different structures and mobility. Although the details of the structure of water on the surface of TiO_2 have not been well elucidated, these results suggest that the adsorbed water regions of the photocatalysts should consist of complex layers in which water molecules take a variety of structures and mobility.

The time profiles of the peak area measured at 358 K for six different TiO_2 photocatalysts are shown in Figure 2A. The relative peak area (the ratio of the peak area to that measured at 295 K) decreased by 40–50% in the first 10 min, and about 20% of the water peak decreased more slowly in the following 2 h. The remaining 30% of the water peak barely decreased even after another 2 h, indicating that the water molecules are highly stabilized in the system. These results imply that about 50% of the water molecules are very mobile and easy to volatilize, 20% are less mobile and harder to volatilize, and the rest (about 30%) are highly stabilized water molecules and/or surface hydroxyl groups. On the basis of this characteristic feature of the time profile, the water region observed by ^1H NMR could be described as three layers as illustrated in Figure 3, that is, (I) the layer with highly stabilized water and/or dissociative water (OH groups) near the solid surface, (II) the intermediate layer consisting of relatively mobile water, and (III) the outermost layer with the most mobile (volatile) water. The ratio of the number of water molecules contained in each layer could be roughly estimated to be 3(I):2(II):5(III). By adsorbing water molecules on TiO_2 powders at 140 K under ultrahigh vacuum conditions, Beck et al. observed temperature-programmed desorption (TPD) spectra of anatase, which presented two water desorption states at about 200 (I) and 300 K (II).¹⁵ The two H_2O peaks in state I were assigned to desorption from islands of molecular H_2O . The nonsaturating peak was assigned to multilayers, whereas the higher-temperature shoulder was assigned to the monolayer. State II was interpreted as water molecules bound to the surface through

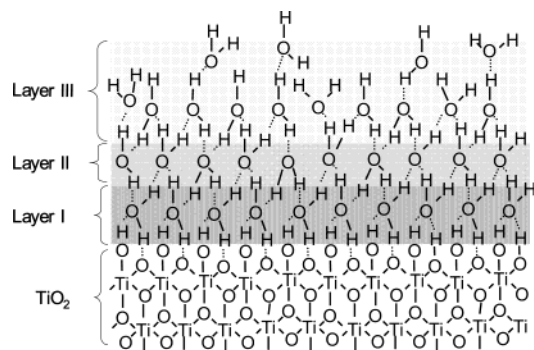


Figure 3. Plausible structure of water layers I, II, and III at the idealized TiO₂ surface deduced from the ¹H NMR observations.

hydrogen bonds to surface oxygen anions. However, from the IR measurement of a TiO₂ film of anatase under flowing dry air, Finnie et al. observed two types of coordinated H₂O species on the TiO₂ surface. The first species at 3696 and 3573 cm⁻¹ (non-H-bonded and H-bonded, respectively) is relatively loosely held and is rapidly desorbed from the surface with mild heating. The second water species with bands at 3634 and 3474 cm⁻¹ (non-H-bonded and H-bonded, respectively) is bound more strongly, and its concentration decreases slowly with heating to below the detection limit at 398 K.²⁹

Figure 2B shows the time profile of peak areas per unit surface area at 358 K. The time profiles for six photocatalysts mainly agree each other and are well correlated with those of relative intensities (Figure 2A). This means that the thickness of the three layers does not differ significantly among the six photocatalysts. Because the value for UV-100 is slightly high, the water layers for UV-100 might be slightly thicker than for the other five photocatalysts. From the weight difference of the TiO₂ powder sample (UV-100) before the temperature increase and after the sample was kept at 358 K for 4 h, the number of water molecules could be roughly estimated to be 4.8×10^{14} , 3.2×10^{14} , and 8.0×10^{14} molecules/cm² for layers I, II, and III, respectively. Because the TiO₂ samples in the present study are anatase abundant powders, the results cannot be directly compared with those reported for rutile. However, for the TiO₂ of the rutile crystal form, the exposure at which the first layer saturated on the (1 × 1) surface of the (100) facet was estimated to be about 7.5×10^{14} molecules/cm² on the basis of the results of TPD measurements by Henderson.²⁰ Because this exposure is approximately equivalent to the surface number density of five coordinate Ti⁴⁺ sites on the (1 × 1) surface (7.36×10^{14} molecules/cm²), he suggested that these sites bind water molecules in the first layer. However, the concentration of H₂O coordinated to the surface of a predried TiO₂ film of anatase was estimated to be 5×10^{14} molecules/cm², corresponding to an initial coordination of H₂O species to 65% of the available Ti⁴⁺ sites at the preferentially exposed anatase (101) surface. The concentration decreased to 0.65×10^{14} molecules/cm² over the temperature range from 300 to 423 K.²⁹

The time profiles of the line width at half peak height measured at 358 K for six TiO₂ photocatalysts are shown in Figure 4. The values at time 0 indicate the line widths measured at 295 K. The line widths became sharper just after the temperature increase and then became broader along with the further vaporization of water. Just after the increase in temperature from 295 to 358 K, most of the mobile (volatile) water molecules still remain in the system. Because of the gained mobility due to the temperature increase, the line width of the mobile water molecules became sharper. The line widths became broader with time, indicating that after the mobile (volatile)

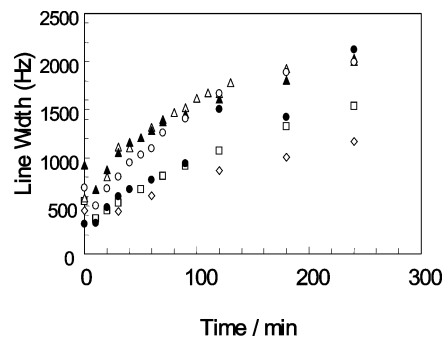


Figure 4. Time profiles of the line width at half peak height of ¹H NMR signals of TiO₂ powders measured at 358 K. (□ UV-100, ◇ ST-01, ▲ AMT-100, △ AMT-600, ○ F4, and ● P25). The line widths measured at 295 K are plotted at time 0.

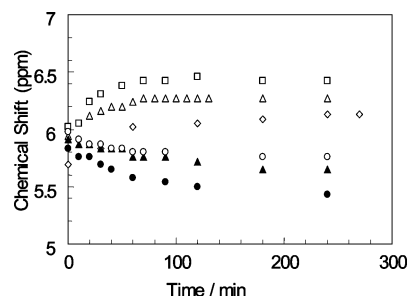


Figure 5. Time profiles of chemical shifts of ¹H NMR signals of TiO₂ powders measured at 358 K. (□ UV-100, ◇ ST-01, ▲ AMT-100, △ AMT-600, ○ F4, and ● P25). The chemical shifts measured at 295 K are plotted at time 0.

water molecules with sharp line widths were evaporated the less-mobile water signals with broader line widths, which were hidden under the more-mobile water signals, successively appeared. The line widths of the water molecules for the six photocatalysts do not differ significantly in the first 10 min. However, after 10 min each photocatalyst began to present the characteristic line width. After 180 min, the line widths of AMT-100, AMT-600, and F4 are almost the same and are much broader than those for ST-01, P25, and UV-100. These results suggest that the mobility and the structure of water molecules in layer III (the outermost layer) are similar among the six photocatalysts, but this is not the case in the inner layer, especially in layer I near the solid surface. Because line widths increased in the order of ST-01 < UV-100 < P25 < AMT-100, AMT-600 and F4, the water molecules in layer I for ST-01 are suspected to take the most mobile structures as compared to those for the other five photocatalysts on the assumption that the line width is determined predominantly by dipole–dipole interactions between protons. Water tends to interact with ionic surfaces by various types of forces and shows the ability for self-association and organization of long-range order on solid surfaces. The molecular motions of water in adsorbed layers and the degree of dissociation likewise depend on the nature of the underlying surface.

The time profiles of chemical shifts measured at 358 K for six TiO₂ photocatalysts are shown in Figure 5. The values at time 0 indicate the chemical shifts measured at 295 K, which correspond to those of the mobile water molecules in layer III that are dominant before the temperature increase. Because the chemical shift difference among the six photocatalysts at 295 K is within 0.5 ppm (6.2–5.7 ppm), the chemical environment of the water molecules in the outermost layer (III) is considered to be similar among the six photocatalysts. When temperature was increased to 385 K for UV-100, AMT-600, and ST-01, the water signal shifted to lower field with time, whereas for F4,

AMT-600, and P25, it shifted to higher field from that at 295 K and thus the chemical shift difference among the six photocatalysts became diverse. The chemical shifts observed 2 h after the temperature increase correspond to those of the water molecules stabilized near the solid surface in layer I. Thus, the fact that the chemical shifts and line widths of the water molecules near the solid surface are characteristic for the six photocatalysts with different properties indicates that the structure, mobility, and chemical environment of the water molecules in layer I are considerably diverse, reflecting the difference in the surface structures and properties of individual photocatalysts.

The adsorbed water is considered to be stabilized by strong hydrogen bonds to form water associates. Hydrogen bonding has a large influence on the ^1H NMR shift and gives a low-field shift of the resonance lines. As expected, the signals of adsorbed water molecules appear in the range from 6.5 to 5.4 ppm, which is lower than that of liquid water (4.8 ppm at 295 K). Because the structure of the water molecules in layer I would be stabilized by stronger hydrogen bonds than those in layer III, the water signals in layer I are expected to appear at lower field than those in layer III. However, for the three photocatalysts (P25, F4, and AMT-600) the water signals shifted to upper field. There must be other factors that affect the chemical shift.

Powders of titanium dioxide characterized by a high specific surface area are prepared using two basic methods: combustion of TiCl_4 in the hydrogen/oxygen flame or hydrolysis of titanium sulfate. Six different photocatalytic samples used in the present study were prepared by the original preparation procedure developed by the supplier; these cause the variation on the solid surface. Proton chemical shifts for the water molecules bonded to different types of surface sites differ significantly. The most important sites are surface hydroxyl groups, and the state of adsorbed water on solid oxide surfaces in general is closely related to the properties, concentration, and configuration of surface hydroxyl groups. The interactions with water molecules are determined mainly by the formation of the hydrogen bond network between water molecules and surface hydroxyl groups. From the temperature dependence of IR spectra of the TiO_2 film of anatase, Finnie et al. reported that the terminally bound hydroxyl species observed at 3730 cm^{-1} is obscured by broadening and red shifting on H bonding with coordinated H_2O but grows in intensity with the dehydration of the surface. In contrast, bridging hydroxyls, which appear at 3670 cm^{-1} , do not undergo H-bonding interactions with H_2O . Above 373 K, the concentration of bridging hydroxyls is reduced by heating but is replenished by the dissociative absorption of H_2O on cooling to 398 K, when the molecular absorption of H_2O begins.²⁹ For the ^1H NMR MAS spectra of anatase TiO_2 samples dehydrated in vacuum at 523 and 773 K, two main peaks at 6.4 (A) and 2.3 (B) ppm were observed.²⁵ Low-field peak A was attributed to the positively charged more acidic protons located on bridged O atoms, whereas high-field peak B was ascribed to more basic H atoms bound to the terminal oxygen. The observed proton signal in layer I in the present study may contain the signals of the adsorbed water molecules hydrogen bonded to the terminally bound hydroxyl species (B). The high-field chemical shift of water signals in layer I observed for P25, F4, and AMT-600 might indicate the existence of the more-abundant basic H atoms bound to the terminal oxygen on the solid surface of these photocatalysts. The isoelectronic points measured for the individual photocatalysts would support this.²⁶ As shown in Table 2, the water peak measured 4 h after the temperature increase to 358 K actually shifts to the higher field

TABLE 2: Chemical Shift of ^1H NMR Signals Measured at 385 K and Isoelectronic Points of TiO_2 Photocatalysts²⁶

TiO_2	chemical shift ^a ppm	isoelectronic point pH
P25	5.4	4.1
F4	5.8	
AMT-600	5.7	5.0
AMT-100	6.3	5.4
ST-01	6.1	5.9
UV-100	6.4	

^a Chemical shift measured 4 h after the temperature increase to 385 K.

with increasing isoelectronic point or basicity of the photocatalysts. Thus, besides the hydrogen bonding, the observed chemical shift of water might reflect the acidity of the solid surface, which is intimately related to the photocatalytic activity.

Six TiO_2 samples exhibit different photocatalytic activities. Together with the particle size, the presence of surface impurities from the various synthetic procedures used is an important factor in such variability of the activities. Therefore, we used the samples as received because the aim of the present study is to investigate the correlation between the photocatalytic activities of commercially available TiO_2 powders and the properties of the adsorbed water. Some commercially available TiO_2 powders contain significant amounts of organic compounds, and we actually detected the ^1H NMR signals. However, for the samples used in the present study, such notable signals were not detected even after the vaporization of the water molecules in layers II and III at 358 K. Therefore, the contribution of the effect of the organic compound to the line widths and chemical shifts of the water molecules in layer I for the TiO_2 samples used in the present study would not be significant. The impurities that significantly affect the line width and chemical shift would be paramagnetic metals. If paramagnetic metals are present in amounts large enough to affect the line width and the chemical shift of the water molecules in layer I, then they must also affect those of the water molecules in layer III to some extent. Because the difference in the chemical shifts and the line widths of water molecules in layer III are small among the six different TiO_2 species, the contribution of paramagnetic metals in the systems to the line width and the chemical shift would also be negligibly small.

As stated above, the chemical shift and line width of the adsorbed water, especially the water in layer I, are quite sensitively affected by the surface properties of the individual photocatalysts. This fact suggests the potential to employ the NMR chemical shifts of the water signal in layer I as one of the parameters assisting in the evaluation of the applicability of the photocatalysts for desired purposes. Further investigations of the relation of the chemical shifts to the various photocatalytic activities and the more detailed water properties with different photocatalysts calcined up to 923 K in an electric furnace are proceeding in our laboratories.

Conclusions

The number of water molecules per surface unit observed by ^1H NMR is found to be almost the same for the six different photocatalysts studied, although they possess different physical properties such as primary particle size, crystal size, crystal form, and BET surface area. The water region observed by ^1H NMR could be described by three layers: (I) the layer with the rigid structured water with restricted mobility near the solid surface; (II) the intermediate layer consisting of relatively mobile water;

and (III) the outermost layer with the most mobile (volatile) water. The number of water molecules contained in each layer could be roughly estimated to be 4.8×10^{14} , 3.2×10^{14} , and 8.0×10^{14} molecules/cm² for layers I, II, and III, respectively. The water molecules in the outermost layer are not significantly affected by the properties of individual photocatalysts. However, the water molecules in the innermost layer (I) are quite sensitively influenced by the surface environment of the individual photocatalysts.

Acknowledgment. This work was supported in part by a Grant-in-Aid on the Priority Area (417) from the Ministry of Education, Culture, Science and Technology (MEXT) and also by the Core Research for Evolution Science and Technology (CREST) from the Japan Science and Technology Agency (JST).

References and Notes

- (1) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (2) Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Photochem. Photobiol., C* **2000**, *1*, 1.
- (3) Sato, S.; Kadowaki, T.; Yamaguti, K. *J. Phys. Chem.* **1984**, *88*, 2930.
- (4) Sato, S. *J. Phys. Chem.* **1987**, *91*, 2895.
- (5) Lopez, A.; Tuilier, M. H.; Guth, J. L.; Delmotte, L.; Popa, J. M. *J. Solid State Chem.* **1993**, *102*, 480.
- (6) Blanchard, J.; Bonhomme, C.; Maquet, J.; Sanchez, C. *J. Mater. Chem.* **1998**, *8*, 985.
- (7) Hugenschmidt, M. B.; Gamble, L.; Campbell, C. T. *Surf. Sci.* **1994**, *302*, 329.
- (8) Boehm, H. P. *Discuss. Faraday Soc.* **1971**, *52*, 264.
- (9) Munuera, G.; Stone, F. S. *Discuss. Faraday Soc.* **1971**, *52*, 205.
- (10) Henderson, M. A. *Surf. Sci.* **1996**, *355*, 151.
- (11) Henderson, M. A. *Langmuir* **1996**, *12*, 5093.
- (12) Jones, P.; Hockey, J. A. *Trans. Faraday Soc.* **1971**, *67*, 2669.
- (13) Jones, P.; Hockey, J. A. *Trans. Faraday Soc.* **1971**, *67*, 2679.
- (14) Primet, M.; Pichat, P.; Mathieu, M. V. *J. Phys. Chem.* **1971**, *75*, 1216.
- (15) Beck, D. D.; White, J. M.; Ratcliffe, C. T. *J. Phys. Chem.* **1986**, *90*, 3123.
- (16) Phillips, L. A.; Raupp, G. B. *J. Mol. Catal.* **1992**, *77*, 297.
- (17) Nakamura, R.; Ueda, K.; Sato, S. *Langmuir* **2001**, *17*, 2298.
- (18) Shao, L.; Zhang, L.; Chen, M.; Lu, H.; Zhou, M. *Chem. Phys. Lett.* **2001**, *343*, 178.
- (19) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. *J. Phys. Chem. B* **2000**, *104*, 9842.
- (20) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *464*, 1.
- (21) Nosaka, A. Y.; Fujiwara, T.; Yagi, H.; Akutsu, H.; Nosaka, Y. *Chem. Lett.* **2002**, 420.
- (22) Nosaka, A. Y.; Fujiwara, T.; Yagi, H.; Akutsu, H.; Nosaka, Y. *Langmuir* **2003**, *19*, 1935.
- (23) Nosaka, A. Y.; Kojima, E.; Fujiwara, T.; Yagi, H.; Akutsu, H.; Nosaka, Y. *J. Phys. Chem. B* **2003**, *107*, 12042.
- (24) Hirakawa, T.; Nakaoka, Y.; Nishino, J.; Nosaka, Y. *J. Phys. Chem. B* **1999**, *103*, 4399.
- (25) Mastikhin, V. M.; Mudrakovsky, I. L.; Nosov, A. V. *Prog. NMR Spectrosc.* **1991**, *23*, 259.
- (26) Teraoka, Y.; Shibata, Y.; Kusaba, H. *Proceeding of 24th Reference Catalysts Meeting, Catalysis Society of Japan* **2003**, 24.
- (27) Theil, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211.
- (28) Suda, Y.; Morimoto, T. *Langmuir* **1987**, *3*, 786.
- (29) Finnie, K. S.; Cassidy, D. J.; Bartlett, J. R.; Woolfrey, J. L. *Langmuir* **2001**, *17*, 816.