

H₂ production from methanol on photoirradiated TiO₂ as studied by electron spin resonance spectroscopy at cryogenic temperature.

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Abstract: Three anatase TiO₂ samples calcined at 573 K for 5, 15, and 240 min (designated as ST01-5, 15, and 240), were photoirradiated (365 nm) with methanol at room temperature or 20 K. ST01-240 showed the highest H₂ production both at 20 K and room temperature. ESR spectra of these TiO₂ samples with methanol at 20 K showed signals attributable to •CH₂O-Ti-(TiO₂) radical (formaldehyde radical adsorbed on Lewis acid sites), Ti³⁺ and holes. Mechanism of the radical formation was discussed.

Keywords: adsorbed formaldehyde radical, Lewis acid sites, *g* value shift

1. Introduction

Temperature range between 573 and 773 K are normally applied for calcination of anatase titanium oxides in usual studies. We have found that a reference catalyst of titanium oxide JRC-TIO-14 (anatase), alias ST01, having specific surface area of 298.0 m²g⁻¹, reduced the surface area almost half of initial one only by 15 min calcination at 573 K. It is interesting to know how the photocatalytic ability changed with the calcination time. In this study, we have tried to evaluate the effect of the calcination as a function of calcined time for photocatalytic H₂ production from methanol. Amounts of H₂ and radicals produced in the samples are determined by microGC and cryogenic electron spin resonance spectroscopy, respectively. The structure of the radical species and the radical formation mechanism will be discussed.

2. Experimental

A reference catalyst of titanium oxide JRC-TIO-14 (anatase), alias ST01, was kindly supplied by Catalysis Society of Japan. The ST01 samples were calcined at 573 K under atmospheric condition for 0, 5, 15, and 240 min (designated as ST01-0, -5, -15, and -240). Each sample was put into a quartz ESR tube and degassed for 10 min (ca. 10⁻² Torr) at room temperature, then equimolar of methanol was introduced. The tube was sealed after He gas injection of 180 Torr as thermal conducting media. ESR measurements with photoirradiation (365 nm) were performed at 20 K for 8 ~120 min. Amounts of produced H₂ at 20 K and room temperature were evaluated at room temperature by a micro GC with Ar-gas carrier by using the same samples for ESR measurements. XRD and diffuse reflectance UV-Vis spectra were also measured for the samples.

3. Results and discussion

Characterization of each calcined samples are summarized in Table 1. Longer calcination time induces decrease in surface area and increase in crystalline sizes. These changes with slight decrease in band gaps indicate that aggregation of first particles with crystal growth has been under progress during the calcination. Amounts of produced H₂ from methanol by photoirradiation at 20 K or room temperature are also summarized in Table 1. ST01-240 at 20 K showed the highest yields, and the yields were larger in longer calcined photocatalysts both at 20 K and room temperature. Increase in H₂ yields cannot be explained by increasing surface area. In addition, the yields at 20 K were larger than those at room temperature.

Table 1. Characterization of calcined ST01 samples, H₂ yields, g_{//} value, and relative line width of Ti³⁺ with methanol.

Calcination time / min	BET surface area / m ² g ⁻¹	Crystalline size / nm	Band gap / eV	H ₂ yields / nmol g ⁻¹		g _{//} of Ti ³⁺	Relative line width of g _⊥ of Ti ³⁺
				20 K	Room temp.		
0	298.0	8.1	3.30	68	41	1.9561	1.0
5	213.3	9.1	3.30	76	44	1.9562	1.4
15	147.3	9.8	3.29	135	73	1.9566	1.5
240	115.9	11.4	3.28	156	78	1.9580	1.6

ESR spectra at 20 K of the photoirradiated ST01-240 with methanol and simulated ones are shown in Figure 1. The experimental signal is reproduced with summation of simulated signals of hole, Ti³⁺ and •CH₂OTi-(TiO₂) radicals. No other radical species was clearly observed such as free •CH₂OH, •H radicals, where •H radicals usually have never been observed even at 4.2 K in organic compounds except CH₄ due to tunneling H atom abstraction reactions. ESR parameters of free •CH₂OH radical was reported as g = 2.0030, |A_{//}| = 2.5 mT, and |A_⊥| = 1.6 mT,¹ but g value in this sample is 1.9997. This minus g shift arises from chemical adsorption of •CH₂O to Ti sites to make •CH₂OTi-(TiO₂) radicals. Theoretical calculation of •CH₂OTi(OH)₃ supports this minus g shift and slight increase in HFCC(A).

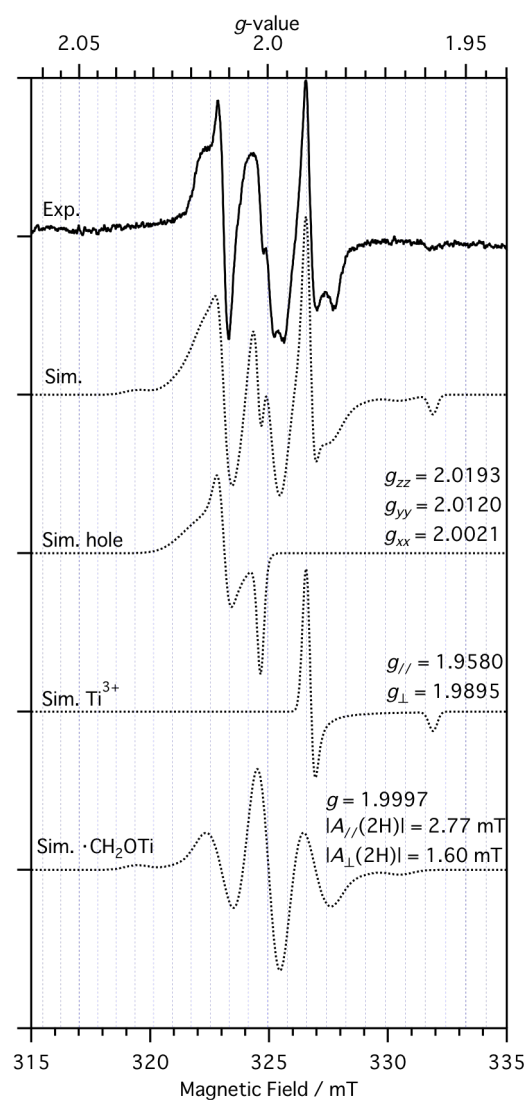
CH₃OH can chemically adsorbed to the surface Ti⁴⁺ as Lewis acid sites to make CH₃OTi-(TiO₂). Protons would be released from CH₃OTi-(TiO₂) by holes making with •CH₂OTi-(TiO₂) radicals, and the released protons would be reduced to be •H radicals by the photoexcited electrons. Otherwise CH₃OTi-(TiO₂) would react with the diffused •H radicals to produce H₂ and •CH₂OTi-(TiO₂) via tunneling reaction at 20 K. Decrease in the yield of H₂ under photoirradiation at room temperature is probably due to increased ratio in desorbed states of CH₃OH, or recombination reactions of electron-hole or radical species such as •CH₂O and H atoms.

Larger g_{//} value shift from ST01-0 to 240 with CH₃OH (Table 1) can be explained by crystal field change around Ti³⁺ by adsorption of CH₃OH. Increase in line width of g_⊥ peak of Ti³⁺ from ST01-0 to 240 with CH₃OH (Table 1) can be explained as an increase in magnetic moment of protons in CH₃OH around Ti³⁺.

These results indicate that the increase in calcination time at 573 K for ST01 induced an increase in the adsorption sites of Ti⁴⁺ (or 3+) as Lewis acid sites for CH₃OH. Because the surface HO-Ti sites in the TiO₂ samples should decrease with increasing calcination time, main adsorption sites for methanol would vary from the HO-Ti sites to the Lewis acid sites. Increase in the Lewis acid sites by calcination should be one of the important factors for the increased photocatalytic activity of producing H₂ from methanol.

References

1. T. Ogawa, G. A. Carlson, G. C. Pimentel, J. Phys. Chem. 74 (1970) 2083.

**Figure 1.** ESR spectrum of photoirradiated ST01-240 at 20 K, and simulated spectra of oxygen hole, Ti³⁺, and •CH₂OTi-(TiO₂).