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ESR AND PHOTOLUMINESCENCE EVIDENCE FOR THE PHOTOCATALYTIC FORMATION OF HYDROXYL RADICALS ON SMALL TiO_2 PARTICLES

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ESR and photoluminescence studies have clarified that UV irradiation of the small TiO_2 particle in the presence of H_2O leads to the formation of $\dot{O}H$ radicals, which are formed by trapping of photo-formed holes by the surface OH^- groups.

From the point of view of the photochemistry of the solid surfaces as well as potential utilization of solar energy, photocatalysis with various semiconductors such as TiO_2 have been investigated by a number of workers. Although it has been proposed that OH radicals would be formed by the trapping of photo-formed hole by OH^- groups, playing a significant role in the photocatalytic reaction over metal oxide catalysts, especially, with TiO_2 catalysts,1) direct evidence for their formation on the catalyst has not been given, except for the report by Bard et al.,2) who detected the $\dot{O}H$ radicals by ESR by using spin-trapping agents. Few studies have been made on the detection of $\dot{O}H$ radicals in the gas-solid system. For this purpose, it has been undertaken to obtain the direct evidence for the formation of $\dot{O}H$ radicals on the synthesized small particle TiO_2 having an average particle size of 50-500 Å and BET surface area of about 1000-200 m^2/g, by using ESR techniques and photoluminescence measurements.

The pure TiO_2 (anatase) samples were prepared by slow hydrolysis of $TiCl_4$ in a dilute solution of $(NH_4)_2SO_4$ and NH_4OH at 280 K, well washed, and then dried at 298 K in vacuum condition. Then, the samples were calcined at the temperature range of 298-775 K. X-Ray diffraction analysis showed that the catalyst consists of only anatase type TiO_2 with particle diameter increasing from 50 to 500 Å with the calcination temperatures. ESR measurements were carried out using a JES-ME-1 (X-band) spectrometer at 77 K under UV irradiation of TiO_2 sample, which had been degassed at 350 K and then adsorbed more than monolayer H_2O on its surfaces. Photoluminescence spectra were measured at 77 K using a Shimadzu RF-501 spectrofluorophotometer equipped with a 500 W Xe lamp.

The TiO_2 sample calcined at 453 K has a particle size of 65 A and BET surface area of 609 m^2/g, and exhibits absorption band at less than 400 nm having a band gap of 3.4 eV and a blue shift of 0.18 eV as compared with those for bulk crystallite of TiO_2. Figure 1 shows the photoluminescence spectrum at 77 K of the TiO_2 having the monolayer of H_2O adsorbed, which had been degassed at temperature above 373 K before the adsorption of H_2O. The spectrum exhibits a maximum at around 500 nm and a maximum of its excitation spectrum at around 340 nm, being in a good agreement with the absorption band of the catalyst. The photoluminescence decreases in intensity with increasing degassing temperature of the catalyst, i. e., decreasing amount of adsorbed H_2O and/or surface OH^- groups on the sample. On the other hand, it was found that an increase in the amount of H_2O adsorbed on the sample leads to an increase in the photoluminescence intensity. The addition of O_2 onto the sample leads to an efficient quenching of the photoluminescence (Fig. 1). These results clearly indicate that the photoluminescence is a surface phenomenon associated with the presence of adsorbed H_2O/or surface OH^- groups. In fact, Maria and McGlynn have reported that the photoluminescence around 450 nm observed with the systems containing the OH^- ion is attributed to the emission of the $\dot{O}H$ radicals,[3)] although its position varies from one system to another, reflecting the environment of the OH^- ions.

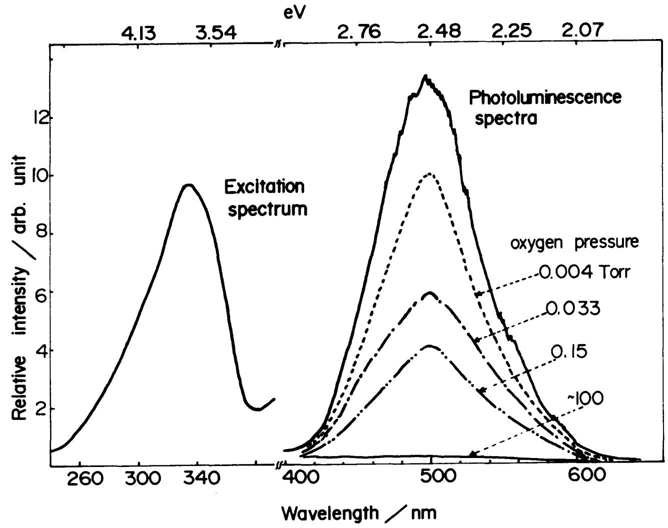

Fig. 1. Photoluminescence spectrum of TiO_2 at 77 K and effect of the addition of O_2 (excitation; 280 ± 10 nm).

As shown in Fig. 2, UV irradiation of the sample containing adsorbed H_2O at 77 K gives rise to ESR signal having $g_1=2.014_6$ and $g_2=2.003_2$, its intensity increasing with the UV irradiation time at 77 K. The formation of this signal accompanied the formation of a much smaller amount of Ti^{3+} ions characterized by its g-values of 1.988. This signal is stable at 77 K. On raising the temperature to around 180 K, however, it immediately disappeared without giving any new signals. The signal could not be detected with the catalyst which had been removed adsorbed H_2O from the surfaces by enough evacuation at around 473-573 K to about 6.6×10^{-4} Pa (5×10^{-6} Torr). This suggests that an appearance of ESR signal is closely associated with the presence of adsorbed H_2O and/or surface OH^- groups. This ESR signal consists of anisotropic two lines due to a hydrogen atom, being characterized by hyperfine splitting of about 20 G. From the good agreement in such shape and g-values of this signal with those in the literatures,4) the signal shown in Fig. 2 could be tentatively assigned to the photo-formed $\dot{O}H$ radicals adsorbed onto the TiO_2 surfaces. Its rather smaller hyperfine splitting due to a hydrogen atom than that observed with the $\dot{O}H$ radicals on zeolites would be attributed to the difference in the strength of the interaction of $\dot{O}H$ radicals with zeolites and TiO_2 catalysts, which results in a slightly different electronic structure of $\dot{O}H$ radicals. In fact, as pointed out by Atkins and Symons, the g-values and the hyperfine splitting of the $\dot{O}H$ radicals vary from one system to another.5) In order to investigate the sources of the $\dot{O}H$ radicals, D_2O was adsorbed onto the catalyst instead of H_2O. UV irradiation of the sample led to the formation of ESR signal, which is almost the same as that shown in Fig. 2. This result suggests that the photo-formed $\dot{O}H$ radicals would stem from the surface OH^- groups on the TiO_2 surfaces. The formation of HO_2 radicals by the reaction of $O_2^- + H^+ \longrightarrow H\dot{O}_2$ has been suggested with the TiO_2 photocatalysts. However, the possibility of this reaction seems to be neglected in this system, since the formation of O_2^- have not been detected by ESR.

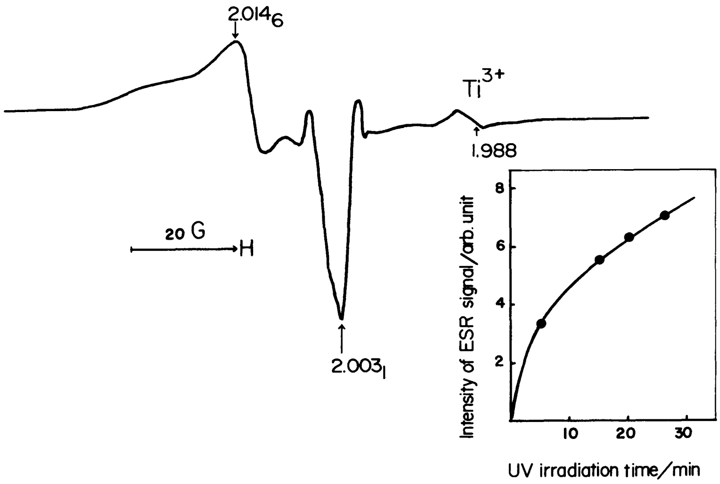

Fig. 2. ESR spectrum of photo-formed $\dot{O}H$ radicals on TiO_2 catalyst and its growth with UV irradiation time at 77 K (ESR was recorded at 77 K).

As proposed by a number of workers, UV irradiation of TiO_2 catalysts containing H_2O and/or surface OH^- groups leads to the formation of Ti^{3+}— $\dot{O}H$, i. e., photo-formed electron-hole pair state, the radiative deactivation of which will bring about the photoluminescence at around 500 nm.[6)] The ESR signal described above would be associated with the formation of the $Ti\overset{4+}{-}\dot{O}H$ species, which is formed from electron transfer from the $Ti\overset{3+}{-}\dot{O}H$ pair state to the adjacent electron acceptors, i. e., H^+; The H^+ ions are supplied from the adsorbed H_2O molecules via the acidic surface OH^- groups.[9)] It is well known that the addition of H_2O, i. e., surface hydroxylation, is a necessary condition for photocatalysis of TiO_2, the results obtained in this work being in a good agreement with the reports.[10)] The reasons enabled the detection of OH radicals would be the high concentration of surface OH^- groups and/or with other factors such as size quantization effect due to a extremely small particle diameter of the used TiO_2 catalysts.[11)]

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