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ESR Studies of Active Surface Titanium Ions on Anchored Ti-Oxide Catalysts

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ESR studies of the photoreduction of Ti-oxide supported onto porous Vycor glass showed that anchored samples exhibit only one type of Ti^{3+} ions, which are in position of low coordination. On the other hand, impregnated catalysts show several types of Ti^{3+} ions with different coordinations.

The anchoring method, which can be used to produce coordinatively unsaturated surface ions, has been widely applied for preparing more active and selective supported catalysts.1-3) Recently, we have reported that photocatalytic activity as well as photoluminescence intensity of titanium oxide anchored onto porous Vycor glass (Ti/PVG oxide) are much larger than those of impregnated titanium oxides as well as bulk TiO_2 catalysts, because of the high dispersion of Ti ions and/or the coordinative unsaturation of surface Ti ions.2) ESR techniques have been used to investigate the coordination of metal ions supported on oxides, such as Ni/SiO_2,4) V/SiO_2,5) Mo/SiO_2,6) etc., by monitoring the photoreduced metal ions. However, there seem to be few reports6,7) to show the specific features of metal ions on the oxide catalysts prepared by the anchoring method. Therefore, it is of special interest to investigate the specific features of the coordination of titanium ions on the anchored Ti/PVG oxide catalysts by using ESR, and to compare them with those of impregnated oxides.

Transparent porous Vycor glass (PVG) (Corning code; 7930, major composition; SiO_2 = 96%, BET surface area; 150-160 m^2/g) was used as an adsorbent. Supported titanium catalysts were prepared either by the anchoring method by reacting gaseous $TiCl_4$ with surface OH groups of PVG (4.0 OH/nm^2) or by the impregnation method using a dilute solution of $TiCl_4$. The concentration of titanium ions anchored or impregnated onto the surfaces of PVG was determined to be (3.2 - 5.2) x 10^{-5} mol/g. The experimental details are described elsewhere.[2,3] The samples were photoreduced in the presence of high-purity H_2 (about 50 Torr) using a high-pressure mercury lamp at 77 K.[4,5] The ESR spectra were recorded in the temperature range of 77 - 298 K on Varian spectrometers (E-3) (X-band). A subharmonic generator with multiple field modulation (Telmore Instruments) was employed for recording third (3rd) derivative spectra.[6] DPPH was taken as a reference sample (g = 2.0036) for measuring g values.

As shown in Fig. 1, after photoreduction by H_2 at 77 K, both the anchored (A) and the impregnated (I) Ti/PVG oxide catalysts present ESR signals due to Ti^{3+} ions (d^1 electronic configuration) in agreement with earlier results.[8] As seen in Fig. 1b, the 3rd derivative ESR spectrum of the sample (A) is composed of only two asymmetric signals corresponding to two different types of Ti^{3+} with $g_\perp$ = 1.979 and 1.9640 (vide infra). The signal at high field is due to H atoms. Figure 2 shows the effect of the addition of H_2O and of the recording temperature upon the spectra. It is clear that the addition of H_2O onto the sample leads to a decrease of intensity of the ESR signal at $g_\perp$ = 1.979, to an extent depending on the amount of H_2O added. Excess H_2O led to the complete disappearance of this signal. Simultaneously, the intensity of the signal at $g_\perp$ = 1.964 increases with the amount of H_2O added. The amount of Ti^{3+} ions which disappeared was roughly equal to that of Ti^{3+} ions which appeared after the addition of H_2O. The change was reversible, i. e., after the evacuation of H_2O in the range 295 - 423 K, the signal at $g_\perp$ = 1.979 could be observed again, though some fractions of the Ti^{3+} ions were destroyed in this treatment, probably because of irreversible reoxidation by H_2O. These results clearly indicate that the Ti^{3+} ions corresponding to the signal at $g_\perp$= 1.9790 are coordinatively unsaturated. The adsorption of H_2O transforms these ions into saturated Ti^{3+} ions corresponding to the signal at $g_\perp$= 1.9640, which coordinations are occupied by either O^{2-}, H_2O,

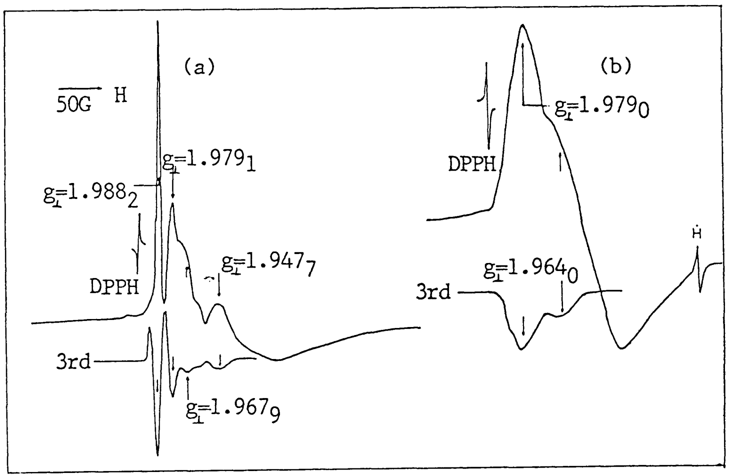

Fig. 1. ESR spectra of photoreduced Ti^{3+} ions on the impregnated (a) and the anchored (b) Ti/PVG oxide at 77 K, and their third derivative spectra at 77 K. (Photoreduction was carried out at 77 K for 80 min. About 70-80% of the anchored Ti^{4+} ions and 30-40% of the impregnated Ti^{4+} ions were photoreduced, respectively.)

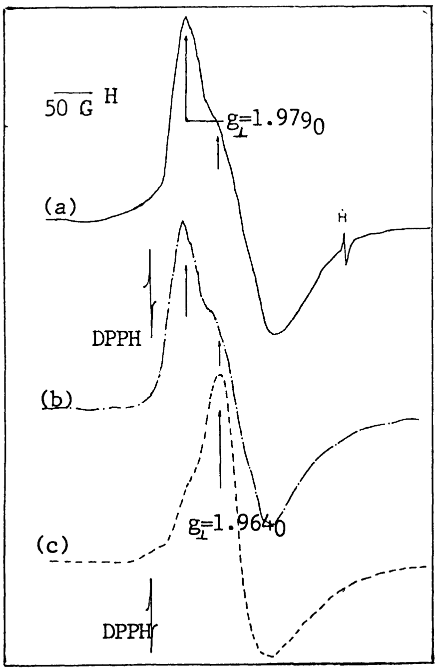

Fig. 2. ESR spectra of photoreduced Ti^{3+} ions on the anchored Ti/PVG oxide at 77 K (a) and at 298 K (b). (c) is the spectrum after the adsorption of H_2O at 298 K; recording temperature ; at 77 K)

or OH^-. The signal at $g_\perp$ = 1.9640 (Fig. 1b), therefore, might be formed by the adsorption of H_2O or OH^-, which would be formed during the photoreduction of Ti^{4+} ions under H_2, or of H_2 molecule, onto the photoformed Ti^{3+} ions, in a way similar to that shown recently for Ni^+ ions.9)

On the other hand, as shown in Fig. 1a, the ESR spectrum of the sample (I) is composed of, at least, four different types of Ti^{3+} ions, with $g_\perp$ values of 1.9882, 1.9791, 1.9679, and 1.9477, respectively. The effect of the addition of H_2O upon the spectrum of the sample (I) was also examined. The most intense and sharp signal with $g_\perp$ = 1.9882 decreased in intensity by the addition of H_2O to an extent depending on the amount of H_2O added. Simultaneously, the signal at $g_\perp$ = 1.9477 increased in intensity. The weak signal at $g_\perp$ = 1.9679 also disappeared by the addition of H_2O. However, the signal at $g_\perp$ = 1.979, which was also observed with the anchored catalyst, scarcely changed by the addition of H_2O, in contrast to that of the sample (A). The effect of the recording temperature upon the signals of the sample (I) was also examined. The signals at $g_\perp$ = 1.9882 and $g_\perp$ = 1.9477 decreased remarkably in intensity by raising the recording temperature. However, the signal at $g_\perp$ = 1.9791 scarcely changed, in agreement with that of the sample (A). Such a temperature effect is closely associated to the spin-lattice relaxation time, shorter for bulk ions than for the surface ions. Thus, the results indicated that with the sample (I) there are, at least, two different types of Ti^{3+} ions. One corresponds to Ti^{3+} ions in position of low coordination, which correspond to the signals at $g_{\perp}$ = 1.9882 and 1.9679. The other corresponds to Ti^{3+} ions located on the support surfaces but covered with other Ti-oxide layers (aggregated TiO_2) or to Ti^{3+} ions located in coordinatively saturated surface sites, leading to the signal at $g_{\perp}$ = 1.9791. Thus, these results were found in great contrast to those obtained with the sample (A), in which there is only one type of Ti^{3+} ions located on the support surfaces.

The results obtained by ESR on titanium ions on anchored Ti/PVG oxides are in good agreement with previous papers:[2,3] High photocatalytic activity and photoluminescence yield of anchored Ti/PVG oxides would arise from the presence of well-dispersed homogeneous titanium ions and/or their coordinative unsaturation, in contrast to the case of impregnated oxide catalysts. Thus, the present work not only provides useful information about anchored and impregnated oxide catalysts, but also shows the usefulness of ESR to characterize the active surface sites on supported oxide catalysts with very low metal oxide contents.

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