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A Common Factor Determining the Features of the Photocatalytic Hydrogenation and Isomerization of Alkenes over Ti–Si Oxides

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Synopsis. On addition of SiO_2 to TiO_2 photocatalysts, it has been found that the yields of C_2H_6 and CH_4 in the photocatalytic hydrogenation of propylene as well as that of 1-butene in the photocatalytic isomerization of *cis*-2-butene decrease simultaneously. This gives some support for the mechanisms for both reactions where $[Ti^{3+}–O^-]$ pairs are important.

It is well-known that in the photocatalytic reactions associated with the decomposition of water over Pt-loaded TiO_2 where charge separation takes place efficiently the reduction reactions by electrons and the oxidation reactions by holes proceed on different parts of the catalyst.[1] We have recently shown that a close association of photo-formed electrons and holes plays a significant role in some photocatalytic reactions.[2] For example, in the photocatalytic hydrogenation of propylene over TiO_2 the photo-formed trapped electron-hole pairs $[Ti^{3+}–O^-]$ play a significant role in formation of the C=C bond fission products such as CH_4 and C_2H_6.[3] Furthermore, in the photocatalytic isomerization of 2-butene the $[Ti^{3+}–O^-]$ pairs or Ti^{3+} (trapped electrons) are important to bring about the double bond shift in the isomerization.[4] According to such a reaction model, it would be expected that the decreases in the yields of CH_4 and C_2H_6 (hydrogenation) and 1-butene (isomerization) take place simultaneously, if removal of the trapped electrons (Ti^{3+}) is caused by in some way. Such features have been actually observed with the photocatalytic reactions over Ti–Si oxides.

Experimental

Propylene and *cis*-2-butene obtained from Takachiho Kagakukogyo Co. were purified by vacuum distillation. Ti–Si oxides with various compositions were prepared by coprecipitation of a mixed solution of $TiCl_4$ and $Si(OC_2H_5)_4$ with aqueous solution of ammonia, and by heating in air for three hours at 500 °C.[5] These catalysts were subjected to oxygen treatment for one hour at 500 °C followed by evacuation at the same temperature. *Cis*-2-butene of 4.0 kPa was introduced over the catalysts (500 mg) which had been spread on the quartz window, having a surface of *ca.* 20 cm^2. The photoisomerization was carried out by UV irradiation from a high pressure mercury lamp (Toshiba, SHL-100UV) without a filter for one hour at the ice-water temperature. The photocatalytic hydrogenation of propylene over water adsorbed catalysts was performed at room temperature in the same experimental conditions as above. Gas samples were analyzed by gas chromatography using silica gel and 2,4-dimethylsulfolane columns.

Results and Discussion

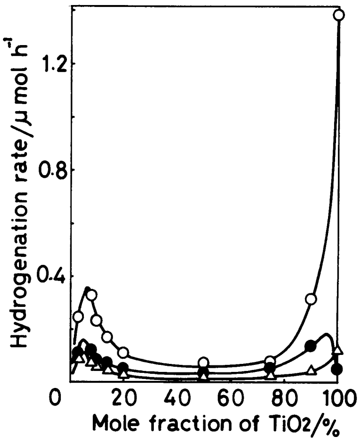

Fig. 1. Photocatalytic hydrogenation of propylene over binary Ti–Si oxides. ○: C_2H_6; ●: C_3H_8; △: CH_4.

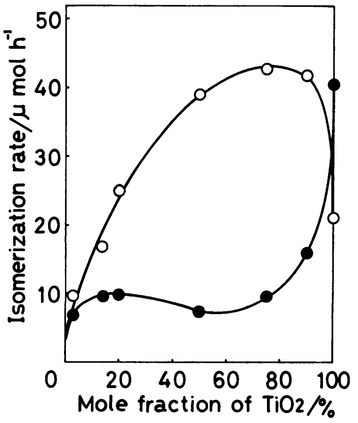

Fig. 2. Photocatalytic isomerization of *cis*-2-butene over binary Ti–Si oxides at 0 °C. ○: *trans*-2-butene; ●: 1-butene.

The hydrocarbon products in the photocatalytic hydrogenation of propylene by adsorbed water (reaction I) are CH_4, C_2H_6, and C_3H_8. As shown in Fig. 1, the formation rates of the products, especially those of CH_4 and C_2H_6 decrease drastically with increasing content of SiO_2 up to 60%. With the photocatalytic hydrogenations of alkenes and alkynes over TiO_2, it has recently been shown that the photo-formed $[Ti^{3+}–O^-]$ pairs participate in formation of the products accompanied by fission of the C=C or C≡C bond.[3] It appears therefore that such a decrease in the yields of C_2H_6 and CH_4 may be explicable by the concept that the concentration of $[Ti^{3+}–O^-]$ pairs decreases on the addition of SiO_2.

In the photocatalytic isomerization of *cis*-2-butene (reaction II) over Ti–Si oxides, both isomerizations to *trans*-2-butene and 1-butene take place, though the isomerizations in the dark scarcely proceed at 0 °C. The rates of formation of *trans*-2-butene and 1-butene, as a function of the TiO_2 content, are shown in Fig. 2. The yield of 1-butene *i.e.* the selectivity toward 1-butene formation decreases in the range up to 60% TiO_2.

According to our recent work[4] in the photocatalytic isomerization of 2-butene the interaction of $[Ti^{3+}-O^-]$ pairs or O^- species with butene results in opening of its C=C bond, *i.e.* in formation of a radical, which participates in the photocatalytic isomerization. In the double bond shift isomerization, H atoms are removed from and added to the radical. Since H atoms are supplied from surface OH groups according to the process $OH^- \rightarrow O^{2-} + H^+$, the neutralization of protons is necessary. For this purpose the electrons trapped on Ti^{4+} ions (Ti^{3+}) are used. Accordingly, if the trapped electrons (Ti^{3+}) are removed, *i.e.* the O^- species are formed in place of the $[Ti^{3+}-O^-]$ pairs, the double bond shift isomerization would be unexpected to occur. The *cis-trans* isomerization will proceed, since it has been shown previously[4] that the interaction of the O^- species with alkene brings about the weakening of its C=C bond.[6] Replacement of the $[Ti^{3+}-O^-]$ pairs by the O^- species would result in simultaneous increase and decrease in the yields of *trans*-2-butene and 1-butene, respectively. Such feature was actually observed with the range above 90% of TiO_2. It was found that the selectivity of *trans*-2-butene formation in the photocatalytic isomerization of *cis*-2-butene is increased with Pt-loaded TiO_2 where removal of the trapped electrons (Ti^{3+}) is expected to occur. This suggests that the occurrence of the *cis-trans* isomerization is closely associated with such removal of the trapped electrons.

The considerations described above suggest that the decrease in the yields of CH_4 and C_2H_6 (reaction I) and 1-butene (reaction II) caused by the addition of SiO_2 is explicable by the same factor, *i.e.* the decrease in the concentration of $[Ti^{3+}-O^-]$ pairs brought about by removal of the trapped electrons(Ti^{3+}). Apart from the nature of such removal, which will be described later, it should be noted that such a simultaneous decrease in the yields of CH_4 and C_2H_6 and of 1-butene in both reactions would give some support for the mechanisms proposed for both reactions where the $[Ti^{3+}-O^-]$ pairs play a significant role.

In the range below 50% of TiO_2, the reversed behavior is observed, *i.e.* simultaneous increase in the yields of CH_4 and C_2H_6 and 1-butene takes place. Such feature might be explained in a similar manner, *i.e.* in the increase in the concentration of $[Ti^{3+}-O^-]$. In any events, those results will again give additional support for the proposed reaction model.

As for the removal of the trapped electrons (Ti^{3+}), the followings may be mentioned. It is well-known that trapping or recombination centers are formed by addition of a foreign material to a semiconductor. This would be the case for the present system, since formation of Lewis acid sites has been reported for Ti–Si oxides.[5] At present the depth of the traps is unknown, they appear deep enough to remove the trapped electrons (Ti^{3+}).

In the region of lower Ti contents, we have recently reported formation of a new active phase arising from a high dispersion of Ti ions.[7] In this state the radiationless transfer of photon energy absorbed by TiO_2 is suppressed because of a high coordination unsaturation. This would be expected to facilitate formation of the $[Ti^{3+}-O^-]$ pairs. Further work is necessary to clarify the nature of such phenomena.

References

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6) The O^- species will trap an electron to form an O^{2-} ion at the end of their life. It seems that its life time is not necessarily the same as the time to complete the isomerization, being probably much longer. Further work is necessary to clarify this point.

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