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# Remarkable Dispersion Effect of $TiO_2$ Catalyst on Silica Support in Propene - Deuterium Addition and Exchange Reaction

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Investigation on the effect of dispersing small particles of $TiO_2$ over silica upon the rate and mechanism of propene-deuterium reaction revealed that lower loading catalysts(1-8 wt%) exhibit markedly different catalytic behavior from that over unloaded $TiO_2$.

Structure sensitivity of supported metal catalysts has been studied in many reactions.$^{1-3)}$ It is caused by the morphological change of the metal with particle sizes and by the electronic interaction between the metal and the support. However, such effect for supported metal oxide catalysts has not so far been investigated in detail. In the present letter, we have studied $C_3H_6$-$D_2$ and $C_3H_6$-$C_3D_6$ reactions over unsupported and silica supported $TiO_2$ catalysts, by applying the isotope tracer technique with microwave spectroscopy.$^{4)}$ We have found that silica supported catalyst, especially in its lower loading region, shows catalytic behavior remarkably different from that of the unsupported catalyst.

Silica supported $TiO_2$ catalysts were prepared by impregnating silica powder (Aerosil 300, evacuated at 723 K for 2 h) with a dry hexane solution of a certain amount of $Ti(OC_3H_7)_4$ under nitrogen atmosphere and then by oxidizing it with $O_2$ at 773 K overnight. Commercial $TiO_2$ powder (Aerosil P25) was employed as an unsupported catalyst. Propene-deuterium reaction was carried out in a closed gas circulation system (total volume: 300 $cm^3$). Before each run, the catalyst (1 g) was freshly oxidized by $O_2$ at 673 K overnight and subsequently evacuated at the same temperature for 30 min. After cooling down to the prescribed reaction temperature, a mixture of $C_3H_6$ (3.4 kPa) and $D_2$ (26.7 kPa) or a mixture of $C_3H_6$ and $C_3D_6$ (1.7 kPa each) was admitted into the system. Deuterium composition in the exchanged propene molecules was determined by mass spectroscopy with an ionization voltage of 12 eV. The location of the deuterium atom in monodeuteropropene (propene-$d_1$) molecules was determined by microwave spectroscopy.$^{4)}$

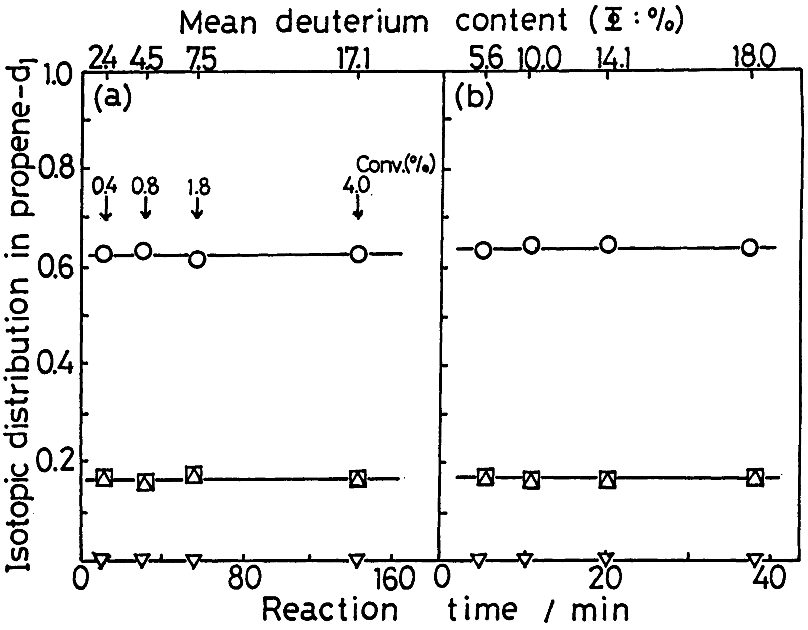

Fig.1. Time courses of deuterium distribution in monodeuteropropene (a) for $C_3H_6$-$D_2$ and (b) for $C_3H_6$-$C_3D_6$ over unsupported $TiO_2$ at 473 K. □ cis-1-$d_1$, △ trans-1-$d_1$, ▽ 2-$d_1$, ○ 3-$d_1$, (a) $\Phi = 1/6 \sum_{i=0}^{6} id_i$ ;(b) $\Phi = (d_1+2d_2+3d_3/2)/3$, Conv. = propane/(propane+propene).

When a mixture of $C_3H_6$ and $D_2$ was introduced onto unsupported $TiO_2$ at 473 K, both deuterium addition and exchange reaction took place simultaneously, the latter proceeding one order of magnitude faster than the former. Figure 1(a) shows the result of the microwave spectroscopic analysis of propene-$d_1$ formed in the exchange process. The identical deuterium distribution pattern was obtained in $C_3H_6$-$C_3D_6$ reaction over the unsupported catalyst at the same reaction temperature, whereas the exchange rate was a few times faster as shown in Fig. 1(b). In the propene-deuterium reaction the activation energy of hydrogen exchange (71 kJ/mol) was much larger than that of propane formation (52 kJ/mol) and similar to that of $C_3H_6$-$C_3D_6$ reaction (75 kJ/mol). These results strongly suggest that hydrogen exchange in $C_3H_6$-$D_2$ reaction proceeds through a different intermediate from that for the deuterium addition process to form propane and through the same intermediate as in $C_3H_6$-$C_3D_6$ reaction. This mechanism is commonly accepted for hydrogenation and hydrogen exchange over unsupported oxide catalysts such as ZnO$^{5,6)}$ and $Cr_2O_3$.$^{7)}$

As shown in Fig. 2, the situation was completely different when $TiO_2$ was supported on silica which is inactive for this reaction (1-8 wt%). In $C_3H_6$-$D_2$ reaction at 473 K over 1 and 8 wt% $TiO_2/SiO_2$ catalysts, both deuterium addition and exchange reactions proceeded simultaneously with similar activation energy (45 kJ/mol). The isotopic distribution pattern of propene-$d_1$ formed in the exchange process was different from that over unsupported $TiO_2$. Propene-2-$d_1$($CH_2$=CD-$CH_3$) was appreciably formed in this case and the relative abundance of propene-3-$d_1$($CH_2$=CH-$CH_2D$) was markedly decreased. However, the isotopic distribution pattern for the $C_3H_6$-$C_3D_6$ reaction was the same as that over unsupported $TiO_2$, and its exchange rate was much smaller than in $C_3H_6$-$D_2$ reaction. Accordingly, it is reasonable to suppose that the hydrogen exchange process in $C_3H_6$-$D_2$ reaction proceeds via the common reaction intermediates as the deuterium addition process, that is, via n-propyl and s-propyl adsorbed species. From the ratio of propene-2-$d_1$ to propene-1-$d_1$($CHD=CH-CH_3$) and 3-$d_1$ shown in Fig. 2(a), it is recognized that s-propyl species is more reactive than n-propyl species in hydrogen exchange process on 8 wt% $TiO_2/SiO_2$ catalyst.

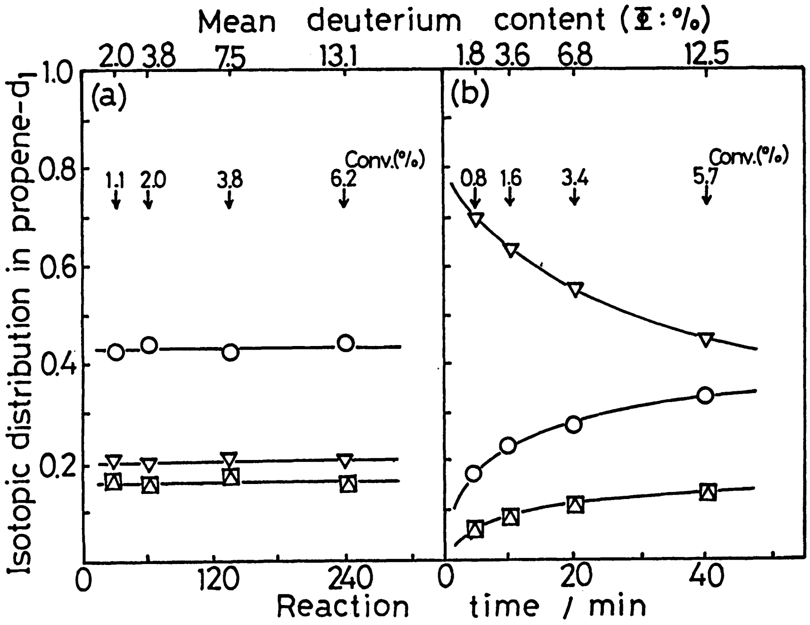

Fig.2. Time courses of deuterium distribution in monodeuteropropene for $C_3H_6$-$D_2$ at 473 K (a) over 8 wt% $TiO_2/SiO_2$ and (b) over 1 wt% $TiO_2/SiO_2$. For other explanation see the caption of Fig.1.

The isotopic distribution pattern over 1 wt% $TiO_2/SiO_2$ catalyst, however, was considerably different from that over 8 wt% loading catalyst, as shown in Fig. 2(b). From the extrapolated ratio of propene-2-$d_1$ to propene-1-$d_1$ and 3-$d_1$, it is realized that the relative activity of the two intermediates changes drastically and that in the exchange process n-propyl species is now much more reactive than s-propyl species. The temporal decrease of propene-2-$d_1$ with the corresponding increase of 3-$d_1$ suggests that there exists an independent intramolecular hydrogen shift process[8] in addition to the deuterium incorporation process through -alkyl adsorbed species.

Figure 3 summarizes the dependence of the initial rates of propane and propene-$d_1$ formation in $C_3H_6$-$D_2$ and $C_3H_6$-$C_3D_6$ reactions upon the amount of $TiO_2$ loading over various $TiO_2/SiO_2$ catalysts. The rate of propane formation was increased monotonously as the loading amount decreased, and 1 wt% catalyst exhibited more than two orders of magnitude larger activity than higher loading catalysts. On the other hand, the rate of propene-$d_1$ formation in $C_3H_6$-$D_2$ reaction showed a minimum at around 10 wt% loading. At lower loading region, the exchange rate was increased in a parallel manner to that of propane formation, indicating that both processes proceed via common σ-alkyl intermediates. At higher loading region, the exchange rate was rather constant in spite of the decrease of propane formation rate and now nearly parallel to the exchange rate of $C_3H_6$-$C_3D_6$ reaction, which was nearly two orders of magnitude larger than that for lower loading catalysts. This result strongly suggests that addition and exchange processes take place through different reaction intermediates in the higher loading region, whose relative rates are similar to those over unsupported $TiO_2$.

XRD and XPS measurments were carried out to clarify the structure of $TiO_2$ particles dispersed on silica. No diffraction pattern was observed for 1 and 8 wt% $TiO_2/SiO_2$ catalysts, which suggested their amorphous structure on silica. On the other hand, broad diffraction peaks were detected in the cases of 16 and 25 wt% catalysts, indicating a certain extent of crystalization of $TiO_2$ particles in the catalysts of higher loading region. From the intensity ratio of Ti 2P and Si 2P peak in XPS, it was suggested that lower loading catalysts may have smaller particle sizes than higher loading ones, although the binding energy of Ti 2P peak was not much different in these catalysts.

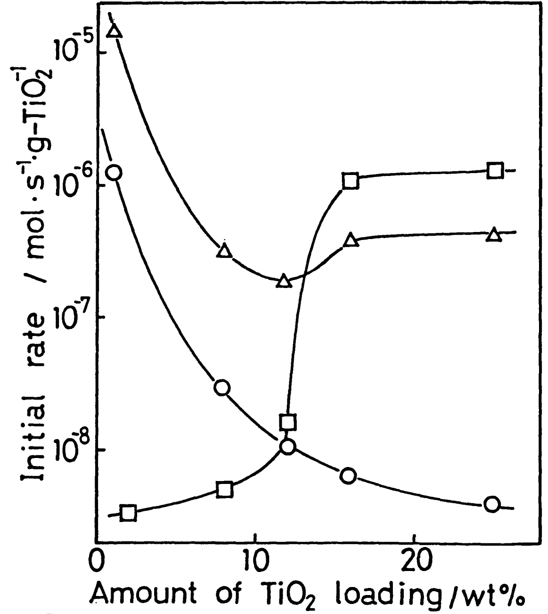

Fig.3. Dependence of the initial rate of propane and propene-$d_1$ formation on the amount of $TiO_2$ loading over $SiO_2$ at 473 K.
○propane in $C_3H_6$-$D_2$ reaction
△propene-$d_1$ in $C_3H_6$-$D_2$ reaction
□propene-$d_1$ in $C_3H_6$-$C_3D_6$ reaction

It is thus concluded that amorphous small particles of $TiO_2$ supported on silica exhibit quite different catalytic behavior from well-crystalized larger $TiO_2$ particles in the propene-deuterium reaction. This marked effect may be reasonably explained by the higher coordinative unsaturation of titanium ions on the surface of smaller $TiO_2$ particles.

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