

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 $\text{C}_3\text{H}_6\text{-D}_2$ and $\text{C}_3\text{H}_6\text{-C}_3\text{D}_6$ 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 $\text{Ti}(\text{OC}_3\text{H}_7)_4$ 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⁾

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

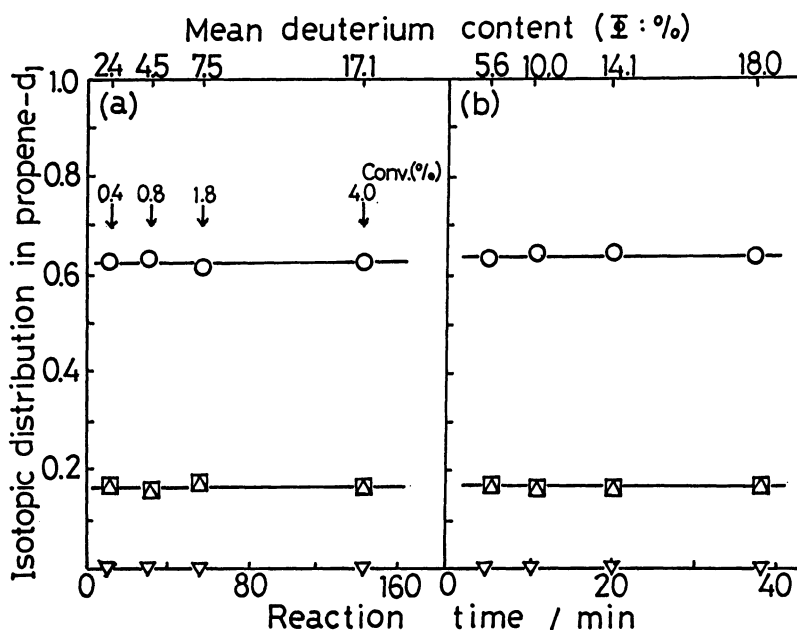


Fig.1. Time courses of deuterium distribution in monodeuteropropene (a) for $C_3H_6-D_2$ and (b) for $C_3H_6-C_3D_6$ over unsupported TiO_2 at 473 K.

□ cis-1- d_1 , Δ trans-1- d_1 , ▽ 2- d_1 , ○ 3- d_1 .

(a) $\phi = \frac{1}{6} \sum_{i=0}^6 i d_i$; (b) $\phi = (d_1 + 2d_2 + 3d_3)/3$.

Conv. = propane/(propane+propene).

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.

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 process⁸⁾ in addition to the deuterium incorporation process through σ -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

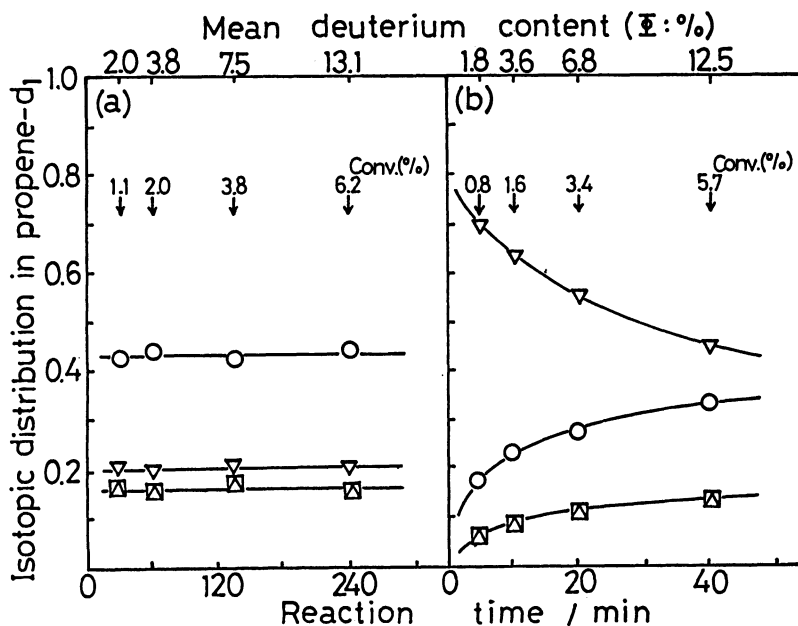


Fig.2. Time courses of deuterium distribution in monodeuteriopropene for $C_3H_6-D_2$ at 473 K (a) over 8 wt% TiO_2/SiO_2 and (b) over 1 wt% TiO_2/SiO_2 . For other explanation see the caption of Fig.1.

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 measurements were carried out to clarify the structure of TiO_2 particles dispersed on silica. No diffraction pattern was observed for 1 and 8 wt% $\text{TiO}_2/\text{SiO}_2$ 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 crystallization 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.

It is thus concluded that amorphous small particles of TiO_2 supported on silica exhibit quite different catalytic behavior from well-crystallized 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.

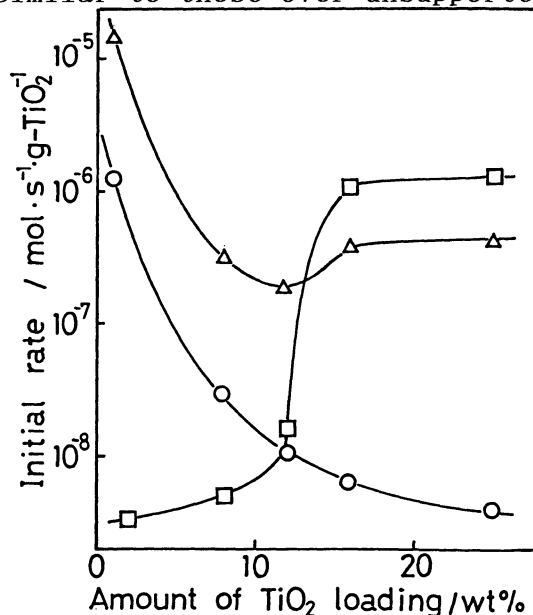


Fig.3. Dependence of the initial rate of propane and propene- d_1 formation on the amount of TiO_2 loading over SiO_2 at 473 K.

○propane in $\text{C}_3\text{H}_6\text{-D}_2$ reaction
 △propene- d_1 in $\text{C}_3\text{H}_6\text{-D}_2$ reaction
 □propene- d_1 in $\text{C}_3\text{H}_6\text{-C}_3\text{D}_6$ reaction

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(Received August 4, 1990)