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Synergetic Ligand Effect in the Hydrogen Exchange Reaction of Propene over Pd-Cu and Pt-Cu Alloy Catalysts

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Marked changes of reaction intermediates on alloying were disclosed by the microwave spectroscopic analysis of the monodeuteriopropene formed during C_3H_6-C_3D_6 exchange reaction over Pd-Cu and Pt-Cu alloy catalysts.

Microwave spectroscopy is a powerful technique for studying hydrogen exchange and isomerization reactions of propene or butene in heterogeneous catalysis.[1,2] Hyperfine distribution of deuterium in exchanged olefins can be determined with this method, and it provides important information on the structure of reaction intermediates on catalyst surfaces.[3,4]

Alloys of group VIII transition metals with IB metals have been considered to exhibit a significant "ensemble effect", which is to reduce the number of large ensembles of active metal atoms that are necessary for a certain type of adsorption or reaction.[5-7] On the other hand, the electronic interaction (ligand effect) between group VIII and IB metals in these alloys has been assumed to be of secondary importance.[8,9] Recent growing experimental evidence indicates the coexistence of some degree of electronic modification with an ensemble effect in these alloys.[10-13]

Recently we reported that when Ni, Pd, and Pt catalysts were alloyed with Cu, the reaction intermediates of C_3H_6-D_2 reaction changed markedly, as disclosed by microwave spectroscopy.[14] In this communication, we have applied the same method to the C_3H_6-C_3D_6 exchange reaction over Pd-Cu and Pt-Cu catalysts. Although the mechanisms are different in the above two exchange reactions, we have observed a similar change of intermediates by alloying, thus confirming the important role of copper in the modification of active sites for these reactions.

Pd-Cu and Pt-Cu alloy catalysts (bulk composition of Cu was 60 mol%) were prepared by coprecipitation method from aqueous solutions of metal hydroxides in their appropriate ratios. The precipitates were calcined in air at 673 K for 2 h.[15] Metallic Pd, Pt, and Cu catalysts were prepared by the similar method: oxide powders were reduced by hydrogen, while the temperature was increased very slowly from room temperature to 723 K, at which it was kept for 20 h. The formation of alloys was confirmed by observing their characteristic X-ray diffraction patterns (approximate lattice constants: 3.71 Å for Pd-Cu and 3.72 Å for Pt-Cu). The cleanliness of the surface was checked by X-ray photoelectron spectroscopy (VG, ESCALAB 5). Surface composition of copper was in the range of 70 - 80% in both Pd-Cu and Pt-Cu catalysts, as estimated from the amount of adsorbed hydrogen at room temperature and the B. E. T. surface area, with the assumption that hydrogen is not adsorbed on copper.[16)]

C_3H_6-C_3D_6 reaction was carried out in a closed gas circulation system (total volume 310 cm^3). Before each run, the catalysts (2 - 3 g) was freshly reduced for 2 h by hydrogen at 473 K and then evacuated at the same temperature for 30 min. After cooling down to the prescribed reaction temperature, a mixture of C_3H_6 and C_3D_6 (1:1, 2 kPa each) was admitted. Deuterium composition in exchanged propene was determined by mass spectrometry (Hitachi RMU-6MG) with an ionization voltage of 12 eV. The location of the deuterium atoms in mono- and dideuteriopropene molecules was determined by microwave spectroscopy.[3,4)]

At the initial stage of C_3H_6-C_3D_6 exchange reaction, the main products were C_3H_5D and C_3HD_5 and the amount of multiply exchanged propene was extremely small. This result indicates the stepwise exchange in the reaction between propene molecules. The exchange rates were two order of magnitude slower than those of C_3H_6-D_2 reaction, for which associative mechanism with σ-alkyl intermediates has been concluded.[3,4,14)] Activation energies for the exchange process over the alloy catalysts were also considerably different: C_3H_6-C_3D_6 : 20-30 kJ mol^{-1}, C_3H_6-D_2 : 30-40 kJ mol^{-1}. It is thus concluded that C_3H_6-C_3D_6 exchange reaction over these catalysts proceeds via dissociative mechanism with n-propenyl, sec-propenyl and σ-allyl intermediates.

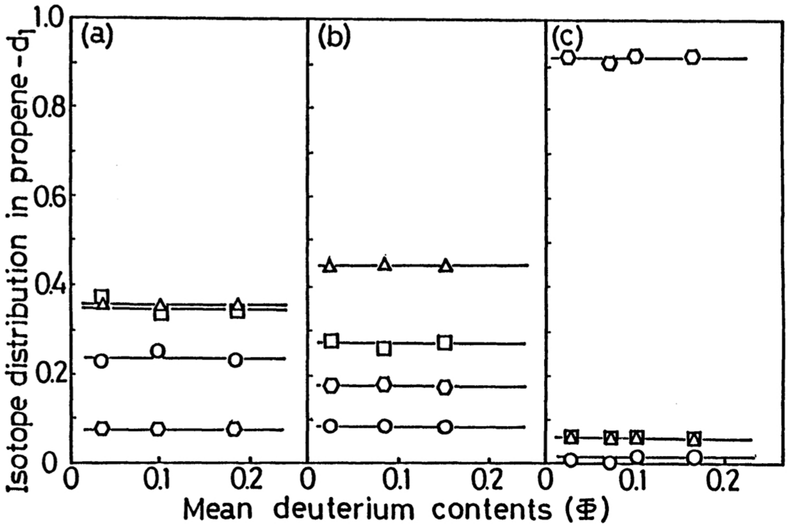

Fig. 1. Isotope distribution in propene-d_1 during C_3H_6-C_3D_6 reaction over Pd, Pt, and Cu catalysts. (a) Pd (260 K), (b) Pt (303 K), (c) Cu (353 K)

□ cis-CHD=CH-CH_3 △ trans-CHD=CH-CH_3
⬡ CH_2=CD-CH_3 ○ CH_2=CH-CH_2D

$\Phi = (d_1+2d_2+1.5d_3)/6$ represents approximately the extent of deuteriation of C_3H_6.

Figure 1 summarizes the result of microwave spectroscopic analysis of monodeuteriopropene formed during C_3H_6-C_3D_6 reaction over Pd, Pt, and Cu metallic catalysts. Deuterium distribution patterns were significantly different among these three metals. Pd metal was the most active and exhibited high exchange activity for the hydrogens attached to C_1 methylene carbon. The main products (70%) were cis- and trans-CHD=CH-CH_3, which were formed through n-propenyl intermediates.[3)] Pt metal also was active for the exchange of the hydrogens attached to C_1 carbon. The most remarkable point is, however, that trans-hydrogen is 1.5 - 2 times more active for exchange than cis-hydrogen, which suggests a large steric hindrance in the adsorbed state of n-propenyl intermediates. On the other hand, Cu metal was more than two orders of magnitude less active for this reaction than Pd and Pt metals. The reaction intermediates over Cu catalyst were completely different from those over Pd and Pt catalysts, since more than 90% of the products over Cu was CH_2=CD-CH_3, which was formed through sec-propenyl intermediates.[3)]

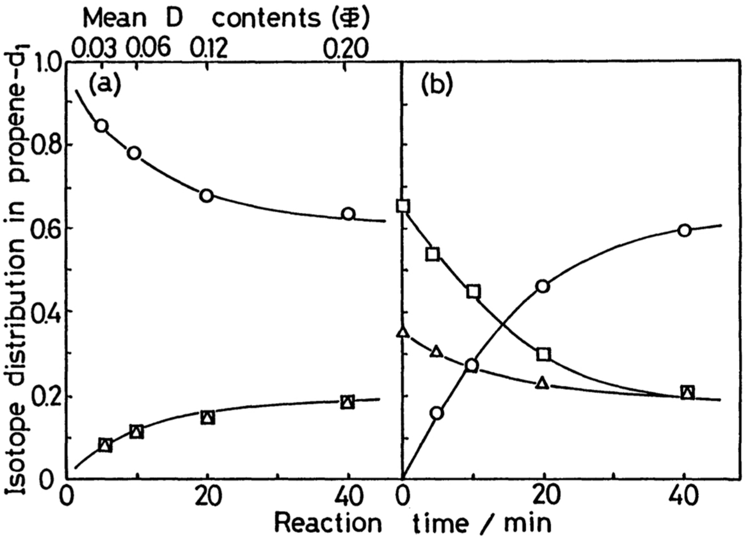

Fig. 2. Time courses of isotope distribution in propene-d_1 over Pd-Cu at 273 K.
(a) C_3H_6-C_3D_6, (b) CHD=CH-CH_3 only
For symbols see Fig. 1.

Figure 2-(a) shows the time courses of isotope distribution in propene-d_1 during C_3H_6-C_3D_6 exchange reaction over Pd-Cu alloy catalyst at 273 K. Although the exchange rate was comparable to that over Pd metal, the deuterium distribution pattern was completely different from that of Fig. 1-(a). It is evident that a marked change takes place in the temporal isotope distribution. The only product at the initial stage was CH_2=CH-CH_2D, formed through σ-allyl intermediate.[3)] CH_2=CH-CH_2D diminished considerably with the corresponding increase of cis- and trans-CHD=CH-CH_3. The hydrogen on C_2 methine carbon was almost inactive for the exchange. This feature may be explained by the rapid equilibration of the hydrogens between C_3 and C_1 carbons after the deuterium incorporation by dissociative mechanism. To confirm this equilibration process, cis- and trans-CHD=CH-CH_3 (65:35) were introduced on the Pd-Cu catalyst. As shown in Fig. 2-(b), the 1,3-hydrogen shift process was observed. This result can not be explained by the repetitive exchange through dissociatively adsorbed σ-allyl intermediate. Hence an intramolecular 1,3-hydrogen shift mechanism should be considered for adsorbed propene molecules in addition to the σ-allyl dissociative mechanism. The intramolecular hydrogen shift was reported for the system involving propene and hydrogen molecule over various metal catalysts.[3,4,14)] The present observation is the first example of the intramolecular hydrogen shift for the system without hydrogen molecule. It is worth noting that the activation energy of the C_3H_6-C_3D_6 exchange reaction over Pd-Cu catalyst was 32 kJ mol^{-1}, which was identical to that of the hydrogen exchange of C_3 carbon in the case of Pd metal. Consequently, it is reasonable to assume that the exchange process through n-propenyl and sec-propenyl adsorbed species is somehow strongly inhibited by the addition of Cu, and only the exchange through σ-allyl adsorbed species is pronounced.

Figure 3 shows the isotope distribution pattern in propene-d_1 during C_3H_6-

C_3D_6 reaction over Pt-Cu alloy catalysts at 293 K. The exchange rate here was comparable to that on Pt metal. However, the distribution pattern was rather similar to the case of Cu (Fig. 1-(c)) than that of Pt (Fig. 1-(b)). The most active hydrogen for exchange was that attached to the C_2 carbon of propene. The activation energy of this process through sec-propenyl adsorbed species was 20 kJ mol^{-1}, which was markedly different from the case of Pt metal (31 kJ mol^{-1}). This result indicates that the active sites for sec-propenyl adsorption is most strongly modified by alloying. The activation energies of other processes were not so much changed; for C_1-hydrogen, Pt: 26 kJ mol^{-1} and Pt-Cu: 27 kJ mol^{-1} and for C_3-hydrogen, Pt: 33 kJ mol^{-1} and Pt-Cu: 32 kJ mol^{-1}.

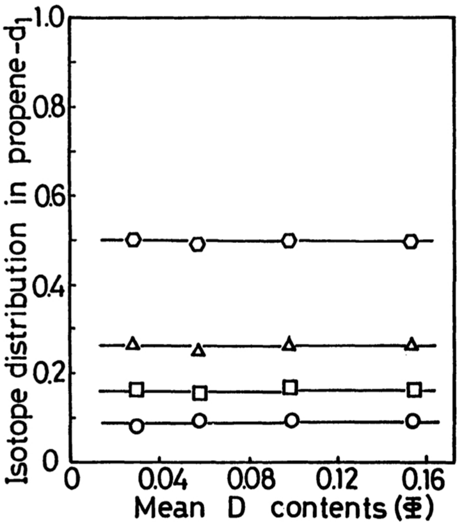

Fig. 3. Isotope distribution in propene-d_1 during C_3H_6-C_3D_6 reaction (293 K) over Pt-Cu catalyst. For symbols see Fig. 1.

The present study has demonstrated an important role of copper in the modification of active sites for dissociative adsorption of propene over Pd-Cu and Pt-Cu alloy catalysts. Experimental results strongly suggest a certain kind of electronic synergetic effect between copper and group VIII metals on the alloy surfaces, which has often been thought to be ineffective in this type of alloys.

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