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Role of Cu in the Deuterium Addition and Exchange of Propene over Pd–Cu and Pt–Cu Alloy Catalysts

SHUICHI NAITO*,[1] AND MITSUTOSHI TANIMOTO†,[2]

*Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, and †Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

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The reaction intermediate and the reaction mechanism of deuterium addition and exchange of propene over a bimetallic alloy have been studied by microwave spectroscopy as well as by kinetic measurements. The isotopic distribution pattern of monodeuteropropene formed during the reaction changed considerably by alloying Pd or Pt with Cu and resembled that over Cu metal. However, the turnover frequency and apparent activation energy of the overall reaction did not change appreciably by alloying. These results indicate the change in the relative activity of reaction intermediates and suggest an important role of Cu in modifying the active sites and the reaction mechanism. It is proposed that a new type of active site is formed by alloying Group VIII metals with Group IB metals; the interaction may be called the "synergetic ligand effect."

INTRODUCTION

The catalytic properties of metallic alloy surfaces have been attracting great attention because alloys sometimes provide enhanced activity and improved selectivity toward various reactions (*1, 2*). Two concepts have been widely proposed to explain this unique character, that is, the "geometric, or ensemble effect," and the "electronic, or ligand effect" (*3–5*). The former effect is concerned with the ensemble size of surface metal atoms required for a particular catalytic reaction. In the case of alloys formed from active and inactive metal components, the effect of the dilution of active metal ensembles by inactive metal atoms will be enhanced. As a result, reactions that proceed through intermediates bound to many adjacent active metal atoms will be inhibited more strongly by alloying than those requiring small ensembles only. On the other hand, the electronic ligand effect results from charge transfer from one of the alloy components to the other at the reaction site. This influences the catalytic activity or selectivity by modifying the chemical bonding of reaction intermediates (*6*).

Sinfelt, Carter, and Yates reported a marked decrease in the rate of hydrogenolysis of ethane with addition of copper to nickel (*7*). They also found that addition of small amounts of copper to nickel led to an increase in the activity for the dehydrogenation of cyclohexane; the activity remained insensitive to further change in the alloy composition. These results seem to be reasonable because hydrogenolysis on metal catalysts is generally accepted as a structure-sensitive reaction which proceeds on large ensembles of active metal atoms, while dehydrogenation is structure-insensitive (*8*). As far as the reaction rate is concerned, many authors have observed similar decrease in hydrogenolysis activity over various Group VIII–IB metal alloy systems (*9, 10*). However, examination of the selectivity for hydrogenolysis in the skeletal reaction of hydrocarbons demonstrated that

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[1] To whom correspondence should be addressed.

[2] Present address: Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422, Japan.

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the effect of alloying an active Group VIII metal with an inactive group IB metal was not so simple. De Jongste and Ponec studied skeletal reactions of several hydrocarbons such as pentane, methylcyclopentane, and hexane over Pt–Cu and Pd–Cu bimetallic catalysts (*11*). In these reactions, the selectivity for hydrogenolysis, compared to that for isomerization, was considerably improved by increasing Cu content in the alloy catalyst. This was a puzzling result because hydrogenolysis had been considered to require larger ensembles than isomerization. Their mechanistic investigations revealed an important role of copper in the formation of chemisorbed complexes favorable to hydrogenolysis (*12, 13*).

Hydrogenation of ethene (*14–16*) and benzene (*17, 18*) has also been studied much over alloy catalysts of Group VIII–IB metals. Since this reaction is classified as a structure-insensitivite reaction, any ensemble effect is supposed to be small. Best and Russell examined the hydrogenation of ethene over Ni–Cu alloy catalysts and observed much higher activity than that over the pure Ni (*19*). Hall and Hassell demonstrated an important role of the hydrogen treatment at higher temperatures in the enhancement effect caused by alloying Ni with Cu (*20*). To elucidate these phenomena more clearly according to the concept of ensemble or ligand effect, it is obviously necessary to examine the change of reaction rates as well as the reaction mechanism caused by alloying. Deuterium addition and exchange of propene (C_3H_6–D_2 and C_3H_6–C_3D_6) would be suitable reactions for this purpose because the fine structure of the reaction has been investigated by applying microwave spectroscopy (*21, 22*). The change of the isotopic distribution in monodeuteropropene formed during the reaction is followed, and the reaction intermediate is thus identified. We have applied this method to C_3H_6–D_2 and C_3H_6–C_3D_6 reactions over Ni-Cu, Pd–Cu, and Pt–Cu catalysts and preliminarily reported on marked changes in the reaction intermediates caused by alloying in both reactions (*23, 24*). These results indicate that copper plays an important role in modifying the active sites and the reaction mechanism. In the present study, we describe this "synergetic ligand effect" in detail and discuss the reaction mechanism in depth.

EXPERIMENTAL

Pd–Cu and Pt–Cu alloy powders and Pd, Pt, and Cu metal powders were prepared by careful reduction of the corresponding oxide powders. Sodium hydroxide solution was added dropwise, with vigorous stirring, to the aqueous chloride or nitrate solutions ($PdCl_2$ and H_2PtCl_4, Nakarai Chemicals, spec pure; $Cu(NO_3)_2$ $3H_2O$, Wako Chemicals, spec pure). The precipitates were filtered, washed thoroughly in distilled water, dried, and calcined in air at 673 K for 2 h. The oxide powders were placed in a U-shaped reaction vessel and reduced with hydrogen, while the temperature was increased very slowly from 298 to 723 K (within about 12 h) and then kept constant for 20 h. After complete reduction the catalysts were examined using X-ray photoelectron spectroscopy (XPS, VG, ESCALAB 5), which exhibited no appreciable surface impurities. The bulk composition of the alloys employed in the present study was 60 mol% of copper.

Table 1 summarizes the characterization of the employed catalysts by means of H_2 chemisorption and X-ray diffraction. The approximate surface composition of the alloy powder was estimated from the total surface area determined by N_2 physisorption at its normal boiling point and by H_2 chemisorption at room temperature. Before the measurement, the catalysts were reduced by H_2 at 623 K for 2 h and evacuated at the same temperature for 0.5 h in a volumetric apparatus (base pressure was 1×10^{-5} Torr, 1 Torr = 133.3 N m^{-2}). The cross-sectional areas of N_2 molecule and H atom were assumed to be 16.2 Å^2 and 6.45 Å^2, respectively. Backsorption method was used to determine the amount of strongly

TABLE 1

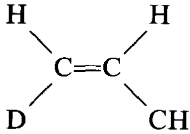
Characterization of the Catalysts by H_2 Chemisorption and X-Ray Diffraction

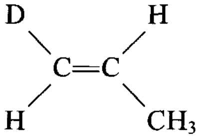
Catalysts	BET surface area ($m^2\ g^{-1}$)	Hydrogen surface density ($\times 10^{15}$ atoms cm^{-2})		Surface Cu atomic fraction	Lattice constants (Å)
		Strongly held	Weakly held		
Pd	1.9	1.5	12.8	0	3.89
Pd–Cu	1.8	0.37	0.52	0.75	3.71
Pt	1.7	1.4	0.36	0	3.91
Pt–Cu	1.5	0.38	0.35	0.73	3.72
Cu	1.1	0	0.01	1	3.61

Note. $P(H_2)$ = 10 Torr, room temp.

adsorbed hydrogen, whose area was taken to be equal to that of the surface Pd or Pt (*25, 26*). A typical surface composition of copper was as follows: 0.75 for the Pd–Cu system and 0.73 for the Pt–Cu system. The surface layer composition was also estimated from the XPS peak areas of Pd $3d_{5/2}$, Pt $4d_{5/2}$ and Cu $2p_{3/2}$, utilizing cross sections reported in the literature (*27*). The obtained surface copper atomic fraction was 0.65–0.75 in both catalysts. The formation of alloys was confirmed by observing their characteristic diffraction patterns, whose approximation lattice constants are listed in Table 1.

H_2 and D_2 gases from commercial cylinders were passed over a heated Pd black catalyst to remove trace amounts of oxygen. C_3H_6 purchased from Takachiho Kagaku KK was purified by a freeze–thaw cycle. $CHD{=}CH{-}CH_3$ and $CH_2{=}CD{-}CH_3$ were prepared from 1-bromo-1-propene and 2-bromo-1-propene according to the procedure reported in the literature (*28*). C_3H_6–D_2 and C_3H_6–C_3D_6 reactions were carried out in a closed gas circulation system (total volume = 310 cm^3). Before each run the catalysts (1–5 g) were freshly reduced by hydrogen at 473 K for 2 h. By this pretreatment, sufficient reproducibility for reaction rates as well as for isotopic distribution patterns was attained. After cooling to the reaction temperature (by a suitable slush bath), a certain amount of reaction gases was introduced into the system and the reaction was started. A few percentages of the circulating gas were sampled at a certain interval and analyzed as follows. Gas chromatographic method (alumina column, He carrier) was used to determine the composition of the gas and to separate the gas into propane and propene. The deuterium contents in propane and exchanged propene were determined with a mass spectrometer (Hitachi, RMU-6MG) using ionization voltage of 15 and 12 eV, respectively. The location of the deuterium atom in monodeuteropropene was determined by recording the microwave absorption line (1_{01}–0_{00} rotational transition) characteristic of each isotopic species. Details of the procedure have been reported previously (*21*). The notation for isotopomers in monodeuteropropene is as follows:


, *c*-1-d_1;


, *t*-1-d_1;

$CH_2{=}CD{-}CH_3$, 2-d_1; $CH_2{=}CH{-}CH_2D$, 3-d_1

TABLE 2

Isotope Distribution of Propane, Propene, and Hydrogen in C_3H_6–D_2 Reaction over Various Catalysts

Catalysts (Reaction temp.) (Reaction time)		Conversion (%)	Isotope distribution (%)							
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{7-8}
Cu	Propane	4.7	5.7	27.6	53.8	10.6	2.0	0.3	0	0
(298 K)	Propene	95.3	86.3	12.5	1.1	0	0	0	0	
(5 min)	Hydrogen		1.6	9.6	88.8					
Pd	Propane	9.5	25.3	29.5	33.4	9.7	1.8	0.2	0	0
(210 K)	Propene	90.5	74.1	19.8	4.6	1.5	0	0	0	
(10 min)	Hydrogen		2.5	10.2	87.3					
Pt	Propane	6.1	4.5	18.7	66.8	8.7	1.3	0	0	0
(235 K)	Propene	93.9	95.1	4.9	0	0	0	0	0	
(10 min)	Hydrogen		1.1	5.5	93.4					
Pd–Cu	Propane	13.1	21.5	30.3	35.8	9.4	2.1	0.9	0	0
(225 K)	Propene	86.9	79.6	17.2	2.3	0.9	0	0	0	
(10 min)	Hydrogen		2.1	9.8	88.1					
Pt–Cu	Propane	12.3	5.1	24.3	59.8	9.3	1.5	0	0	0
(248 K)	Propene	87.7	91.5	8.0	0.5	0	0	0	0	
(20 min)	Hydrogen		1.8	7.8	90.4					

Note. $P(D_2)$ = 50 Torr, $P(C_3H_6)$ = 25 Torr.

RESULTS

C_3H_6–D_2 and C_3H_6–C_3D_6 Reactions over Cu Powder

When a mixture of D_2 (50 Torr) and C_3H_6 (25 Torr) was introduced onto Cu powder at 298 K, both deuterium addition and exchange reactions took place simultaneously. Table 2 demonstrates the isotopic distributions of propane, propene, and hydrogen in C_3H_6–D_2 reaction over Cu. The main product of the exchange process was C_3H_5D, whose formation rate was about three times faster than that of propane. The amount of highly exchanged propene was very small at the initial stage of the reaction, which indicated a stepwise exchange process. The deuterium distribution in propane is roughly explained by considering the deuterium distributions of both exchanged propene and hydrogen molecules in the gas phase. On the other hand, hydrogen exchange reaction of propene in the mixture of C_3H_6 and C_3D_6 (1 : 1, 12.5 Torr each) was recognized to be nearly two orders of magnitude slower than that in the C_3H_6–D_2 reaction. To obtain a similar rate of C_3H_5D formation, it was necessary to raise the reaction temperature to 360–370 K. At the initial stage the main products were C_3H_5D and C_3HD_5, again suggesting the stepwise exchange reaction. Because of such a large difference in the reaction rate, it is reasonable to suppose that C_3H_6–D_2 and C_3H_6–C_3D_6 reactions proceed via two different mechanisms: dissociative and associative.

Figure 1 summarizes the microwave spectroscopic analysis of monodeuteropropene formed in these exchange processes. In the C_3H_6–C_3D_6 reaction, there was no change with time in the isotopic distribution during the reaction. The hydrogen attached to the C_2 carbon of propene was most active and $CH_2{=}CD{-}CH_3$ (2-d_1) was the main product (90%). On the other hand, in the C_3H_6–D_2 reaction, a considerable change occurred in the isotopic distribution with time. Also in this reaction, the hydrogen attached to the C_2 carbon was the most active and 2-d_1 was the most abundant product (80%) at the initial stage. As the reac-

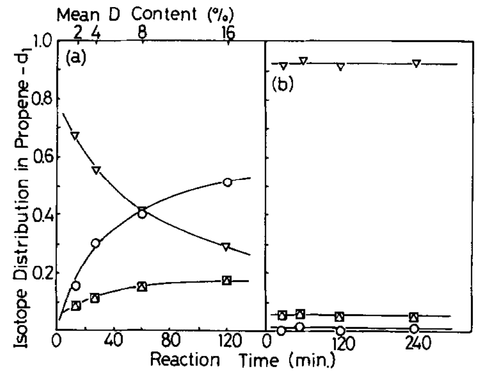


Fig. 1. Time courses of the isotopic distribution in monodeuteropropene during (a) C_3H_6 + D_2 at 298 K and (b) C_3H_6–C_3D_6 at 363 K over Cu powder (5.1 g). (a) $P(D_2)$ = 50 Torr, $P(C_3H_6)$ = 25 Torr; (b) $P(C_3H_6)$ = $P(C_3D_6)$ = 12.5 Torr. (□) *c*-1-d_1, (△) *t*-1-d_1, (▽) 2-d_1, (○) 3-d_1.

tion proceeded, its amount rapidly decreased with the corresponding increase in $CH_2{=}CH{-}CH_2D$ (3-d_1), while $CHD{=}CH{-}CH_3$ (*c*- and *t*-1-d_1) increased slightly. This feature in the exchange process is similar to those observed in the case of Au and Ag catalysts (*29*). As discussed previously (*21, 22, 29*), if the hydrogen exchange process in C_3H_6–D_2 reaction takes place only via the *n*-propyl and the *sec*-propyl adsorbed species, the isotopic distribution pattern should stay constant at the initial stage of the reaction where isotope dilution of deuterium by the repeated exchange through these adsorbed species is not significant. Accordingly it is reasonable to suppose that there exists an intramolecular hydrogen shift process in addition to the associative mechanism. By comparing Figs. 1a and 1b, it is clear that this intramolecular process occurs only in the presence of gaseous hydrogen.

As has been previously demonstrated, $CHD{=}CH{-}CH_3$ + H_2 or $CH_2{=}CD{-}CH_3$ + H_2 is a useful reaction to investigate the intramolecular hydrogen shift process in more detail (*21, 22, 29*). Since initially the reactant molecules possess one deuterium atom on one side of the carbon double bond, these reactions enable us to distinguish the intramolecular process from the deuterium incorporation process. Use of a large isotope ratio of H/D (25/1) permits the neglect of the change of isotopic distribution pattern caused by the repeated exchange. Figures 2a and 2b represent the time courses of the isotopic distribution in monodeuteropropene formed during these reactions over Cu catalyst. In both cases, rapid increase in 3-d_1 was observed with a corresponding decrease in the reactant 1-d_1 or 2-d_1. These results clearly indicate the existence of 1,3- as well as 2,3-intramolecular hydrogen shift in propene during the C_3H_6–D_2 reaction. The closed symbols in Fig. 2b represent the result when only 2-d_1 was introduced onto Cu. The absence of exchange in this case suggests that these processes took place only in the presence of gaseous hydrogen. By comparing Figs. 2a and 2b, it is realized that the 1,3- hydrogen shift process is more than three times faster than the 2,3-hydrogen shift over Cu, as is the case with Au and Ag catalysts (*29*).

C_3H_6–D_2 Reaction over Pd, Pt, Pd–Cu, and Pt–Cu Powders

C_3H_6–D_2 reaction over Pd and Pt powders took place in a similar manner to that over Cu metal mentioned above, although

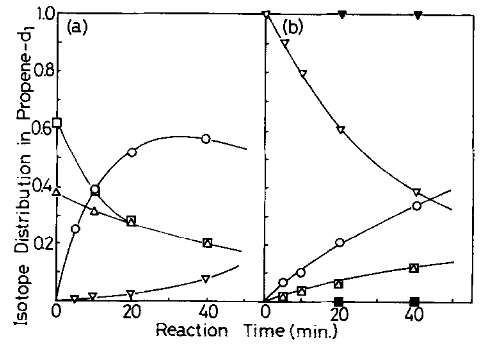


FIG. 2. Time courses of the isotopic distribution in monodeuteropropene during (a) $CHD{=}CH{-}CH_3$ + H_2 and (b) $CH_2{=}CD{-}CH_3$ + H_2 reactions over Cu powder (5.1 g) at 298 K. $P(H_2)$ = 50 Torr, P(propene) = 25 Torr. Closed symbols: $CH_2{=}CD{-}CH_3$ only; (□) *c*-1-d_1, (△) *t*-1-d_1, (▽) 2-d_1, (○) 3-d_1.

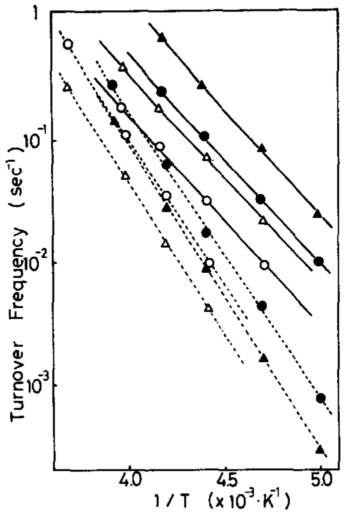


FIG. 3. Arrhenius plots of the initial rates (TOF) of C_3H_6–D_2 reaction over Pd, Pt, Pd–Cu, and Pt–Cu alloy powders. Closed symbols with solid line: Pd metal (1.3 g). Closed symbols with broken line: Pt metal (1.3 g). Open symbols with solid line: Pd–Cu alloy (3.1 g). Open symbols with broken line: Pt–Cu alloy (2.6 g). (○, ●) Initial rate of propane formation; (△, ▲) initial rate of C_3H_5D formation.

the reaction rates were more than two orders of magnitude faster than in the case of Cu. To obtain a similar formation rate of C_3H_5D in the exchange process, it was necessary to lower the reaction temperature from 300 K (Cu) to 220 K (Pt) or 200 K (Pd). The closed symbols in Fig. 3 represent the temperature dependence of the initial rates (turnover frequency) of deuterium addition (propane formation) and exchange process (C_3H_5D formation) over Pd (solid line) and Pt (broken line) catalysts. From the slope of these plots, it is possible to estimate the apparent activation energies of the addition (E_h) and exchange (E_e) processes as follows: $E_h = E_e = 33.9 \pm 0.9$ kJ/mol for Pd; $E_h = 43.9 \pm 1.1$ kJ/mol and $E_e = 45.6 \pm 1.2$ kJ/mol for Pt. Table 2 summarizes the isotopic distribution of propane, propene, and hydrogen during the reaction on these catalysts. In the case of Pd catalyst, the initial rate of C_3H_5D formation was two to three times faster than that of propane formation. The situation was reversed in the case of Pt catalyst where propane formation was two to three times faster than C_3H_5D formation. The deuterium distributions of formed propane were also considerably different over these two metals. Almost the same amounts of d_0-, d_1-, and d_2-propane were formed over Pd catalyst, which indicates that the surface H/D ratio available for hydrogenation is almost unity and totally different from the isotopic ratio in the gaseous hydrogen. On the other hand, the main product over Pt catalyst was d_2-propane, indicating that the dilution of dissociatively adsorbed deuterium by hydrogen of adsorbed propene is slow. By comparing the results with the reaction rates and activation energies of the C_3H_6–C_3D_6 reaction on these catalysts (as discussed below, the rates of the C_3H_6–C_3D_6 and C_3H_6–D_2 reactions are different by two orders of magnitude), it is clearly demonstrated that the C_3H_6–D_2 reaction proceeds via associative mechanism through *n*-propyl and *sec*-propyl adsorbed species.

Open symbols in Fig. 3 represent the temperature dependence of the initial rate of the C_3H_6–D_2 reaction over Pd–Cu (solid line) and Pt–Cu (broken line) alloy catalysts. TOF was estimated by assuming that only Pd or Pt atoms on the alloy surface were active sites and that surface Cu atoms were inactive in this reaction. The kinetic behavior over alloy catalysts was almost identical with that over pure metal catalysts, except that the decrease in TOF was half or one-third of the pure metal. Isotopic distribution patterns of propane formed are also similar to those on pure metal catalysts as shown in Table 2. The apparent activation energies of the addition and exchange processes were as follows: $E_h = E_e = 35.1 \pm 0.8$ kJ/mol for Pd–Cu; $E_h = 43.5 \pm 1.2$ kJ/mol and $E_e = 44.3 \pm 1.3$ kJ/mol for Pt–Cu. These values are also very close to those over pure metal catalysts. From these results, it is easily conceivable that intrinsic activity of Pd and Pt metals for deuterium addition and exchange is not significantly affected by alloying them with copper,

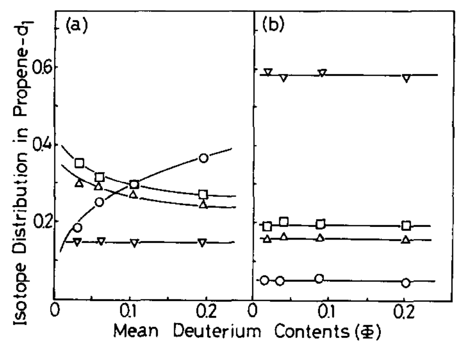


FIG. 4. Time courses of the isotopic distribution in monodeuteropropene during C_3H_6–D_2 reaction over (a) Pd powder (1.3 g) at 210 K and (b) Pd–Cu alloy (3.1 g) at 225 K. $P(D_2)$ = 50 Torr, $P(C_3H_6)$ = 25 Torr. (□) *c*-1-d_1, (△) *t*-1-d_1, (▽) 2-d_1, (○) 3-d_1. $\Phi = \frac{1}{6}\sum_{i=0}^{6} i \times [C_3H_{6-i}D_i]$: mean deuterium contents in propene.

which is consistent with the consensus that hydrogenation is a structure-insensitive reaction (*8*).

However, once we looked into the fine structure of the reaction mechanism, we noticed considerable changes in the structure of the reaction intermediates by alloying. Figure 4 shows the isotopic distribution of monodeuteropropene formed in the exchange process of the C_3H_6–D_2 reaction over Pd and Pd–Cu alloy catalysts. As mentioned above, this reaction proceeds via associative mechanism through *n*-propyl and *sec*-propyl adsorbed species. In the case of pure Pd, there exists a considerable change in the isotopic distribution during the reaction, indicating the presence of intramolecular hydrogen shift in propene molecule after deuterium incorporation. From the value extraporated to zero deuterium content in Fig. 4a, it is recognized that *c*- and *t*-1-d_1 are the main products in the deuterium incorporation process. This result implies that the exchange rate through *sec*-propyl intermediate is much higher than that through *n*-propyl species over pure Pd catalyst. Once Pd was alloyed with Cu, the situation completely changed as shown in Fig. 4b. The main product of the exchange process is now 2-d_1, which is formed through *n*-propyl intermediate. Moreover, the change of the isotopic distribution with time is negligible. This suggests that the intramolecular hydrogen shift process becomes very slow by alloying.

Figure 5 shows the isotopic distribution of monodeuteropropene formed in the exchange process of the C_3H_6–D_2 reaction over Pt and Pt–Cu alloy catalysts. The situation is similar to the case of Pd metal mentioned above. The main product of the exchange process on pure Pt was *t*-1-d_1, which gradually decreased with the corresponding increase of *c*-1-d_1, whereas 2-d_1 remained almost constant and 3-d_1 increased slightly. It may be considered that this reaction also proceeds via associative mechanism through *n*-propyl and *sec*-propyl adsorbed species. In that case the ratio of *t*-1-d_1 and *c*-1-d_1 should be unity and the ratio of (*t*- and *c*-1-d_1) : 3-d_1 should be 2 : 3. The experimental result in Fig. 5, however, is considerably different from the above expectation and suggests that the two methyl groups of *sec*-propyl intermediate are not equivalent to each other for abstraction of a hydrogen atom. In addition, moderate change in the isotopic distribution suggests the existence of the intramolecular hydrogen shift process. When alloyed, the isotopic distribution drastically changed as shown in Fig. 5b and now 2-d_1 was the main

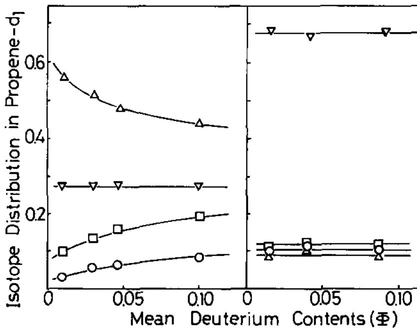


FIG. 5. Time courses of the isotopic distribution in monodeuteropropene during C_3H_6–D_2 reaction over (a) Pt powder (1.3 g) at 235 K and (b) Pt–Cu (2.6 g) alloy at 248 K. $P(D_2)$ = 50 Torr, $P(C_3H_6)$ = 25 Torr. (□) *c*-1-d_1, (△) *t*-1-d_1, (▽) 2-d_1, (○) 3-d_1.

product through *n*-propyl intermediate. Again the intramolecular process became negligible by alloying.

C_3H_6–C_3D_6 *Reaction over Pd, Pt, Pd–Cu, and Pt–Cu Catalysts*

Intermolecular hydrogen exchange between propene (C_3H_6–C_3D_6) was studied over Pd and Pt catalysts. The main products at the initial stage were C_3H_5D and C_3HD_5 and the amount of multiply exchanged propene was very small, indicating the stepwise exchange between propene molecules. Temperature dependences of the exchange rate (TOF of C_3H_5D formation) of each hydrogen in propene are demonstrated in Figs. 6 and 7. Apparent activation energy of each product was estimated from the slope of these plots. In the case of Pd metal (Fig. 6), the main products were 1-d_1 (50–60%) and 3-d_1 (30–40%), whose activation energies were considerably different from each other: E_e(1-d_1) = 23.8 ± 1.0 kJ/mol and E_e(3-d_1) = 32.2 ± 1.1 kJ/mol. The amount of 2-d_1 was less than 10% at any temperatures investigated. The activation energy for the formation of 2-d_1 was 30.8 ± 1.3 kJ/mol. There was no temporal change in the isotopic distribution at the initial stage of the exchange reaction, suggesting that intramolecular hydrogen shift was negligible in the absence of hydrogen gas even at higher temperatures. In the case of Pt metal (Fig. 7), apparent activation energies of each product and their isotopic distributions (in parenthesis) were: E_e(*t*-1-d_1) = 25.5 ± 0.9 kJ/mol (35–45%), E_e(*c*-1-d_1) = 25.5 ± 1.1 kJ/mol (20–25%), E_e(3-d_1) = 33.4 ± 1.3 kJ/mol (15–20%) and E_e(2-d_1) = 31.3 ± 1.4 kJ/mol (5–10%). The ratio of *t*-1-d_1/*c*-1-d_1 is 1.5–2, again suggesting some steric hindrance in adsorbed intermediates.

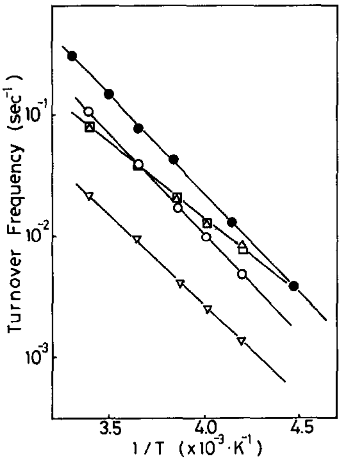


FIG. 6. Arrhenius plots of the initial rates (TOF) of C_3H_6–C_3D_6 reaction over Pd and Pd–Cu alloy. $P(C_3H_6)$ = $P(C_3D_6)$ = 12.5 Torr. Open symbols: Pd metal (1.3 g); closed symbols: Pd–Cu alloy (3.1 g). (□) *c*-1-d_1, (△) *t*-1-d_1, (▽) 2-d_1, (○) 3-d_1.

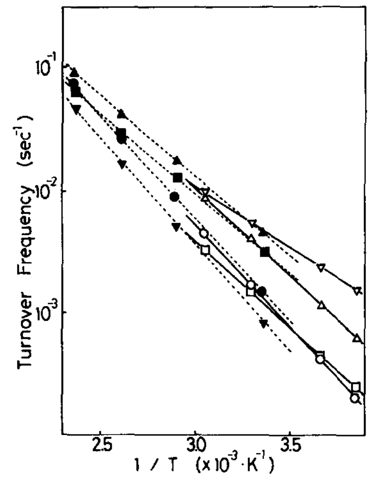


FIG. 7. Arrhenius plots of the initial rates (TOF) of the C_3H_6–C_3D_6 reaction over Pt and Pt–Cu alloy. $P(C_3H_6)$ = $P(C_3D_6)$ = 12.5 Torr. Open symbols with solid line: Pt–Cu alloy (2.6 g); closed symbols with broken line: Pt metal (1.3 g). (□, ■) *c*-1-d_1, (△, ▲) *t*-1-d_1, (▽, ▼) 2-d_1, (○, ●) 3-d_1.

By comparing Figs. 3, 6, and 7, it is recognized that the exchange rates in C_3H_6–C_3D_6 reaction are nearly two orders of magnitude slower than that of the C_3H_6–D_2 reaction and that activation energies are also considerably different. Accordingly it is most probable that the reactions proceed via completely different reaction mechanisms, that is, associative and dissociative. In the case of the C_3H_6–C_3D_6 reaction, results mentioned above are satisfactorily elucidated if we consider *c*- and *t*-*n*-propenyl, *sec*-propenyl, and σ-allyl dissociatively adsorbed species as reaction intermediates. This mechanism is identical with that proposed for Cu in the previous section, but the exchange rate itself is several hundred times faster than in the case of Cu.

Figures 6 and 7 also represent the temperature dependences of the TOF and C_3H_5D formation in C_3H_6–C_3D_6 reaction over Pd–Cu and Pt–Cu alloy catalysts. The overall exchange rates did not change much by alloying on both metals, but microwave spectroscopic analysis exhibited completely different features caused by alloying with copper, especially in the case of Pd metal. There was a marked change in the isotopic distribution of monodeuteropropene with time during C_3H_6–C_3D_6 reaction over Pd–Cu. The only product at the initial stage was 3-d_1, which decreased considerably with the corresponding increase in *c*- and *t*-1-d_1. This behavior is different from that over pure Pd metal and suggests the existence of the rapid equilibration process of the hydrogens between C_3 and C_1 carbons. Figure 6 shows the initial rates of 3-d_1 formation, and the activation energy is estimated to be 33.5 ± 1.1 kJ/mol. The situation is similar to that in the case of Pt–Cu catalyst. As seen from Fig. 7, the overall exchange rate was almost identical with that over pure Pt, but the isotopic distribution was considerably different. The most abundant product was 2-d_1 which should be formed through *sec*-propenyl adsorbed species. The activation energies for the formation of each product were determined as follows: $E_e(2\text{-}d_1) = 19.6 \pm 0.8$ kJ/mol, $E_e(c\text{-}1\text{-}d_1) = E_e(t\text{-}1\text{-}d_1) = 27.2 \pm 1.2$ kJ/mol and $E_e(3\text{-}d_1) = 31.8 \pm 0.8$ kJ/mol. The most remarkable change by alloying was the decrease in the activation energy for 2-d_1 formation by 10 kJ/mol.

DISCUSSION

Hydrogenation of olefins over alloy catalysts is favorable to the investigation of the ligand effect caused by alloying because it has been classified as a structure-insensitive reaction (*8*) and hence the ensemble effect will be small. Although extensive studies have been carried out on the hydrogenation of olefins over Ni–Cu alloy catalysts (*14–20*) investigations on Pd–Cu and Pt–Cu catalysts have rarely been carried out. As mentioned briefly under Introduction, the hydrogenation activity over Ni–Cu catalyst is extremely sensitive to the pretreatment conditions. Much higher activity was observed over the catalyst which was cooled down to the reaction temperature under hydrogen atmosphere after high temperature reduction than over the catalyst which was evacuated at the same high temperature just after hydrogen reduction (*20*). It has not been clarified whether this enhanced effect results from the strongly adsorbed hydrogen which can only be desorbed at higher temperatures or from some reconstruction of the alloy surface by evacuation at high temperature. Accordingly Ni–Cu alloy does not seem to be a good system to specify the intrinsic ligand effect. In this study we have also examined the effect of the same pretreatment on the hydrogenation of propene over Pd–Cu and Pt–Cu catalysts and found that the reaction rates were not affected by the pretreatment. Consequently these would be excellent systems to study any ligand effect on the hydrogenation of olefins over Group VIII–IB metal alloys.

Chemisorption as well as XPS measurements have revealed that the alloy catalysts prepared in this study (bulk Cu composition was 60%) possess the surface composition of Pd : Cu = 25 : 75 and Pt : Cu = 27 : 73. These values are reasonable because the surface enrichment of IB metals is usually observed in these alloy systems (*30, 31*). If the surface is ideally uniform, every Pd or Pt surface atom may be surrounded by Cu surface atoms only, and ensemble effect should operate strongly if it is important.

As discussed under Results the reaction mechanism of deuterium addition and exchange of propene over Pd, Pt, and Cu powders is identical to those over silicasupported Pd, Pt, Ag, or Au (*21, 22, 29*). The first step is the adsorption of propene molecules by π- or di-σ-bonding. Two alternative pathways of addition or abstraction of hydrogen are possible as a next step for adsorbed propene, depending on the concentration of adsorbed hydrogen. In the presence of gaseous deuterium, addition of deuterium gives exclusively *n*-propyl or *sec*-propyl adsorbed species. Propane and deuterated propene are formed through these intermediates. At the same time, intramolecular hydrogen shift process takes place via different intermediates. On the other hand, in the absence of gaseous deuterium, hydrogen is predominantly abstracted to form dissociatively adsorbed *n*-propenyl, *sec*-propenyl, and σ-allyl species. The hydrogen exchange process of propene proceeds through these intermediates.

The sequence of the catalytic reaction pathways is similar over Group VIII and IB metal catalysts. However, the reactivity of the individual reaction intermediate, the relative rate of each elementary step, and the overall reaction rates are considerably dependent on the metals employed. In the case of the C_3H_6–D_2 reaction over Pd and Pt catalysts, *sec*-propyl intermediate is more active than *n*-propyl species, which is completely the opposite of the case of Cu. Relative rates of deuterium exchange (V_e) to deuterium addition (V_h) and to intramolecular process (V_i) are also different for metals used: $V_h/V_e = 3$ (Pt), 0.5 (Pd), and 0.3 (Cu) and $V_i/V_e = 0.1$ (Pt), 1 (Pd), and 3 (Cu). On the other hand, in the case of the C_3H_6–C_3D_6 reaction over Pd and Pt, *n*-propenyl intermediate is more active than *sec*-propenyl species, and again the situation is the opposite of the case of Cu. Deuterium exchange via associative process is one to two orders of magnitude faster than that via dissociative process in all the metals investigated. Overall activities in these processes are two to three orders of magnitude larger over Pd and Pt than those over Cu.

When Pd and Pt metals were alloyed with Cu, the activation energies of deuterium addition and exchange in the C_3H_6–D_2 reaction did not change considerably, while the TOF diminished to half or one-third of that over pure metals. The relative activity of each reaction intermediate was remarkably changed by alloying. Isotopic distribution patterns of the C_3H_6–D_2 reaction over Pd–Cu and Pt–Cu alloy catalysts were considerably different from those over Pd and Pt catalysts, and 2-d_1 was the main product, which was formed through the *n*-propyl intermediate. This is the active intermediate on the Cu surface, suggesting an important role of copper in modifying the adsorbed states of intermediates and their reactivity toward the C_3H_6–D_2 reaction. Intramolecular hydrogen shift on Pd metal almost disappeared by alloying, which indicated that this process might require larger ensemble size of surface Pd metal.

In the case of C_3H_6–C_3D_6 reaction over Pd–Cu and Pt–Cu alloy catalysts, the TOF was not affected at all by alloying. Isotopic distribution pattern over Pt–Cu catalyst resembles that over Cu metal, again suggesting a certain modification of the active site by copper. The situation, however, is considerably different over Pd–Cu alloy catalyst, where the isotopic distribution pattern exhibited considerable change with time. One explanation for this is that a rapid intramolecular 1,3-hydrogen shift process follows deuterium incorporation through dissociatively adsorbed σ-allyl intermediate. Another explanation is that the reaction proceeds through single π-allyl species adsorbed dissociatively, and the repeated intermolecular exchange through this intermediate causes the change in the isotopic distribution pattern with time. If this is the case, 1,3-hydrogen transfer process should exhibit the same rate as deuterium incorporation process. We compared the rate of 3-d_1 formation in the C_3H_6–C_3D_6 reaction (deuterium incorporation process) with that in the reaction of 1-d_1 alone (intramolecular process). Similar rates were obtained in both reactions, suggesting that the C_3H_6–

C_3D_6 reaction over Pd–Cu proceeds via π-allyl intermediate. This implies that copper atoms adjacent to a palladium atom make it possible to transform σ-allyl adsorbed species to π-allyl species.

The role of Cu in Pd–Cu and Pt–Cu alloys demonstrated in this study for the hydrogenation and hydrogen exchange for propene is similar to that which De Jongste and Ponec (*11*) reported for the hydrogenolysis of pentane over various Cu alloy catalysts. As they suggested, it is not so easy to derive some concrete features for these phenomena. However, from the experimental results obtained in this study, we propose that new active sites are formed by alloying Group VIII metals with Group IB metals; the interaction between them may well be called the "synergetic ligand effect" (*23, 24*).

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