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Effect of a Hydrogen Pretreatment on the Mechanism of Deuterium Addition and Exchange of Propene over Ni-Cu Alloy Catalysts

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The effects of a hydrogen pretreatment on the activity and reaction intermediate in a C_3H_6-D_2 reaction over a Ni-Cu alloy as well as Ni metal catalysts were investigated in detail by applying an isotope tracer technique. Ni metal and Ni-rich alloy catalysts, cooled down to the reaction temperature under a hydrogen atmosphere (D-surface), exhibited low activity compared to that of a surface evacuated before cooling (E-surface). For Cu-rich alloy catalysts, however, the E-surface exhibited a lower activity and a higher activation energy than did the D-surface. A comparison of the TPD spectra of adsorbed hydrogen with the dependence of the activity upon the evacuation temperature suggests that strongly adsorbed hydrogen retards the reaction over Ni and Ni-rich alloy catalysts at lower temperature. Microwave spectroscopic analysis demonstrated that the reaction intermediates over D- and E-surfaces of Cu-rich alloy catalysts were similar to those over Cu and Ni metals, respectively. This result suggests that a hydrogen pretreatment of Cu-rich alloys forms a specific surface structure which is destroyed by evacuation at elevated temperatures.

Bimetallic alloy systems comprising an active group-VIII metal and an inactive group-IB metal have extensively been investigated, since they allow one to study the role of the "geometric, or ensemble, effect" as well as the "electronic, or ligand, effect" in alloy catalysts.[1–3] Among them, a nickel-copper alloy system has received particular attention from the viewpoint of both the surface structure and the catalytic behavior in hydrogen exchange,[4–6] hydrogenation,[7–12] hydrogenolysis[13] or dehydrogenation[14] of various hydrocarbons. Analyses of its surface composition by various methods, such as selective chemisorption,[15,16] work function change,[17–19] and AES (Auger Electron Spectroscopy) measurements,[20,21] have disclosed a considerable enrichment of copper on the surface, which is inactive for the reactions mentioned above. Accordingly, the dilution effect of active metal ensembles by inactive atoms would be significantly pronounced in these systems (ensemble effect). In fact, it is well known that reactions involving C-C bond fission or formation are suppressed much more efficiently by alloying than reactions involving C-H bonds on this catalyst.[1,4,6,13] The situation is somewhat different in the case of the hydrogenation reaction, which proceeds at a much lower temperature than does hydrogenolysis or dehydrogenation.

Best and Russell[7] examined the hydrogenation of ethene over Ni-Cu alloy catalysts of various composition and observed several orders of magnitude higher activity in the copper-rich range than over a pure Ni catalyst. Hall and Emmett[8] reported a remarkable dependence of the activity for this reaction upon the pretreatment over Ni-Cu alloy catalysts as well as pure Ni catalysts. When the catalysts were evacuated at the temperature at which the reduction had been carried out, and then cooled in vacuo or in flowing helium, the activity decreased as the copper content of the catalyst increased. On the other hand, if the catalysts were cooled in a hydrogen atmosphere the activity showed two maxima at around 30 and 70 atm% of copper in the alloy composition.[9] Hall and Hassell further demonstrated that these results could be explained in terms of a promotion effect of strongly adsorbed hydrogen on the hydrogenation rate over alloy catalysts and a suppression effect over pure Ni metal.[10] To clarify the intrinsic nature of this effect, it is obviously necessary to study changes not only in the reaction rates, but also in the reaction mechanism by these pretreatments.

Deuterium addition and exchange of propene (C_3H_6-D_2 reaction) would be an excellent probe reaction for this purpose, since it enables one to investigate the fine structure of the reaction mechanism by applying microwave spectroscopy.[22] The temporal changes in the isotope distribution in monodeuteriopropene formed during the reaction can be followed. We have examined the effect of a pretreatment on the C_3H_6-D_2 reaction over Ni-Cu alloy catalysts of various compositions and found the same phenomena as in the case of the C_2H_4-H_2 reaction. Moreover, the relative activity of the reaction intermediates, propyl and isopropyl adsorbed species, was demonstrated to change with the manner of pretreatment, as well as the surface composition of Ni and Cu. In the present paper we describe in detail the experimental results and discuss in depth possible features of this effect.

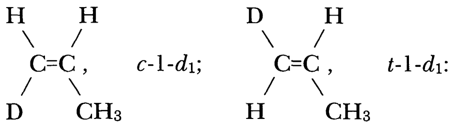
Experimental

Catalyst Preparation. Powders of Ni-Cu alloy and pure metals (Ni and Cu) were prepared by carefully reducing the corresponding oxide powders according to a method described in the literature.[15] First of all, carbonate powders were coprecipitated by adding aqueous nitrate solutions ($Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$; Wako Chemicals, spec. pure) dropwise to aqueous NH_4HCO_3 solutions (Wako Chemicals, spec. pure) with vigorous stirring. The precipitates were filtered, washed thoroughly with distilled water, dried, and calcined in air at 673 K for 2 h. The oxide powders were placed in an U-shaped reactor and reduced with flowing hydrogen by increasing the temperature very slowly from 298 to 773 K (within about 12 h) and then maintaining that temperature for 20 h. The bulk composition of the alloys employed were 0.5, 25, 60, and 90 atom% of copper.

Catalyst Characterizations. The surface areas and surface compositions in alloy catalysts were determined by N_2 physisorption at its normal boiling point and H_2 chemisorption at room temperature. About a one-order-of-magnitude larger amount of the catalysts (10—15 g) than that used for the catalytic reaction were employed in order to obtain precise values for adsorption experiments. Before measurements, the catalysts were reduced with H_2 at 623 K for 2 h and then evacuated at the same temperature for 0.5 h in a volumetric apparatus (base pressure was 1×10^{-3} Pa). The crosssectional areas of the N_2 molecule and the H atom were assumed to be 16.2 and 6.45 Å^2, respectively. Hydrogen was chemisorbed at room temperature in order to obtain total uptake. The catalyst was then evacuated under vacuum for 30 min at room temperature. Readsorption measurements were carried out in order to determine the amount of weakly adsorbed hydrogen. The amount of strongly adsorbed hydrogen was determined from the difference between these two values. The surface area of this strongly adsorbed hydrogen was assumed to correspond to that of surface Ni. Comparing this with the total surface area obtained by the BET method, the surface compositions of Ni and Cu could be estimated. The obtained results were as follows: 0.5 mol% bulk Cu=0.55 surface Cu, 25 mol% bulk Cu=0.77 surface Cu, 60 mol% bulk Cu=0.78 surface Cu, 90 mol% bulk Cu=0.91 surface Cu. These surface compositions were qualitatively confirmed by XPS (X-ray photoelectron spectroscopy) analysis (ESCALAB 5). The formation of a monophase homogeneous alloy was confirmed by observing their characteristic X-ray diffraction pattern. The lattice constants of alloy powders obtained were consistent with Vegard's law: Ni=3.52 Å, Ni-Cu(0.5)=3.52 Å, Ni-Cu(25)=3.54 Å, Ni-Cu(60)=3.58 Å, Ni-Cu(90)=3.60 Å, and Cu=3.61 Å.

Reaction Procedure, Detection Method, and TPD Procedure. H_2 and D_2 gases from commercial cylinders were purified by circulating over a heated palladium black catalyst to remove trace amount of oxygen. C_3H_6 purchased from Takachiho Kagaku K.K. was purified by a freeze-thaw cycle. The C_3H_6-D_2 reaction was carried out in a closed gas circulation system (total volume: 310 cm^3). Before each run the catalyst was freshly reduced by D_2 at 473 K for 2 h. For a reaction over a deuterium pretreated surface (D-surface), the catalyst was cooled to the reaction temperature without evacuating deuterium gas. For a reaction over an evacuated surface (E-surface), the catalyst was evacuated at 473 K for 1 h and then cooled down to the reaction temperature under vacuum. A certain amount of the C_3H_6-D_2 mixture was introduced into the system and the reaction started. The reaction temperature was maintained with suitable slush bathes.

At certain intervals during the reaction, a few percent of the circulating gas was sampled and analyzed. The composition of the gas was determined by gas chromatography (alumina column, He carrier). The deuterium contents in the exchanged propene and formed propane were determined with a mass spectrometer (Hitachi, RMU-6MG) using ionization voltages of 12 and 15 eV, respectively. The location of the deuterium atom in mono- and dideuteriopropene was determined by recording the microwave absorption line (1_{01}—0_{00} rotational transition) characteristic of each isotopic species. The notation for isotopic isomers in monodeuteriopropene is:



c-1-d_1; t-1-d_1:

CH_2=CD-CH_3, 2-d_1. CH_2=CH-CH_2D, 3-d_1.

TPD (Temperature programmed desorption) experiments were carried out in a separate UHV apparatus (base pressure: 1×10^{-7} Pa), equipped with a mass spectrometer (UTI 100). The heating part was made of a quartz cell, in which about 10 mg of catalyst was placed. The heating rate was set to 15 K min^{-1}.

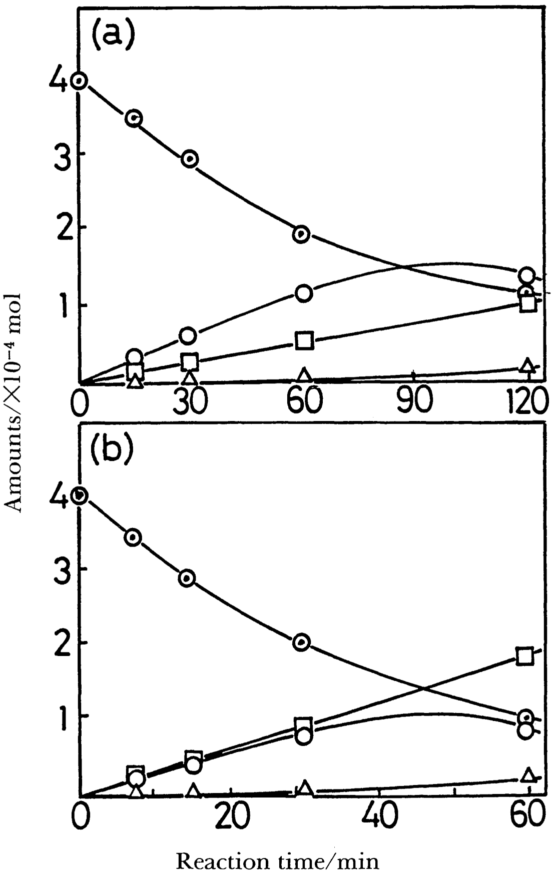


Fig. 1. Time courses of C_3H_6-D_2 reaction (D-surface) over (a) Ni metal at 210 K and (b) Ni-Cu(25) at 180 K.
p_{D_2}=6.7 kPa, $p_{C_3H_6}$=2.0 kPa, Catalysts=1 g.
⊙: Propene- d_0, ○: Propene-d_1, △: Propene-d_2, □: Propane.

Results

Kinetics of C_3H_6-D_2 Reaction over D-Surfaces. When a mixture of D_2 (6.7 kPa) and C_3H_6 (2.0 kPa) was introduced over D-surfaces of Ni and Ni-Cu alloy catalysts at 170—220 K, both deuterium addition and exchange reaction took place simultaneously. The D-surface was prepared by D_2 reduction at 473 K or 2 h, followed by cooling down to the reaction temperature without evacuation. Typical time courses of the reaction over Ni metal and Ni-Cu(25) (25 mol% bulk Cu) catalysts are shown in Fig. 1. In the case of Ni metal (Fig. 1(a)), the main product in the exchange process was C_3H_5D (propene-d_1), the formation rate of which was twice as fast as that of propane. During a later stage of the reaction, $C_3H_4D_2$ (propene-d_2) was detected, suggesting a successive reaction in the exchange process. The reaction over Ni-Cu(25) was nearly two orders of magnitude faster than that over Ni metal (Fig. 1(b)). The time course was similar to that over Ni, except that C_3H_5D and propane were formed in comparable amounts. The reaction behavior of other catalysts could be divided into these two categories: Ni-Cu(0.5) alloy was similar to Ni metal; Ni-Cu(60) and (90) alloys were similar to Ni-Cu(25).

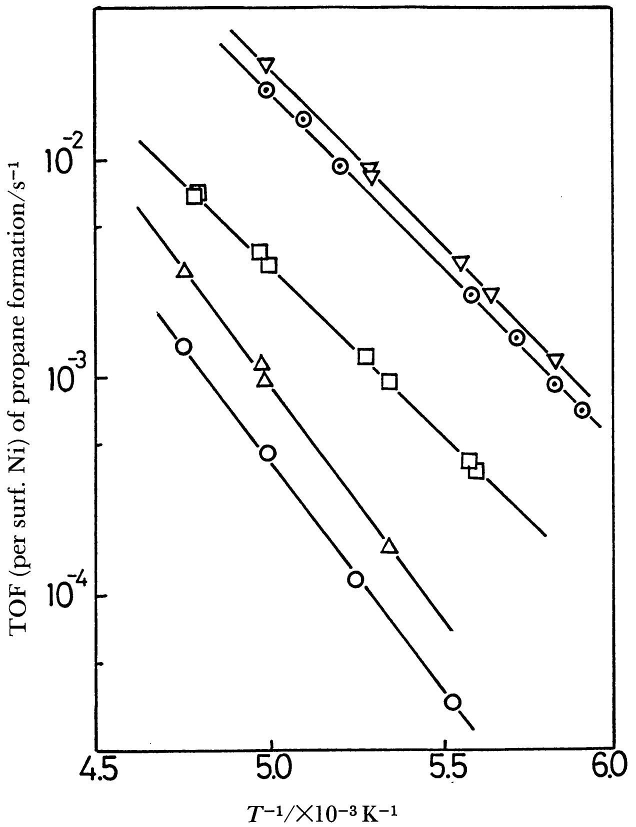


Fig. 2. Temperature dependence of TOF of propane formation (D-surface) over various catalysts. $p_{D_2}=6.7$ kPa, $p_{C_3H_6}=2.0$ kPa, Catalyst=1 g. ○: Ni, △: Ni-Cu(0.5), ⊙: Ni-Cu(25), ▽: Ni-Cu(60), □: Ni-Cu(90).

The temperature dependence of the turnover frequency (TOF) of propane formation over various catalysts is displayed in Fig. 2. The TOF was estimated assuming that only the surface Ni atoms are active for this reaction. The activity for propane formation decreased in the following order: Ni-Cu(60)≈Ni-Cu(25)>Ni-Cu(90)>Ni-Cu(0.5)<Ni metal. The activation energies of the reaction were also classified into two categories. Ni-Cu(0.5) catalyst exhibited an activation energy (41 kJ mo^{-1}) similar to that of Ni metal (39 kJ mol^{-1}). The activation energy considerably decreased by alloying, and the same value (31 kJ mol^{-1}) was observed for Ni-Cu(25), (60), and (90) alloy catalysts.

The pressure dependence of the turnover frequency for propane formation over Ni and Ni-Cu(25) catalysts is demonstrated in Fig. 3. Over a Ni catalyst the reaction orders for the partial pressures of hydrogen and propene were 0.37 and 0.07, respectively. Upon alloying, they decreased as follows: 0.45 for the partial pressure of hydrogen and −0.15 for propene; this suggests an increase in the adsorption strength of propene by alloying.

Kinetics of C_3H_6-D_2 Reaction over E-Surfaces. Figure 4 demonstrates the temperature dependence of propane formation over the E-surfaces of Ni and Ni-Cu alloy catalysts. The E-surfaces were prepared by D_2 reduction at 473 K, followed by evacuation at the same temperature for 1 h. It was recognized that this evacuation treatment drastically accelerates the propane formation rate over both Ni and Ni-Cu(0.5) catalysts, although their activation energies did not change at all. The situation was completely different over

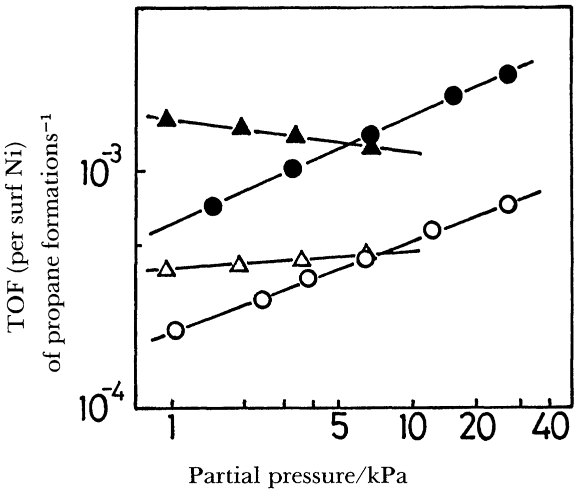


Fig. 3. Pressure dependence of TOF of propane formation (D-surface) over (a) Ni metal at 210 K (open symbols), and (b) Ni-Cu(25) alloy catalyst at 180 K (closed symbols).
○●: Dependence of H_2 partial pressure ($p_{C_3H_6}=3.3$ kPa, constant). △▲: Dependence of C_3H_6 partial pressure ($p_{H_2}=6.7$ kPa, constant).

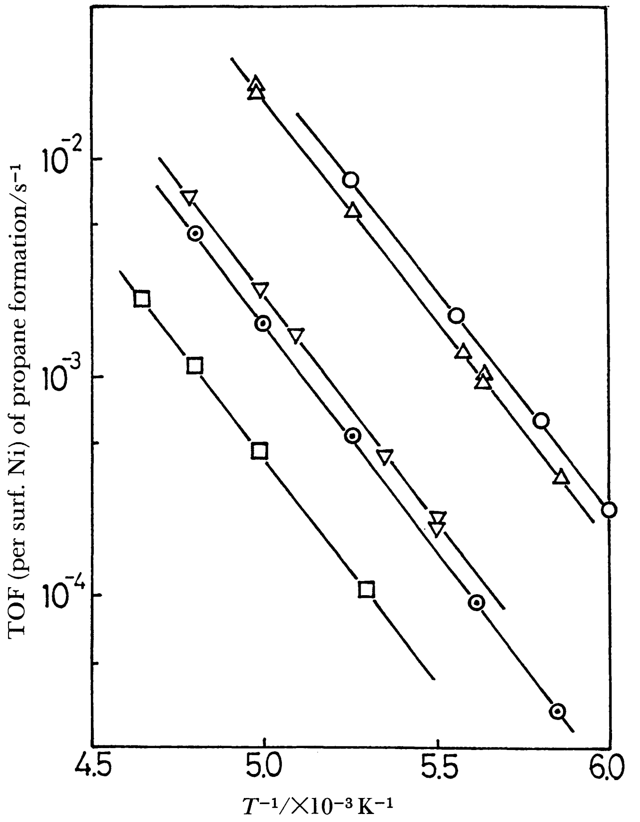


Fig. 4. Temperature dependence of TOF of propane formation (E-surface) over various catalysts.
p_{D_2}=6.7 kPa, p_{D_2}=2.0 kPa, Catalyst=1 g.
○: Ni, △: Ni-Cu(0.5), ⊙: Ni-Cu(25), ▽: Ni-Cu(60).
□: Ni-Cu(90).

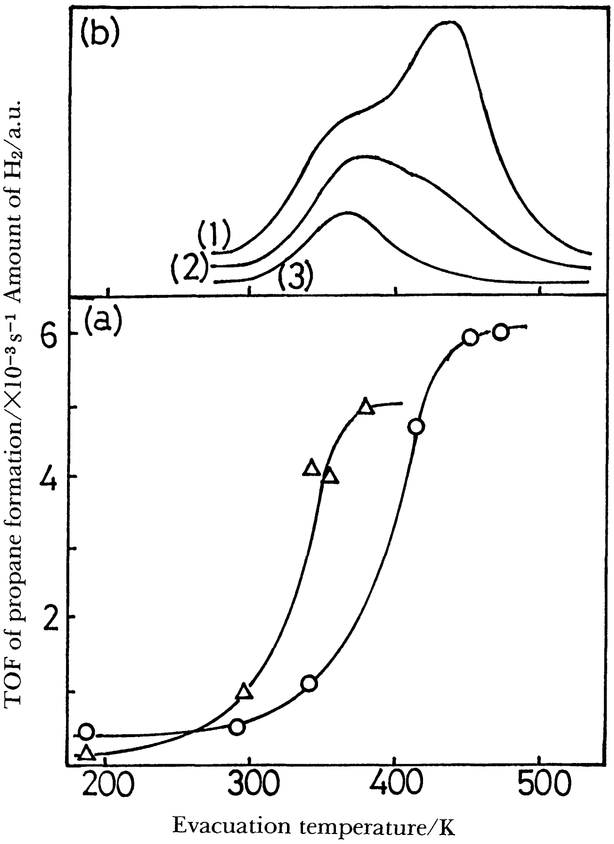


Fig. 5. (a) Effect of evacuation temperature on TOF of propane formation over Ni metal at 190 K, and over Ni-Cu(0.5) catalyst at 210 K.
p_{D_2}=6.7 kPa, $p_{C_3H_6}$=2.0 kPa, Catalyst=1 g.
○: Ni, △: Ni-Cu(0.5).
(b) TPD spectra of adsorbed H(a) over various catalysts.
(1) Ni, (2) Ni-Cu(0.5), (3) Ni-Cu(25).
Adsorption temperature=273 K for 1 h. (p_{H_2}=6.7 kPa).

other alloy catalysts: the rate decreased more than one order of magnitude with an increase in the activation energy to 40 kJ mol^{-1} for Ni-Cu(25), (60), and (90) catalysts.

To investigate the relation between the D- and E-surfaces of Ni and Ni-Cu(0.5) catalysts, the effect of the evacuation temperature upon the rate of propane formation was examined, as summarized in Fig. 5(a). After reduction by D_2 at 623 K for 2 h, the catalyst was evacuated for 1 h at various temperatures from 190 to 623 K and then cooled down to the reaction temperature (190 K for Ni and 210 K for Ni-Cu(5)), before C_3H_6-D_2 reaction was carried out. In the case of the Ni catalyst, the rate gradually increased as the evacuation temperature was increased, and reached a plateau activity at around 450 K. Over a Ni-Cu(0.5) catalyst, this plateau temperature was considerably lowered (360 K). Fig. 5(b) demonstrates the TPD spectra of adsorbed hydrogen over pure Ni, Ni-Cu(0.5) and Ni-Cu(25) alloy catalysts. The adsorption was carried out at 273 K for 1 h (P_{H_2}=6.7 kPa). After evacuation up to 10^{-7} Pa, the catalyst was heated at a rate of 15 K min^{-1}. Two maximum peaks were observed in the case of Ni. The higher temperature peak was considerably diminished and disappeared in the Ni-Cu(25) catalyst.

Microwave Spectroscopic Study of C_3H_6-D_2 Reaction. It has been well established that deuterium addition and exchange processes in the C_3H_6-D_2 reaction over Ni and Cu metal catalysts proceed through common σ-alkyl intermediates: propyl and isopropyl adsorbed species (associative mechanism).[23,24] The situation seemed to be identical over Ni-Cu alloy catalysts in the present study, because the rates of both addition and exchange processes exhibited similar temperature dependences, indicating equal activation energies. Moreover, the rate of the hydrogen exchange in the C_3H_6-C_3D_6 reaction, which should proceed via a dissociative mechanism, was more than two orders of magnitudes slower than that in the C_3H_6-D_2 reaction. Consequently, it is evident that hydrogen exchange in the C_3H_6-D_2 reaction over alloy catalysts takes place via a reverse process of the σ-alkyl intermediate formation, as in Ni and Cu catalysts.

The isotopic distributions of formed propane over

Table 1. Isotopic Distribution of Propane and Propene-d_2 in C_3H_6-D_2 Reaction over D-Surfaces of Various Catalysts

Catalysts	Ni	Ni-Cu (0.5)	Ni-Cu (25)	Cu
Reac. Temp	190	190	180	263
Reac. Time/min	60	60	120	600
Conversion	0.41	0.45	0.32	0.35
C_3H_8	0.33	0.30	0.05	0.04
C_3H_7D	0.28	0.29	0.26	0.25
$C_3H_6D_2$	0.29	0.32	0.55	0.58
$C_3H_5D_3$	0.09	0.09	0.11	0.12
$C_3H_4D_4$	0.01	0.01	0.02	0.02
$C_3H_3D_5$-C_3D_8	0.00	0.00	0.00	0.00
CD_2=CH-CH_3	0.03	0.04	0.06	0.07
CHD=CD-CH_3	0.85	0.85	0.80	0.79
CHD=CH-CH_2D	0.01	0.00	0.03	0.02
CH_2=CD-CH_2D	0.12	0.12	0.11	0.12
CH_2=CH-CHD_2	0.00	0.00	0.00	0.00

these catalysts are summarized in Table 1. Propane-d_2 was the main product over Cu (24), whereas comparable amounts of propane-d_0, -d_1, and -d_2 were formed over Ni catalyst.[23)] The latter phenomenon corresponds well to the first observation by Turkevich et al.[25)] that C_2H_6 was mainly formed during the initial stage of the C_2H_4-D_2 reaction over Ni, which was reasonably explained by an associative mechanism.[26)]

The relative reactivity of propyl and isopropyl intermediates can be estimated by observing the isotopic distribution of monodeuteriopropene formed in the exchange process of the C_3H_6-D_2 reaction. Microwave spectroscopic results over the D-surface are summarized in Figs. 6 and 7. Over a Ni catalyst (Fig. 6(a)) more than 90% of the exchanged products was propene-2-d_1, which would be formed through a propyl adsorbed intermediate. The remainder of the products were equal amounts of propene *cis*- and *trans*-1-d_1 with a small amount of propene-3-d_1. This result suggests that the isopropyl species is adsorbed in a distorted manner, so that hydrogen exchange takes place mainly on the C_1 carbon of the double bond. On the other hand, over a Cu catalyst (Fig.6(b)), the proportion of propene-2-d_1 decreased from 93 to 73%, with an increase of *cis*- and *trans*-1-d_1. As on the Ni catalyst, the amount of propene-3-d_1 was slight during the reaction, suggesting a sterically distorted adsorption of the isopropyl intermediate. Figure 7 demonstrates the isotopic distribution pattern in the case of Ni-Cu(0.5) and (25) catalysts. This pattern is quite similar to that of Ni metal in the case of a Ni-Cu(0.5) catalyst (Fig. 7(a)), whereas it resembles that of Cu metal in the case of a Ni-Cu(25) catalyst (Fig. 7(b)).

The closed symbols in the figures represent data for

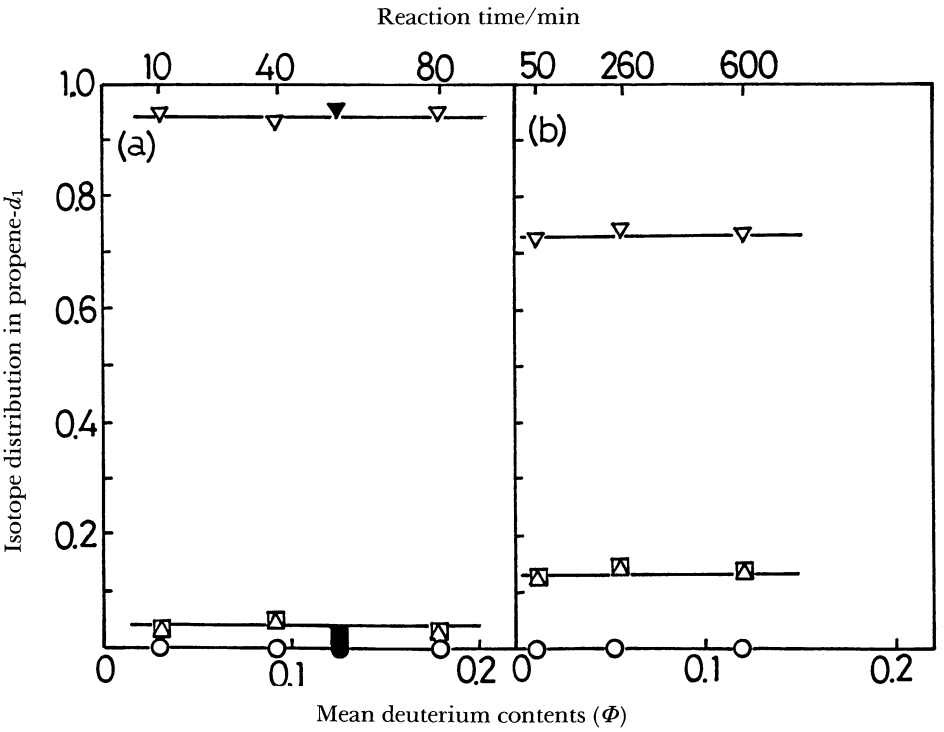


Fig. 6. Time course of the isotopic distribution in monodeuteriopropene during C_3H_6-D_2 reaction over (a) Ni metal at 200 K, and (b) Cu metal at 263 K. p_{D_2}=6.7 kPa, $p_{C_3H_6}$=2.0 kPa, Catalyst=1 g. Open symbols: over D-surfaces, closed symbols: over E-surfaces.
□■: *c*-1-d_1, △▲: *t*-1-d_1, ▽▼: 2-d_1, ○●: 3-d_1.

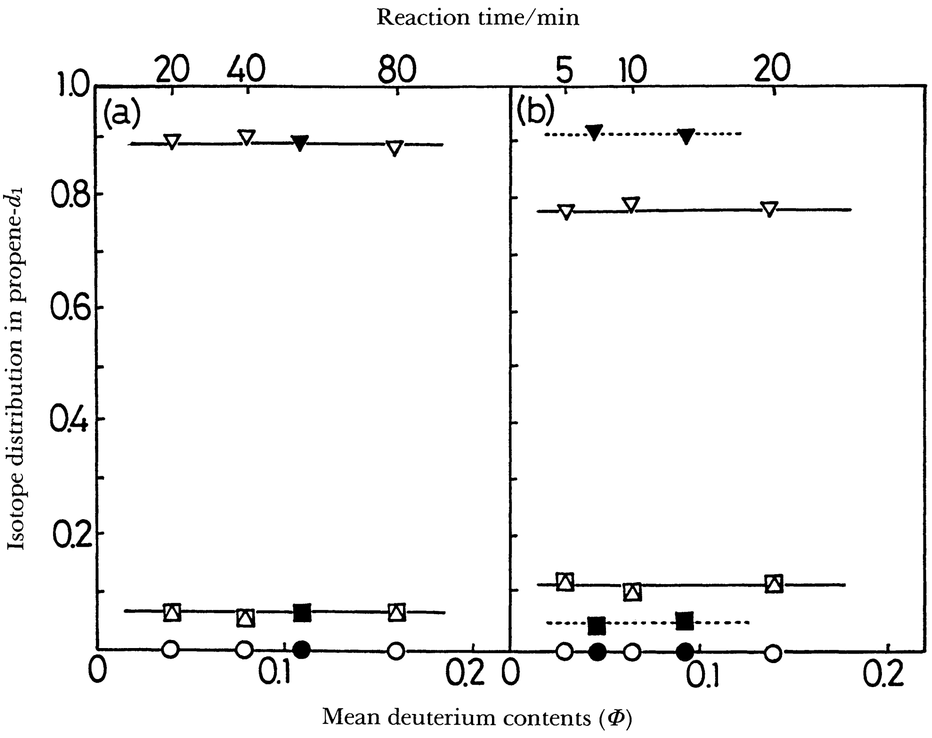


Fig. 7. Time course of the isotopic distribution of monodeuteriopropene during C_3H_6-D_2 reaction over (a) Ni-Cu(0.5) alloy at 190 K, and (b) Ni-Cu(25) alloy at 180 K.
p_{D_2}=6.7 kPa, p_{D_2}=2.0 kPa, Catalyst=1 g. Open symbols: D-surfaces, closed symbols: E-surfaces.
□■: *c*-1-d_1, △▲: *t*-1-d_1, ▽▼: 2-d_1, ○●: 3-d_1.

the corresponding E-surfaces. The time-course curves on the E-surface do not differ from those on the D-surfaces in the case of Ni and Ni-Cu(0.5) catalysts, whereas a clear difference can be seen for the Ni-Cu(25) catalyst. Its pattern resembles that on pure Ni metal. Similar results were observed in the cases of Ni-Cu(60) and (90) catalysts.

The results of a microwave spectroscopic analysis of propene-d_2 over D-surfaces of these catalysts are summarized in Table 1. The main d_2-product was propene-1,2-d_2, which can be reasonably explained by a successive reaction in the exchange process; dideuteriopropene may be formed by a repetitive exchange of monodeuteriopropene through σ-alkyl intermediates.

Discussion

It is well known that the surface composition of alloy catalysts is different from the bulk composition.[2,3] In the case of a Ni-Cu alloy, segregation and enrichment of copper on the surface is demonstrated by various methods.[15-21] In the present study, a hydrogen treatment at 773 K realized homogenization of alloys, which was confirmed by their characteristic X-ray diffraction patterns, as described in the experimental section. The surface compositions of alloys were determined by hydrogen chemisorption at room

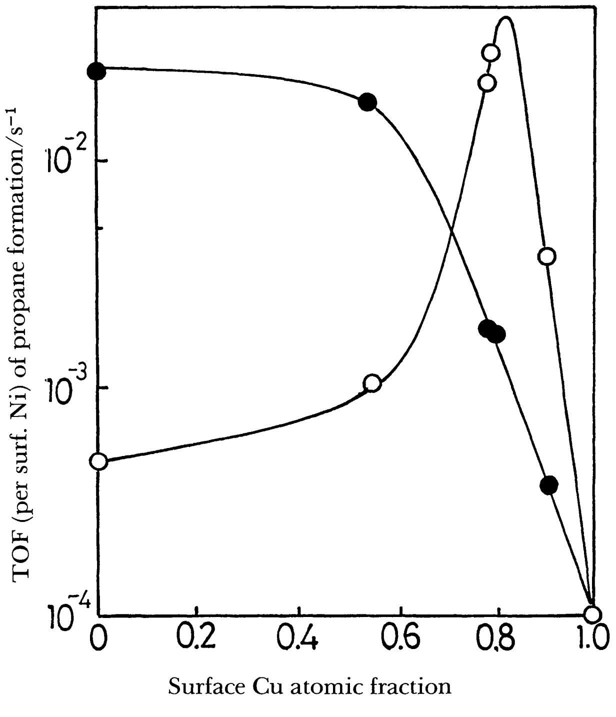


Fig. 8. Dependence of TOF of propane formation at 200 K upon the surface Cu atomic fraction.
○: D-surfaces, ●: E-surfaces:

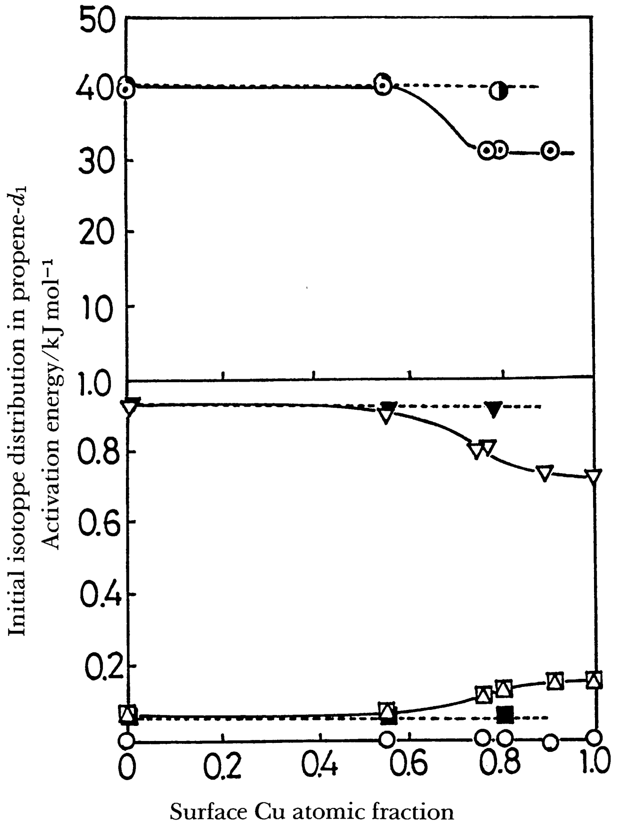


Fig. 9. Dependence of (a) the initial isotopic distribution of monodeuteriopropene and (b) activation energy upon the surface Cu atomic fraction.
Open symbols: D-surfaces, closed symbols: E-surfaces.
□■: c-1-d_1, △▲: t-1-d_1, ▽▼: 2-d_1, ○●: 3-d_1, ⦿◑: Activation energy.

temperature, under the assumption that strong adsorption of hydrogen occurs only on surface nickel atoms. Since adsorption was measured after evacuation at 623 K, the estimated values should correspond to the surface composition of the E-surfaces. It is impossible to determine the surface composition of the D-surfaces by this method. We therefore assumed that the number of surface Ni atoms does not change upon evacuation of hydrogen gas and the surface composition of E-surfaces was used to estimate the TOF over the D-surfaces.

Figure 8 demonstrates the change in the TOF of propane formation (estimated from Figs. 2 and 4) over D- and E-surfaces against surface copper atomic fractions. The catalytic behavior can be divided into two parts, the boundary being at around 60% of surface copper fraction. Over pure Ni and Ni-Cu(0.5) catalysts (nickel-rich alloy catalyst), the activity of the E-surface is much higher than that of the D-surface. The situation is opposite over Ni-Cu(25), (60), and (90) catalysts (copper-rich alloy catalyst); the D-surface is much more active than is the E- surface. Figure 9 summarizes the change in the initial isotope distribution pattern of monodeuteriopropene formed during a C_3H_6-D_2 reaction, as well as the activation energy of propane formation against surface copper atomic fractions. A similar change in the catalytic behavior was observed at around 60% of the surface copper atomic fraction. Over D-surfaces of nickel rich alloy catalysts, the isotopic distribution pattern as well as the activation energy were similar to those of Ni metal, itself. Over D-surfaces of copper-rich alloy catalysts, the distribution pattern considerably changed and became similar to that of Cu metal. On the other hand, over E-surfaces such changes were not observed even in the copper-rich alloy regions, and isotopic distribution pattern as well as activation energy remained similar to those of Ni metal.

The activity decrease over D-surfaces of Ni and Ni-rich alloy catalyst may be explained by an inhibition effect caused by strongly adsorbed hydrogen at lower temperatures. The existence of such strongly adsorbed hydrogen has been observed in TPD experiments of adsorbed hydrogen over a Ni surface.16,27,28) Three desorption peaks have been reported in the literature, whose maxima are at temperatures β_1=250 K, β_2=329 K and α=370 K.

We also examined the TPD spectra of H_2 on catalysts employed in this study, displayed in Fig. 5(b). Only two peaks were observed, corresponding to β_2 and α, whose peak maxima shifted by about 50 K to higher temperatures than those reported in the literature. Can be seen from the spectra, the amount of strongly adsorbed hydrogen drastically decreased as the surface copper composition increased in the alloy catalysts. By comparing Figs. 5(a) and (b) it was realized that the hydrogen desorption temperature corresponds well to the temperature of steeply increasing catalytic activity. Accordingly, it is reasonable to suppose that α hydrogen may be responsible for the inhibition of hydrogenation of propene at lower temperatures. Because of the lack of this α hydrogen peak, such inhibition does not occur in Cu-rich alloy catalysts. During a C_3H_6-D_2 reaction over the E-surface at lower temperatures, no drastic decrease in the reaction rate was observed, indicating a slow rate of α hydrogen adsorption at low temperatures. Moreover, the results of a pressure-dependence study indicate that the surface was mostly covered by adsorbed propene during the reaction, which also retards the adsorption rate of α hydrogen. However, once the E-surface was exposed to hydrogen at room temperature, the reaction rate at lower temperatures was considerably reduced, which is consistent with the above-mentioned consideration.

Another interesting point regarding these systems is the high activity of the D-surface in the case of Cu-rich alloy catalysts. Hall suggested that the catalytic activity of the surface alloy phase is increased by enrichment with Ni.29) The present microwave spectroscopic investigation, however, clearly demonstrated that the structure of the reaction intermediate is similar to that on Cu metal. Accordingly, the hydrogen treatment effect is not ascribed to surface-enriched Ni alone, but to some novel sites involving both Cu and Ni atoms. Such an effect was really observed only on the Cu-rich alloy surface, where every surface Ni atom might be surrounded by surface Cu atoms. A marked decrease in the activity over the E-surface suggests that evacuation at higher temperatures causes a reconstruction of the pertinent surface structure.

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