

Marked Changes of Reaction Intermediates caused by Alloying: Deuterium Addition and Exchange of Propene over Ni-Cu, Pd-Cu, and Pt-Cu Catalysts

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Microwave spectroscopic analysis of the monodeuteriopropene formed during $C_3H_6-D_2$ reaction over Ni-Cu, Pd-Cu, and Pt-Cu catalysts disclosed marked changes in the reaction intermediates for deuterium addition and exchange caused by alloying.

The main interest of alloying metals in the field of heterogeneous catalysis is the effect it can produce on the activity and the selectivity of catalytic reactions.¹⁻⁴ For alloy catalysts consisting of active group 8 metals and inactive group 1B metals, alloying has been considered to reduce the number of 'ensembles' of active metal atoms that are necessary for a certain type of adsorption or product formation.^{5,6} Accordingly, the effect is large for the structure-sensitive reactions⁷ such as hydrogenolysis⁸ but small for the structure-insensitive reactions such as hydrogenation.⁹ On the other hand, the changes in the electronic structure (ligand effect⁴) due to alloying are not very pronounced in these systems, although the coexistence of a certain electronic modification with ensemble effect has been recognized in some cases.¹⁰⁻¹³ In this communication we report that the reaction intermediates of the $C_3H_6-D_2$ reaction change markedly when Ni, Pd, and Pt

catalysts are alloyed with Cu. The result indicates an important role of copper in the modification of active sites and reaction mechanisms.

Alloy catalysts and their component metals were prepared by coprecipitation of metal carbonates (Ni, Ni-Cu, and Cu) or metal hydroxides (Pd, Pd-Cu, Pt, and Pt-Cu).^{14,15} Carbonate or hydroxide powders were calcined in air at 673 K for 2 h and then reduced by hydrogen while the temperature was very slowly increased from room temperature to 723 K at which it was kept for 20 h. After complete reduction the catalysts were examined using X-ray photoelectron spectroscopy (X.p.s.) (VG. ESCALAB 5), and exhibited no appreciable surface impurities. The formation of alloys was confirmed by observing their characteristic X-ray diffraction patterns. The bulk composition of the alloys employed was 60 mol% of copper. Approximate surface composition of copper was 70-80% in

Table 1. Isotope distribution in monodeuteriopropene formed during $C_3H_6-D_2$ reaction over various catalysts [$P(D_2) = 4$ kPa, $P(C_3H_6) = 2$ kPa].

Catalyst	Reac. temp./K	$E_{exc.}/$ kJ mol ⁻¹	$E_{hyd.}/$ kJ mol ⁻¹	Mean D ^a content (ϕ)	<i>cis</i> -1-[² H ₁] (%)	<i>trans</i> -1-[² H ₁] (%)	2-[² H ₁] (%)	3-[² H ₁] (%)
Ni	200	41	39	0.03	2	3	95	0
				0.24	3	3	94	0
Pd	210	34	33	0.03	35	33	16	16
				0.10	28	28	14	30
				0.19	23	22	14	41
				0.01	9	57	28	6
Pt	235	45	43	0.05	16	48	28	8
				0.10	20	42	28	10
				0.03	11	12	77	0
Ni-Cu	180	35	33	0.14	11	11	78	0
				0.02	20	17	58	5
Pd-Cu	225	36	35	0.20	20	18	57	5
				0.01	13	9	68	10
Pt-Cu	248	44	43	0.09	12	10	67	11
				0.01	14	14	72	0
Cu	263	-	-	0.01	14	14	72	0
				0.05	13	14	73	0

^a $\phi = 1/600 \sum_{i=1}^6 i \times [^2H_i]$ (mean deuterium content in propene molecule).

all the alloys employed [estimated from the amount of adsorbed hydrogen at room temperature and Brunauer-Emmett-Teller (B.E.T.) surface area, and confirmed qualitatively by X.p.s.].

Reaction of propene and deuterium was carried out in a closed gas circulation system. Before each run the catalysts were freshly reduced by H_2 or D_2 at 473 K for 2 h and cooled to the reaction temperature without evacuating hydrogen gas. The composition of the gas phase was analysed during the reaction by gas chromatography (alumina column, He carrier). Deuterium contents in the exchanged propene were determined by mass spectrometry (Hitachi, RMU-6MG) with an ionization voltage of 12 eV.¹⁶ The location of the deuterium atom in monodeuteriopropene was determined by microwave spectroscopy.¹⁷

When a mixture of D_2 (4 kPa) and C_3H_6 (2 kPa) was introduced onto a freshly reduced Ni, Pd, or Pt powder catalyst (2–3 g), deuterium addition and exchange took place simultaneously. These processes exhibited identical temperature and pressure dependence behaviour; Langmuir type rate equations are valid in all cases and the activation energies are summarized in Table 1. These results indicate that both addition and exchange processes proceed *via* the same reaction intermediate, presumably the σ -alkyl species as has been concluded in the case of silica-supported catalysts.^{18,19} Table 1 demonstrates the isotope distribution in [²H₁]propene formed during $C_3H_6-D_2$ reaction over these catalysts. At the beginning of the reaction ($\phi = 0.01$ – 0.03 ; mean deuterium content in propene), deuterium addition to adsorbed propene and hydrogen abstraction from σ -alkyl species take place only on the double bond carbons (C-1 and C-2) producing mainly 1-[²H₁] (on Pd and Pt) or 2-[²H₁] (on Ni). The methyl carbon (C-3) of propene, however, is inactive in this deuterium incorporation process. The intramolecular isomerization process, proposed in the study of silica-supported catalysts,^{18,19} also proceeds on these powder catalysts and drastic changes in isotopic composition of monodeuteriopropene are observed at the initial stage of the reaction (up to $\phi = 0.15$ – 0.20), where isotope dilution of deuterium by the repeated adsorption and desorption of σ -alkyl species is not significant. This mechanism can convert *trans*-1-[²H₁] into *cis*-1-[²H₁]propene (on Pt and Ni) and 3-[²H₁]propene (on Pd).

When these metals were alloyed with copper, the kinetic parameters of the $C_3H_6-D_2$ reaction did not change considerably. The pressure dependence in the addition and exchange processes obeyed the Langmuir type rate equations and the temperature dependence was also the same in both processes as summarized in Table 1. These results seemingly suggest that alloying with copper does not affect the mechanism of the $C_3H_6-D_2$ reaction and that an associative mechanism with σ -alkyl intermediates may operate on the alloy catalysts too. The turnover frequency of propane formation over Ni-Cu, however, was more than one order of magnitude larger than that over Ni powder. This phenomenon has already been reported by Hall and Emmett,²⁰ who attributed it to the effect of hydrogen treatment at elevated temperatures. Over Pd-Cu and Pt-Cu alloy catalysts, the turnover frequencies of propane formation, based on the number of surface Pd or Pt atoms (surface copper was assumed to be inactive for this reaction), were approximately half or one third of those on Pd or Pt, which were still more than two orders of magnitude larger than that for Cu powder. These results indicate that the intrinsic activity of these metals for deuterium addition and exchange is not significantly affected by alloying and are consistent with the consensus that hydrogenation is a structure-insensitive reaction.

However, the isotope distribution of the monodeuteriopropene formed over these alloy catalysts suggests considerable change in the structure of the reaction intermediates. In the case of Ni-Cu alloy, the relative activity of the C-1 carbon (s-propyl species) for exchange (22%) is higher than that of Ni (6%). For Pd-Cu and Pt-Cu alloy catalysts, the C-2 carbon (n-propyl species) becomes more active than the C-1 carbon (s-propyl species) on alloying: from 16 to 58% for 2-[²H₁] on Pd-Cu and from 28 to 68% for 2-[²H₁] on Pt-Cu. Moreover, the intramolecular isomerization process becomes very slow on using alloys. The most striking point is that these isotope distribution patterns over alloy catalysts resemble that over Cu, whereas the reaction rates are quite different from those over Cu, and the activation energies are still close to those of the individual metals.

This study has demonstrated an important role of copper in the hydrogenation of alkenes over Ni-Cu, Pd-Cu, and Pt-Cu alloy catalysts. From these experimental results we propose

the following model for active sites to elucidate the role of the copper component in alloy catalysts. The surface composition (70–80% Cu) indicates a surface where the group 8 metals are isolated atomically from each other and surrounded by copper atoms. In this situation, copper metal clusters or mixed clusters of copper–group 8 metal become the active sites for alkene as well as hydrogen activation. This model implies the important role of electronic interaction between surface copper and group 8 metal in alloy catalysis, which has often been thought to be ineffective.

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