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Preparation of supported bimetallic catalysts by means of selective deposition using mobile metal compounds as precursors

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Abstract

The preparation of supported bimetallic catalysts was examined by selective deposition of metal complex precursors on the surface of the first metal particles. A Pt–Ru/SiO_2 catalyst was prepared using Pt/SiO_2 and ruthenocene as starting materials. Analysis of the surface structure by means of O_2–CO titration suggested that Ru metals covered the surface Pt atoms without forming separate Ru particles. This technique was applied for the preparation of an egg-shell type of the Pd–Fe bimetallic catalyst supported on alumina, using ferrocene as a precursor of iron. Pt–Sn bimetallic catalysts were prepared by selective deposition of tetramethyl tin on Pt particles. Liquid-phase deposition was tried in the case of Pd–Ag and Pd–Au catalysts supported on alumina. Selective deposition of Ag and Au on Pd surface was observed, and the selectivity to 1-butene was increased in the partial hydrogenation of 1,3-butadiene.

Keywords: Supported bimetallic catalysts; Selective deposition; Mobile metal compounds

1. Introduction

Supported bimetallic catalysts are frequently used in the industry, but the preparation method has not been well established. Because bimetallic interaction appears only when the two metallic components form bimetallic clusters instead of separate particles, it is desirable to develop a preparation method in which the deposition of the second metallic component preferentially takes place on the surface of the first metal particle. We have tried this selective deposition using volatile complexes as the precursor of the second metallic component. In this paper, we first tried the deposition of Ru on a Pt gauze using ruthenocene (bis-η-cyclopentadienyl ruthenium(II)) as the precursor in flowing hydrogen. Because Ru deposited selectively on the Pt surface, we applied this method for the preparation of some supported bimetallic catalysts. The method is effective especially in the case of egg-shell types of pellet catalysts which contain metallic components only in the outer layers of catalyst pellets to control the distribution of the metallic components. We also tried liquid-phase deposition of Ag and Au, as volatile precursors of these metals were not available.

2. Experimental

2.1. CVD of ruthenocene on Pt gauze

The Pt gauze (100 mesh, 99.9%) was placed in a Pyrex tube (10 mm o.d.) and heated at 450 K, as shown in Fig. 1. In the lower part of the reactor, ruthenocene (Aldrich, reagent grade)

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was vaporized in flowing hydrogen at 400 K. The resulting thin films of Ru were analyzed with EPMA (Shimazu EMX-SM) and XPS (Ulvac Phi ESCA558UP).

2.2. Catalyst preparation

A silica supported Pt catalyst was prepared by impregnation of SiO_2 (aerosil 380) with an aqueous solution of H_2PtCl_6, followed by drying and hydrogen reduction at 600 K for 3 h. The egg-shell type samples of Pd/Al_2O_3 (supplied by Nissan) and Pt/Al_2O_3 (supplied by NE Chemcat) have a structure, as illustrated in Fig. 2, in which the noble metals are supported only in the outer layers of cylindrical pellets. These supported mono-metallic catalysts were used as the starting materials of supported bimetallic catalysts. Details of the preparation of bimetallic catalysts are described individually together with the experimental results. The amount of deposited metals was measured by X-ray fluorescence.

2.3. Measurement of the surface composition of Pt–Ru

The surface composition of Pt–Ru bimetallic particles was determined by means of O_2–CO titration [1,2]. The amount of O_2 adsorbed was determined by pulse adsorption at room temperature. The surface oxygen was then titrated by

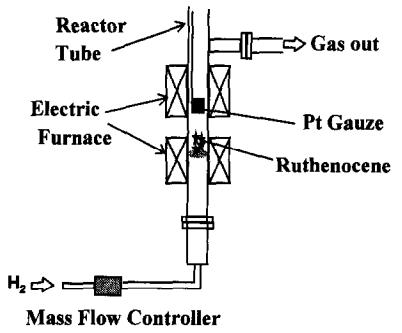

Fig. 1. Apparatus used for the deposition of Ru on Pt gauze in a flow of hydrogen.

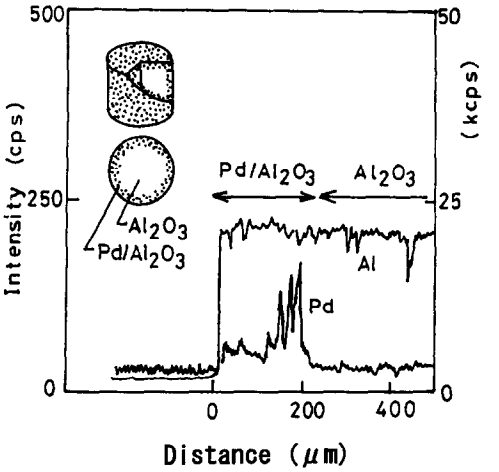

Fig. 2. Analysis of the cross section of a typical egg-shell type of Pd/Al_2O_3 catalyst. Zero in distance represents the edge of the pellet. Dots indicate the distribution of Pd.

CO pulses, forming CO_2. The ratio of O_2:CO:CO_2 was 1:4:2 on Pt and 1:1:0.3 on Ru. Using the titrated values of $O_2(N_{O_2})$, $CO(N_{CO})$ and $CO_2(N_{CO_2})$ on the Pt–Ru bimetallic catalysts, the numbers of surface Pt (Pt_s) and Ru(Ru_s) atoms are calculated as the solution of the following Eqs. (1) and (2). The observed N_{CO_2} was found to agree with the calculated value using Pt_s and Ru_s in the Eq. (3).

$$0.5Pt_s + Ru_s = N_{O_2} \quad (1)$$

$$2Pt_s + Ru_s = N_{CO} \quad (2)$$

$$Pt_s + 0.3Ru_s = N_{CO_2} \quad (3)$$

2.4. EPMA analysis

The egg-shell type of catalyst pellets were embedded in an epoxide resin and were cut off by a diamond cutter. The distribution of the metal components in the cross-section of the catalyst pellets was analyzed by EPMA, as shown in Fig. 2.

2.5. TEM observation

The bimetallic particles of $Pt–Ru/Al_2O_3$ and $Pd–Ru/Al_2O_3$ catalysts were observed by TEM

(Akasi Beam Technology EM-002B), and the composition was analyzed by EDX.

3. Results and discussion

3.1. CVD of ruthenocene on Pt gauze in H_2

Ruthenocene is a volatile compound and stable enough in hydrogen at temperatures less than 500 K. The deposition temperature of 450 K was found to be optimal, because the deposition of $Ru(cp)_2$ occurred selectively only on the Pt surface. At temperatures in excess of 450 K, the deposition occurred nonselectively on the Pt gauze, quartz wool and on the Pyrex tube. At temperatures below 450 K, the ruthenocene passed through the reactor without chemical reaction and deposited down stream of the Pt gauze. The results of EPMA analysis of the Ru deposition on Pt are shown in Fig. 3. Prior to deposition of Ru, the EPMA spectrum shows that only Pt is present. After 1 h of treatment in the ruthenocene vapor in a hydrogen flow, a small signal of Ru appeared. The signal intensity of Ru increased with the time of treatment for 6 h.

The corresponding XPS spectra of the surface of a Pt gauze are shown in Fig. 4. The spectrum in Fig. 4B shows a strong signal of

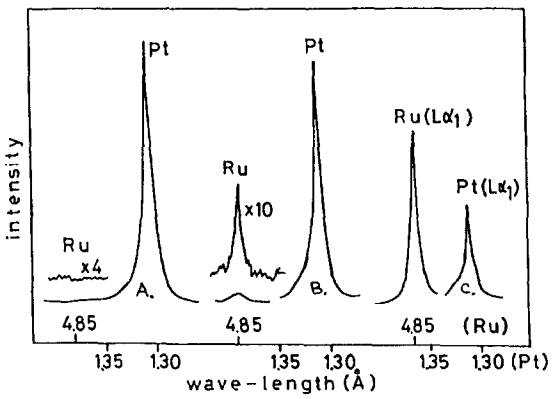

Fig. 3. The effect of ruthenocene treatment time on the deposition of Ru over a Pt gauze, as studied using EPMA. (A) Before deposition, (B) depositions for 1 h, (C) deposition for 6 h.

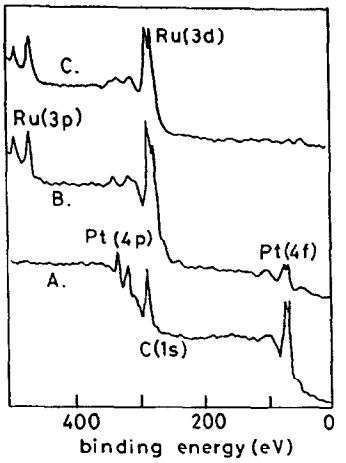

Fig. 4. XPS spectra of the same samples as shown in Fig. 3. (A) Before deposition, (B) deposition for 1 h, (C) deposition for 6 h.

Ru, so only 1 h of treatment was enough to cover most of the Pt surface. These results show that the Pt surface is covered with an ultra-thin film of Ru metal, because the analyzing depth of XPS is much smaller than that of EPMA.

3.2. Preparation of supported Pt–Ru bimetallic catalysts by successive impregnation

We first tried to prepare a silica-supported Ru catalyst using ruthenocene as a halogen-free Ru precursor. Ruthenocene was supported on silica by impregnation using its benzene solution. When the catalyst was heated up slowly in flowing hydrogen, ruthenocene vaporized before its reduction and condensed downstream the catalyst bed. The remaining catalyst contained only trace amounts of Ru.

A similar preparation was tried using Pt/SiO_2 instead of SiO_2. In this case ruthenocene was decomposed to metallic Ru on Pt and most of the Ru remained in the catalyst. Clearly, the presence of Pt particles in the catalyst accelerated the decomposition of ruthenocene to metallic Ru. When the ruthenocene was heated up, it started to migrate on the support surface through the gas phase because of its high vapor pressure. When it migrated on the Pt particle in a hydrogen stream, it was catalytically decom-

posed and Ru metal deposited on the Pt surface, because the precursor contained ligands which hydrogenated easily.

The surface composition of the Pt–Ru bimetallic particles was measured by means of O_2–CO titration and the results are shown in Fig. 5. As the amount of Ru increased, the number of surface Pt atoms decreased and that of Ru increased. The total number of surface metal atoms (Pt + Ru) increased slightly, but the number of metal particles per weight of SiO_2 was kept constant. These results suggest that Ru deposited only on the surface of Pt particles without forming separate Ru particles. Particle growth by deposition of Ru resulted in lower dispersion.

$RuCl_3$ was used instead of ruthenocene but the number of surface Pt atoms did not decrease in proportion to the amount of Ru added because of segregation of Ru and Pt particles.

3.3. Preparation of bimetallic catalysts with an egg-shell type of structure

Many commercial noble metal catalysts have the so called 'egg-shell' structure, in which the metallic component distributes only in the outer layer of pellet catalysts. It is not easy to prepare egg-shell type of bimetallic catalysts because

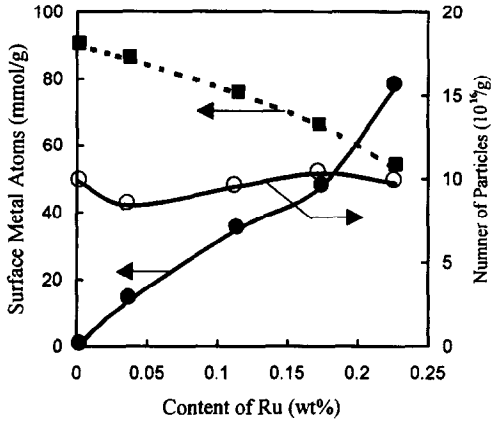

Fig. 5. Number of surface Pt and Ru atoms and metal particles in Pt–Ru/Al_2O_3 catalysts measured by O_2–CO titration. ■; number of surface Pt atoms, ●; number of surface Ru atoms, ○; number of metal particles.

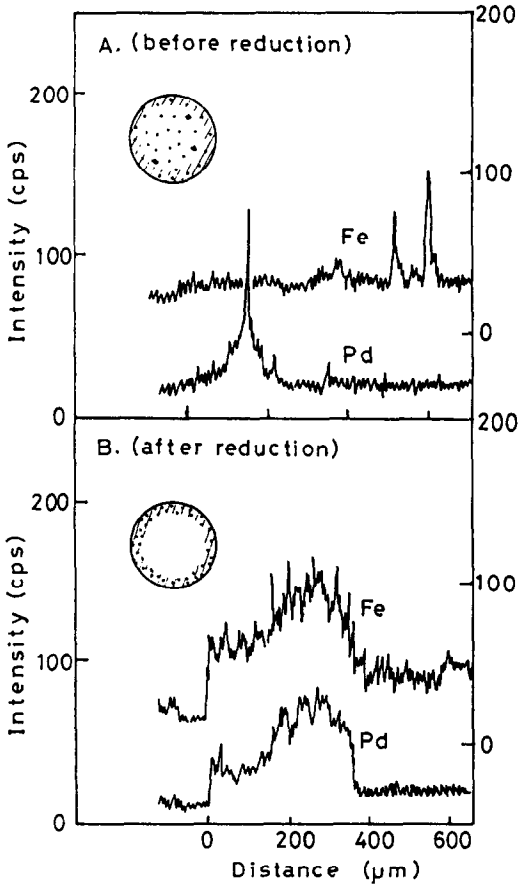

Fig. 6. Analysis of the cross section of the Pd–Fe/Al_2O_3 catalyst by EPMA. (A) Before reduction, (B) after reduction. Dots indicate the distribution of Fe.

the two metallic components should distribute in the same area without forming separate particles. We tried selective deposition of a second metallic component on the metal particles of egg-shell type of supported monometallic catalysts.

The starting egg-shell catalysts, Pd/Al_2O_3 and Pt/Al_2O_3, were cylinders of 4.5 mm diameter in which Pd and Pt were supported on the outer 0.2 mm layers, as illustrated in Fig. 2.

We prepared a Pd–Fe/Al_2O_3 catalyst using a Pd/Al_2O_3 egg-shell catalyst and ferrocene as starting materials. The Pd/Al_2O_3 catalyst was prereduced, impregnated in a benzene solution of ferrocene and dried. It was then heated up slowly in a hydrogen flow and reduced at 600 K

for 3 h. Fig. 6 shows the distribution of Fe of the cross-section of the Pd–Fe/Al_2O_3 before and after reduction. Before reduction Fe was distributed uniformly in the pellet, forming some crystals. However, after hydrogen reduction Fe was distributed only in the outer layer in the same manner as the Pd, suggesting clearly that the Fe moved in the catalyst to concentrate in the same region as Pd.

An egg-shell type of Pt–Ru/Al_2O_3 catalyst was prepared in a similar manner, using Pt/Al_2O_3 and ruthenocene. The Ru was distributed uniformly before reduction, but it distributed in the same region as the Pt. We carried out TEM observation of the individual Pt–Ru bimetallic particles and confirmed by EDX analysis that each metal particle contained both Pt and Ru.

3.4. Preparation of Pt–Sn / $ZnAl_2O_4$ catalysts

We have reported [3] that the selectivity of Pt/Al_2O_3 in the dehydrogenation of isobutane was improved by the addition of ZnO in the support. Addition of Sn was also effective in the reaction. We tried to prepare a Pt–Sn catalyst supported on $ZnAl_2O_4$ by selective deposition using alkyl tin compounds as the precursors. Because the vapor pressure of tetramethyl tin (TMT) and tetrabutyl tin (TBT) is much higher than that of ferrocene or ruthenocene, these precursors tend to escape from the catalyst before reduction. We therefore tried to provide the precursor directly from the gas phase. The monometallic catalyst, Pt/$ZnAl_2O_4$, was packed and heated in the reactor of the conventional flow reaction system used for dehydrogenation of isobutane, and a cyclohexane solution of TMT (or TBT) was introduced by a micropump in a flow of hydrogen.

Fig. 7 shows the amount of Sn deposited on the catalyst. When $ZnAl_2O_4$ was packed in the reactor the precursors passed through without deposition. However, deposition occurred when the Pt-supported catalyst was used. Selective deposition on Pt surface occurred in the temperature range 420–500 K. At 520 K, Sn deposited not only on the Pt but also on the support surface.

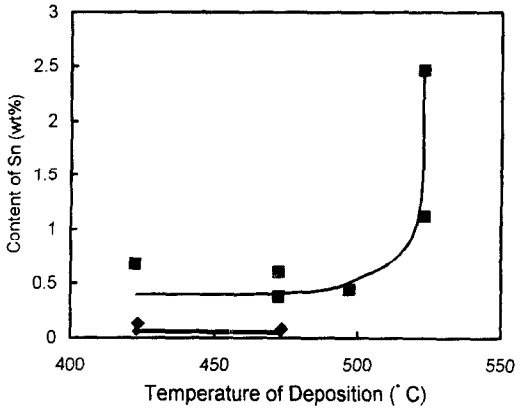

Fig. 7. The effect of the deposition temperature on the content of Sn in Pt–Sn/Al_2O_3 catalyst using TMT as the precursor of Sn. ■; deposition on Pt/$ZnAl_2O_4$, ◆; deposition on $ZnAl_2O_4$.

Fig. 8 shows the amount of CO adsorption on the Pt–Sn/$ZnAl_2O_4$ catalysts. The amount of CO adsorption decreased with increase in the Sn content, because the surface Pt atoms are covered with Sn. When TMT was used as the precursor of Sn, the decrease in CO adsorption was equal to the amount of Sn deposited, suggesting that all the Sn atoms were effectively used to cover the Pt surfaces. However, when a nonvolatile precursor ($SnCl_2(acac)_2$) was used, the amount of CO adsorption was larger than

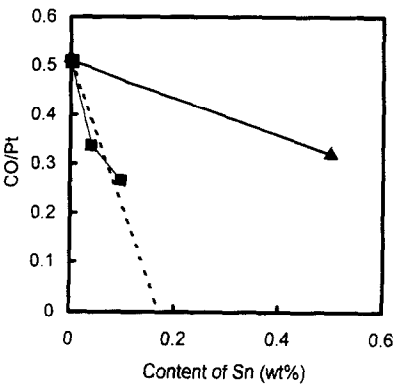

Fig. 8. The effect of Sn content on the amount of CO adsorption of Pt–Sn/Al_2O_3. The broken line indicates the estimated value on the assumption that all the Sn covered the surface Pt atoms. ■: $Sn(CH_3)_4$ precursor, ▲: $SnCl_2(acac)_2$ precursor.

Table 1
Composition of the solutions used for deposition of Ag and Au on Pd/Al_2O_3 to form Pd–Ag and Pd–Au bimetallic catalysts

Compound	Composition (mmol/l)
Solution for deposition of Au	
$HAuCl_4$	0.54
$Na_2S_2O_3$	4.32
Na_2SO_3	21.8
Sodium ascorbate	54.0
Temperature (K)	337
Solutions for deposition of Ag	
[solution I]	
AgCN	1.1
NaCN	2.2
NaOH	18.8
$BH_3 \cdot NH(CH_3)_2$	11.0
Temperature (K)	273
[solution II]	
$AgNO_3$	0.51
Na_2SO_3	9.03
$Na_2S_2O_3$	85.5
$N_2H_4 \cdot H_2O$	20.0
Temperature (K)	313

the calculated value, because most of the Sn was distributed on the support surface.

We have confirmed [4] that the Pt–Sn/$ZnAl_2O_4$ was an effective catalyst in the dehydrogenation of isobutane.

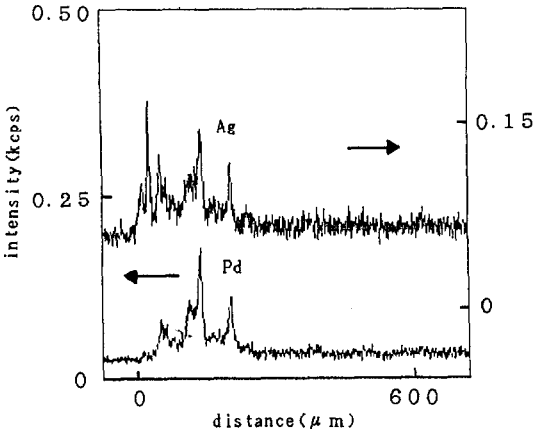

Fig. 9. Distributions of Pd and Ag in the cross-section of a Pd–Ag/Al_2O_3 catalyst of egg-shell structure studied by using EPMA.

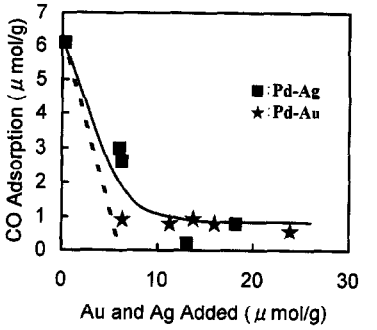

Fig. 10. The effect of the content of Ag and Au on the amount of CO adsorption on Pd–Ag and Pd–Au/Al_2O_3. The broken line indicates the estimated value on the assumption that all the Ag (or Au) covered the surface of Pd particles.

3.5. Liquid phase preparation of Pd–Ag and Pd–Au catalysts

The preparation of Pd–Ag and Pd–Au bimetallic catalysts was examined and these materials were used for selective hydrogenation of 1,3-butadiene. Because we could not find any suitable complexes of Ag and Au volatile and stable enough for selective deposition in hydrogen, we examined selective deposition in the liquid phase, using dimethyl-amineborane and hydrazine for the reduction of AgCN in aqueous solution, and sodium ascorbate for the reduction of Au. The composition of the solutions used for the deposition of Ag and Au are shown in Table 1 [5]. The egg-shell Pd/Al_2O_3 catalyst

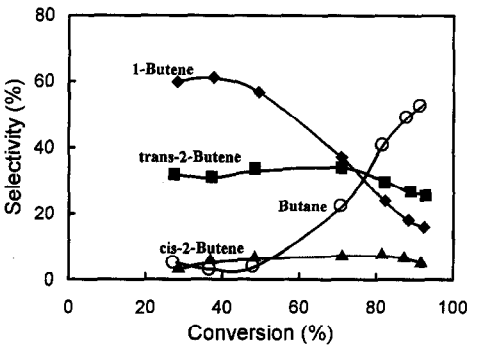

Fig. 11. The relation between conversion and selectivity in hydrogenation of 1,3-butadiene over Pd/Al_2O_3. ◆: 1-butene, ■; *trans*-2-butene, ▲: *cis*-2-butene, ○: butane.

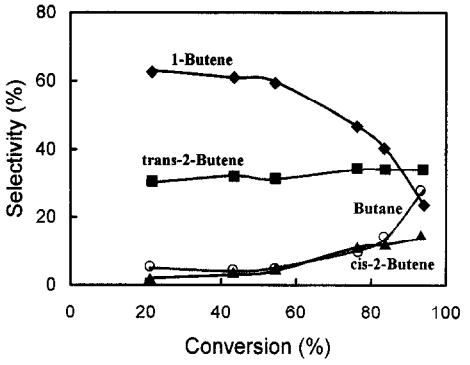

Fig. 12. The relation between conversion and selectivity in hydrogenation of 1,3-butadiene over Pd–Au/Al_2O_3. ◆: 1-butene, ■: *trans*-2-butene, ▲: *cis*-2-butene, ○: butane.

was impregnated in the solution for 3–24 h while stirring slowly. After decantation and washing with water bimetallic catalysts were obtained.

Fig. 9 illustrates the distribution of Ag in the Pd–Ag/Al_2O_3 pellet catalyst. Ag is distributed in the same manner as Pd. The adsorption of CO was examined at room temperature and it was found to decrease as the amount of Ag increased. The Pd–Au/Al_2O_3 sample also suggested similar results.

The partial hydrogenation of 1,3-butadiene was examined over Pd/Al_2O_3, Pd–Au/Al_2O_3 and Pd–Ag/Al_2O_3 catalysts (Figs. 10–12). As shown in Fig. 11, the Pd/Al_2O_3 catalyst was selective for butene formation at conversions less than 40%, but the formation of butane increased as the conversion increased above 40%. On the Pd–Au/Al_2O_3 catalyst, in contrast, the formation of butane was suppressed, even at a conversion of 80%. A similar high selectivity for partial hydrogenation was observed on the Pd–Ag/Al_2O_3 catalyst.

4. Conclusions

The preparation of supported bimetallic catalysts was examined using metal complex precursors which could migrate on the support. By means of selective chemical vapor deposition of ruthenocene, ferrocene and tetramethyl tin, the metals of Ru, Fe and Sn deposited on the surface of Pt or Pd particles and supported bimetallic catalysts such as Pt–Ru, Pd–Fe and Pt–Sn were prepared. Precursor complexes were catalytically decomposed on the noble metal surfaces and deposited selectively on the metal particles. Egg-shell type of supported bimetallic catalysts were prepared by means of selective deposition on egg-shell type of monometallic catalysts. Both Pd and Fe were distributed in the same manner after reduction. Liquid phase deposition was also examined in the preparation of Pd–Ag and Pd–Au catalysts. The amount of CO adsorption decreased as the amount of Ag or Au increased. Egg-shell types of Pd–Au and Pd–Ag catalysts were prepared by this technique. These catalysts had high selectivity to 1-butene in the partial hydrogenation of 1,3-butadiene.

References

[1] H. Miura and R.D. Gonzalez, J. Catal., 74 (1982) 216.
[2] H. Miura, T. Suzuki, Y. Ushikubo, K. Sugiyama, T. Matsuda and R.D. Gonzalez, J. Catal., 85 (1984) 331.
[3] H. Sato, H. Taguchi and H. Miura, Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.), 38 (1995) 34.
[4] T. Ito, H. Miura and H. Sato, Proc. 37th Annu. Meet. Jpn. Petroleum Soc., B17, 1994, Tokyo.
[5] H. Miura, M. Terasaka, K. Oki and T. Matsuda, Proc. 10th Intern. Congr. Catal., 1992, Budapest, Hungary, p. 2379.