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New catalytic functions of Pd–Zn, Pd–Ga, Pd–In, Pt–Zn, Pt–Ga and Pt–In alloys in the conversions of methanol

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Pd and Pt supported on ZnO, Ga_2O_3 and In_2O_3 exhibit high catalytic performance for the steam reforming of methanol, $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$, and the dehydrogenation of methanol to $HCOOCH_3$, $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$. Combined results with temperature-programmed reduction (TPR) and XRD method revealed that Pd–Zn, Pd–Ga, Pd–In, Pt–Zn, Pt–Ga and Pt–In alloys were produced upon reduction. Over the catalysts having the alloy phase, the reactions proceeded selectively, whereas the catalysts having metallic phase exhibited poor selectivities.

Keywords: methanol, steam reforming, dehydrogenation, Pd alloy, Pt alloy

1. Introduction

Catalytic functions of group 8–10 metals are markedly different from those of copper for the conversions of methanol such as steam reforming and dehydrogenation to $HCOOCH_3$ [1–13]. For the steam reforming of methanol, group 8–10 metal catalysts exhibit poor selectivity [1–3], whereas over copper catalysts the reaction occurs in high selectivity [1,4–8]. Over group 8–10 metal catalysts, methanol is decomposed to CO and H_2 [9–12], while over copper catalysts it is dehydrogenated to $HCOOCH_3$ [1].

In previous work [1,12–16], we showed that the catalytic functions of Pd and Pt were greatly modified in the presence of ZnO. The steam reforming of methanol and the dehydrogenation of methanol to $HCOOCH_3$ occurred with high selectivity over Pd/ZnO and Pt/ZnO catalysts [1,12–16]. Involvement of PdZn and PtZn alloys was suggested [14–16].

In the present study, the steam reforming and the dehydrogenation of methanol are carried out over various supported group 8–10 metal catalysts. We show that the selectivities for the steam reforming and the dehydrogenation to $HCOOCH_3$ are greatly improved upon the formation of Pd and Pt alloys.

2. Experimental

Catalysts used were Pd, Pt, Ni and Co supported on various metal oxides, i.e., ZnO (Kanto Chemicals Co., Ltd.), In_2O_3 (Wako Pure Chemicals Co., Ltd.), Ga_2O_3 (Wako Pure Chemicals Co., Ltd.), SiO_2 (Nihon Chromato Kogyo, Ltd.), MgO (Kishida Chemicals Co., Ltd.), CeO_2 and ZrO_2. CeO_2 and ZrO_2 were prepared by thermal decomposition of zirconium oxynitrate (Kanto Chemicals Co., Ltd.) and cerium carbonate (Wako Pure Chemicals Co., Ltd.), respectively. Metal loading of each catalyst was kept at 10 wt% unless otherwise stated. Supported Pd, Ni and Co catalysts were prepared by impregnation of the metal oxides with a solution of $Pd(NO_3)_2$ (Tanaka Noble Metals Ind. Co.), $Ni(NO_3)_2$ (Wako Pure Chemicals Co., Ltd.) and $Co(NO_3)_2$ (Wako Pure Chemicals Co., Ltd.) at 353 K, respectively. Supported Pt catalysts were prepared by impregnation with a solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich Chemical Co., Inc.) at 353 K.

The catalysts thus prepared were then dried at 383 K overnight, pressed into granules in sizes of 60–80 meshes (Tyler meshes), and were subjected to calcination in air at 773 K for 3 h. The catalysts (1.0 g) were then packed in reactors and calcined again at 773 K for 2 h in a stream of O_2 (20 vol% O_2) diluted with nitrogen at a total flow rate of 100 cm^3 STP/min.

Prior to the reaction, the catalysts were reduced in a hydrogen stream (4 vol% H_2) diluted with nitrogen under temperature-programmed conditions at a heating rate of 5 K/min up to 773 K.

The steam reforming and the dehydrogenation of methanol were carried out in a conventional flow reactor at 493 and 473 K, respectively. For the steam reforming of methanol, the inlet partial pressures of methanol and water were both kept at 10.1 kPa. For the dehydrogenation of methanol, the inlet partial pressure of methanol was kept at 10.1 kPa. Nitrogen was used as a diluent. Gases in the effluent were analyzed by gas chromatography. The selectivity was evaluated on the carbon basis.

Temperature-programmed reduction (referred to as TPR) of the catalysts was carried out in a flow of a hydrogen–argon mixture (4 vol% H_2) at a total flow rate of 50 cm^3/min and at a heating rate of 5 K/min to 773 or 1073 K. Hydrogen from the reactor was collected every 2 min in a sampling tube attached to the outlet of the reactor and analyzed by

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gas chromatography. X-ray diffraction (referred to as XRD) spectra of the catalysts were obtained with a JEOL JDX-8020 X-ray diffractometer. The number of metal surface sites of Pt, Ni and Co catalysts were determined by hydrogen chemisorption at room temperature, whereas those of Pd catalysts were determined at 373 K to avoid hydride phase formation [17]. The metal surface areas were calculated from the number of metal surface sites and the average surface densities of metal atoms [18]. The turnover frequency for the hydrogen formation was estimated from the number of metal surface sites and the outflow rate of hydrogen.

3. Results and discussion

3.1. Steam reforming of methanol

When a mixture of methanol and water was fed over the catalyst, H_2 and CO_2 were produced together with CO. The steam reforming of methanol ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) occurred along with the decomposition of methanol ($CH_3OH \rightarrow CO + 2H_2$).

Table 1 summarizes the conversion of methanol, selectivity and turnover frequency for the hydrogen production obtained over various supported group 8–10 metal catalysts along with the metal surface area and the dispersion. The kinetic parameters such as conversion, selectivity and turnover frequency were greatly affected by the kinds of supports as well as those of metals used. The selectivity for the steam reforming was greatly improved when Pd or Pt was supported on ZnO, In_2O_3 and Ga_2O_3. Over the other group 8–10 metal catalysts, CO and H_2 were produced predominantly. The methanol decomposition occurred in preference to the steam reforming. No reaction took place over ZnO, Ga_2O_3 and In_2O_3 alone. The turnover frequencies obtained over Pd/ZnO and Pt/ZnO catalysts exceeded those obtained over the other supported Pd and Pt catalysts. In comparison with previous results for copper-based catalysts [7], it is to be noted that the turnover frequencies obtained over Pd/ZnO and Pt/ZnO are greatly in excess of those (0.04–0.1 s^{-1}) over copper-based catalysts.

Table 1
Steam reforming of methanol over various supported group 8–10 metal catalysts.[a]

Catalyst	Conv. (%)	Selectivity (%)		SA[b] ($m^2\,g^{-1}$)	Dispersion (%)	TOF[c] (s^{-1})
		CO_2	CO			
Pd black	10.9	0.0	100.0	9.9	2.1	0.0071
Pd/ZnO	54.2	99.2	0.8	10.4	2.2	0.497
Pd/In_2O_3[d]	28.3	95.5	4.5	9.9	2.1	0.291
Pd/Ga_2O_3	21.2	94.6	5.4	12.3	2.6	0.177
Pd/SiO_2	15.7	0.0	100.0	42.4	9.0	0.021
Pd/MgO	41.0	6.6	93.4	49.0	10.4	0.053
Pd/ZrO_2	64.3	18.4	81.6	31.1	6.6	0.139
Pd/CeO_2	62.4	22.7	77.3	170.6	36.2	0.025
Pt black	3.0	56.7	43.3	1.65	0.60	0.019
Pt/ZnO	27.6	95.4	4.6	7.1	2.58	0.391
Pt/In_2O_3[c]	30.6	98.3	1.7	7.7	2.81	0.420
Pt/Ga_2O_3	5.4	75.5	24.5	7.2	2.63	0.065
Pt/SiO_2	10.3	18.8	81.2	92.3	33.5	0.0087
Ni/ZnO	19.1	3.0	97.0	2.7	0.40	0.365
Co/ZnO	13.1	13.3	86.7	6.2	0.92	0.117

[a] Reaction temperature: 493 K. Inlet partial pressures of methanol and water: 10.1 kPa.
[b] Metal surface area.
[c] Turnover frequency for the H_2 formation.
[d] Reduction temperature: 523 K.

3.2. TPR

Upon feeding of hydrogen over the various supported Pd catalysts at room temperature, hydrogen consumption occurred rapidly. This suggests that PdO formed on the supports was reduced, being converted to PdH_x [14]. After completion of the H_2 consumption at room temperature, TPR experiments were conducted. Figure 1 illustrates TPR profiles for various supported Pd catalysts. With increasing temperature, inverse peaks are observed around 360 K where PdH_x is decomposed [14]. With further increase in temperature, peaks appear in a temperature range of 600–700 K over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3. However, no hydrogen consumption peaks appear over the other sup-

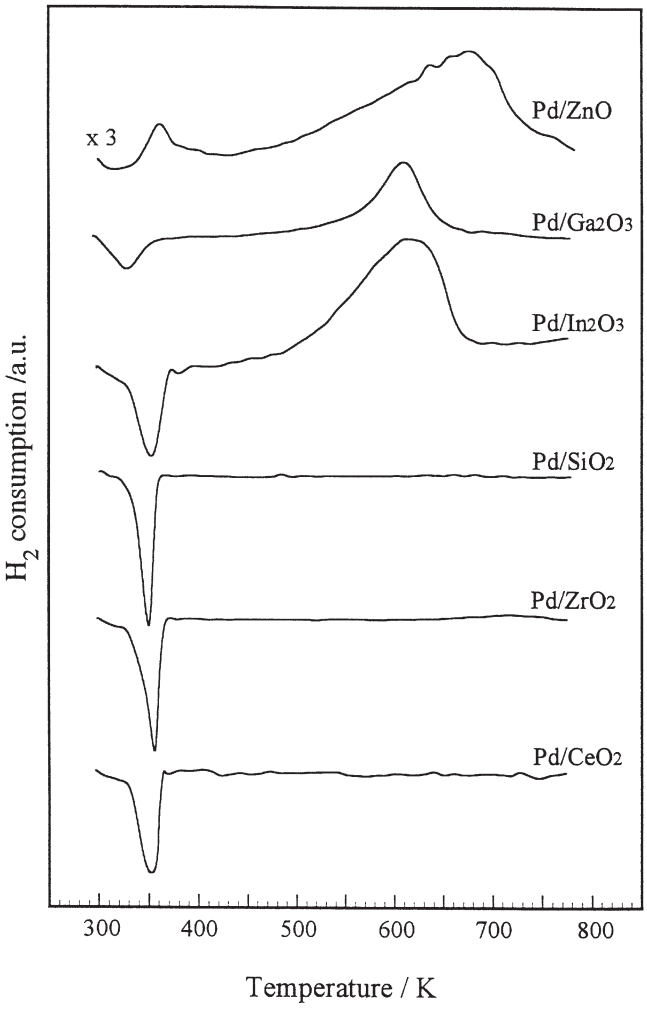

Figure 1. TPR profiles for various supported Pd catalysts.

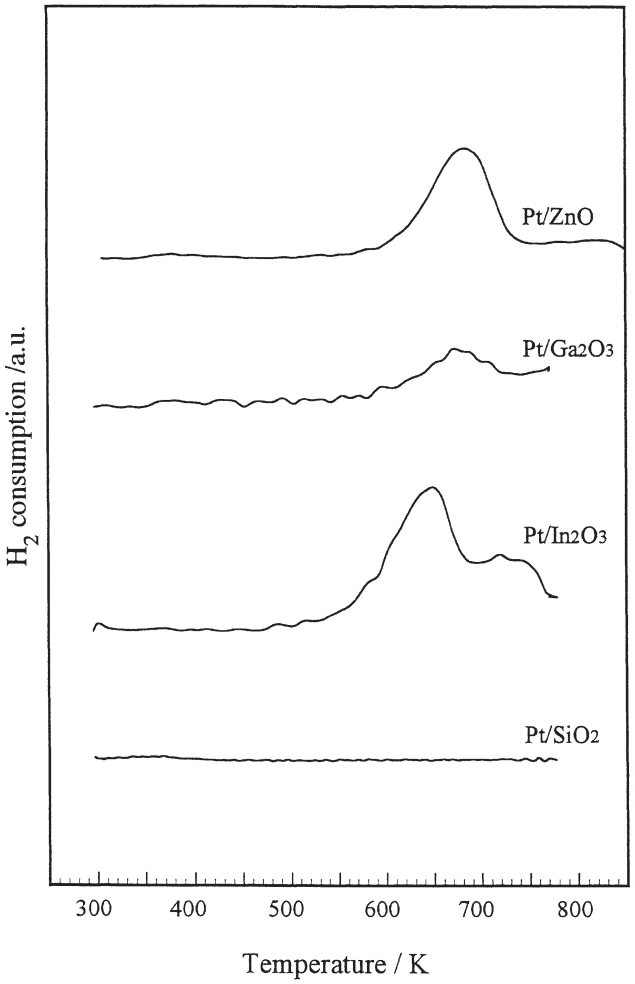

Figure 2. TPR profiles for various supported Pt catalysts.

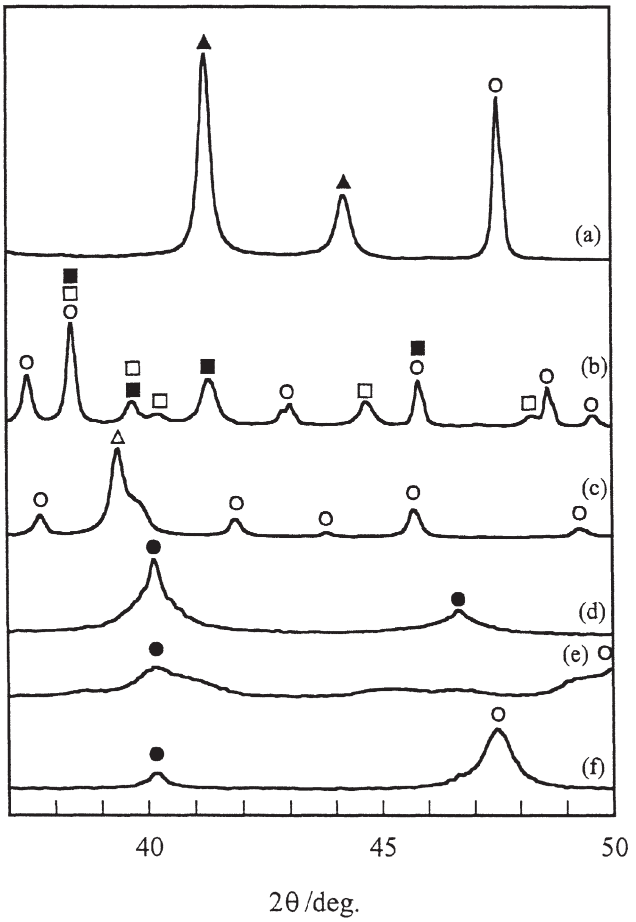

Figure 3. XRD pattern for various supported Pd catalysts reduced at 773 K. (a) Pd/ZnO, (b) Pd/Ga_2O_3, (c) Pd/In_2O_3, (d) Pd/SiO_2, (e) Pd/ZrO_2 and (f) Pd/CeO_2; (▲) PdZn, (□) Ga_2Pd_5, (■) Ga_5Pd, (△) $In_{0.52}Pd_{0.48}$, (●) Pd and (○) support metal oxides.

ported Pd catalysts. Over ZnO, Ga_2O_3 and In_2O_3 alone, no peaks of hydrogen consumption or desorption were discerned over the whole temperature range studied. Similar experiments were carried out over supported Pt catalysts. For Pt/ZnO, Pt/Ga_2O_3 and Pt/In_2O_3, the consumption of H_2 becomes appreciable around 500 K and increases, yielding a peak at 680, 670 and 650 K, respectively. By contrast, the hydrogen consumption is practically negligible over Pd/SiO_2 at higher temperatures (figure 2).

3.3. XRD

The structures of the catalysts reduced to 773 K under the temperature-programmed conditions were inspected by the XRD measurement. Figure 3 shows XRD spectra of various supported Pd catalysts. In the spectra, peaks for Pd species appear along with those for support metal oxides. Peaks for PdZn alloy [19] are discerned at $2\theta = 41.2$ and 44.1° and that for $Pd_{0.52}In_{0.48}$ alloy [20] appears at $2\theta = 39.3°$ in the respective spectrum for Pd/ZnO and Pd/In_2O_3 catalysts. For Pd/Ga_2O_3 catalyst, peaks ascribed to Ga_5Pd [21] or Ga_2Pd_5 alloy [22] grow at $2\theta = 39.5$, 41.3 and 45.9° or at $2\theta = 38.2$, 39.9, 40.2, 44.4 and 47.9°, though some peaks overlap with those of Ga_2O_3. For the other supported Pd catalysts, broad peaks ascribed to metallic Pd [23] are observed at $2\theta = 40.1°$ upon the reduction. Similar experiments were carried out over supported Pt, Ni and Co catalysts. Figure 4 depicts XRD spectra for the catalysts reduced to 773 K. For Pt/ZnO, Pt/In_2O_3 and Pt/Ga_2O_3 catalysts, PtZn, Ga_3Pt_5, $Ga_{5.4}Pt_{10.6}$ and In_2Pt alloy phases were evolved, respectively, whereas for Pt/SiO_2, Ni/ZnO and Co/ZnO catalysts, only metallic phases were developed after the reduction of the catalysts at 773 K. After the steam reforming, XRD spectra were also recorded. It was found that the original alloy phases were maintained over these catalysts subjected to the reaction. These findings indicate that the steam reforming of methanol selectively proceeds over the catalysts having alloy phases.

3.4. Reaction mechanisms

In previous work [2], we showed that the steam reforming of methanol proceeds through pathways

$$\begin{tikzcd} CH_3OH \arrow[r] \arrow[drr] & HCHO \arrow[r] & HCOOH \arrow[r] & CO_2 + H_2 \\ & & HCOOCH_3 \arrow[u, "H_2O"'] & \end{tikzcd} \tag{1}$$

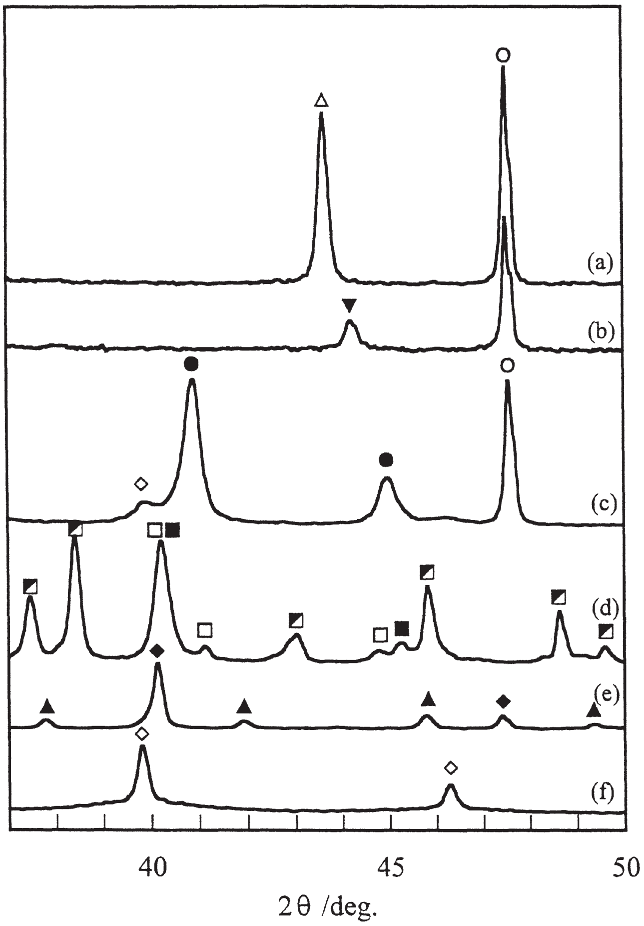

Figure 4. XRD pattern for various supported Pt, Ni and Co catalysts reduced to 773 K. (a) Ni/ZnO, (b) Co/ZnO, (c) Pt/ZnO, (d) Pt/Ga_2O_3, (e) Pt/In_2O_3 and (f) Pt/SiO_2; (△) Ni, (○) ZnO, (▼) Co, (●) PtZn, (◩) Ga_2O_3, (□) $Ga_{5.4}Pt_{10.6}$, (■) Ga_3Pt_5, (▲) In_2O_3, (◆) In_2Pt and (◇) Pt.

and

$$CH_3OH \rightarrow HCHO \rightarrow CO \xrightarrow{H_2O} CO_2 + H_2 \qquad (2)$$

respectively, over Cu/SiO_2 and Pt/SiO_2 catalysts. Over Cu/SiO_2 catalysts, HCHO species formed in the reaction were attacked by H_2O and/or CH_3OH, and finally transformed to CO_2 and H_2. In contrast, over Pt/SiO_2 catalysts, HCHO species were rapidly decomposed to CO and H_2, and partly transformed to CO_2 and H_2 through the water–gas shift reaction.

Recently, we found that over Pd/ZnO catalysts when PdZn alloy phases are developed, the steam reforming of methanol occurred through pathway (1) [14]. Consistent with the proposed reaction mechanisms, the formation of $HCOOCH_3$ occurred selectively upon the dehydrogenation of methanol over Pd/ZnO.

Dehydrogenation of methanol was carried out over various supported Pd and Pt catalysts, $HCOOCH_3$ was produced along with CO and H_2, suggesting that the reactions, $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$, and $CH_3OH \rightarrow CO + 2H_2$ occurred. Table 2 lists the conversion of methanol and the selectivities to $HCOOCH_3$ and CO over various supported Pd and Pt catalysts. The conversions and selectivity are greatly affected by the kinds of supports. The catalysts, Pd/ZnO, Pd/Ga_2O_3, Pd/In_2O_3, Pt/ZnO, Pt/In_2O_3 and Pt/Ga_2O_3, exhibiting high selectivity for the steam reforming show high selectivity to $HCOOCH_3$. Over the other catalysts, such as Pd/SiO_2, Pd/ZrO_2 and Pt/SiO_2, the decomposition of methanol occurs exclusively. Original catalytic functions of metallic Pd and Pt for the conversions of methanol are greatly modified upon the formation of the alloys.

Table 2
Dehydrogenation of methanol over various supported group 8–10 metal catalysts.[a]

Catalyst	Conv. (%)	Selectivity (%) HCOOCH$_3$	Selectivity (%) CO
Pd black	21.6	0.0	100.0
Pd/ZnO	8.9	94.1	5.9
Pd/In_2O_3[b]	18.2	76.0	24.0
Pd/Ga_2O_3	12.3	96.3	4.7
Pd/ZrO_2	41.5	0.0	100.0
Pd/SiO_2	13.0	0.0	100.0
Pt black	1.7	0.0	100.0
Pt/ZnO	3.7	89.5	10.5
Pt/Ga_2O_3	3.9	71.8	28.2
Pt/In_2O_3[b]	12.7	86.9	13.1
Pt/SiO_2	9.8	0.0	100.0

[a] Reaction temperature: 473 K. Inlet partial pressure of methanol: 10.1 kPa.

[b] Reduced to 523 K.

4. Conclusion

Catalytic performances of group 8–10 metal catalysts for the conversions of methanol are markedly affected by the kinds of supports as well as those of metals used. The selectivities for the steam reforming, $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$, and the dehydrogenation to $HCOOCH_3$, $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$, are greatly improved when Pd or Pt is supported on ZnO, Ga_2O_3 and In_2O_3. Over the other group 8–10 metal catalysts, the decomposition of methanol, $CH_3OH \rightarrow CO + 2H_2$, occurs exclusively. Combined results with TPR and XRD method revealed that the support metal oxides of Pd or Pt supported on ZnO, Ga_2O_3 and In_2O_3 were reduced in the course of the TPR with H_2 being transformed to Pd–Zn, Pd–Ga, Pd–In, Pt–Zn, Pt–Ga and Pt–In alloys. Original catalytic functions of metallic Pd and Pt are greatly modified upon the formation of the Pd and Pt alloys.

References

[1] N. Takezawa and N. Iwasa, Catal. Today 36 (1997) 45.
[2] K. Takahashi, H. Kobayashi and N. Takezawa, Chem. Lett. (1985) 759.
[3] K. Mizuno, Y. Yokoyama, N. Wakejima, Y. Takeuchi and A. Watanabe, Chem. Lett. (1986) 1969.
[4] H. Kobayashi, N. Takezawa and C. Minochi, Chem. Lett. (1976) 1347.

[5] J. Barton and V. Pour, Coll. Czech. Chem. Commun. (1980) 45.
[6] H. Kobayashi, N. Takezawa and C. Minochi, J. Catal. 69 (1981) 487.
[7] N. Takezawa, H. Kobayashi, A. Hirose, M. Shimokawabe and K. Takahashi, Appl. Catal. 4 (1982) 127.
[8] H. Agaras and G. Carrella, Appl. Catal. 45 (1988) 53.
[9] I. Yasumori, T. Nakamura and E. Miyazaki, Bull. Chem. Soc. Jpn. 40 (1967) 1372.
[10] G.C. Bond, *Catalysis by Metals* (Academic Press, New York, 1964).
[11] D.W. McKee, Trans. Faraday Soc. 64 (1968) 2200.
[12] N. Iwasa, O. Yamamoto, A. Akazawa, S. Ohyama and N. Takezawa, J. Chem. Soc. Chem. Commun. (1991) 1322.
[13] N. Iwasa, S. Kudo, H. Takahashi, S. Masuda and N. Takezawa, Catal. Lett. 19 (1993) 211.
[14] N. Iwasa, S. Masuda, N. Ogawa and N. Takezawa, Appl. Catal. A 125 (1995) 145.
[15] N. Iwasa, T. Akazawa, S. Ohyama, K. Fujikawa and N. Takezawa, React. Kinet. Catal. Lett. 55 (1995) 245.
[16] N. Iwasa, S. Masuda and N. Takezawa, React. Kinet. Catal. Lett. 55 (1995) 349.
[17] P.C. Aben, J. Catal. 10 (1968) 224.
[18] J.R. Anderson, *Structure of Metallic Catalysts* (Academic Press, New York, 1975).
[19] X-ray Powder Data File, ASTM 6-620.
[20] X-ray Powder Data File, ASTM 46-1011.
[21] X-ray Powder Data File, ASTM 15-577.
[22] X-ray Powder Data File, ASTM 27-232.
[23] X-ray Powder Data File, ASTM 46-1043.