Difference in the reactivity of acetaldehyde intermediates in the dehydrogenation of ethanol over supported Pd catalysts

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Catalytic performances of supported Pd catalysts for the dehydrogenation of ethanol were greatly modified upon the formation of Pd alloy phases. Over Pd–Zn, Pd–Ga and Pd–In alloys, acetaldehyde was selectively produced at lower conversion levels. With the increased conversion level, ethyl acetate was produced at the expense of acetaldehyde. The selectivities for the ethyl acetate formation exceeded that over a Cu/ZnO catalyst. Over metallic Pd, the decomposition of ethanol, $C_2H_5OH \rightarrow CO + CH_4 + H_2$, occurred to a considerable extent. It was shown that the reactivity of acetaldehyde species over the Pd alloys was markedly different from that over metallic Pd. Over the Pd alloys, acetaldehyde species were stabilized and transformed into ethyl acetate by the nucleophilic addition of ethanol. By contrast, over metallic Pd, aldehyde species were rapidly decarbonylated to methane and carbon monoxide.

Keywords: ethanol, dehydrogenation, acetaldehyde, ethyl acetate, Pd alloy

1. Introduction

Bimetallic catalysts frequently exhibit different catalytic performances from those of monometallic catalysts [1]. Recently, it has been reported that Pd–Zn bimetallic catalysts show anomalous catalytic functions for conversions of methanol [2–9], hydrogenolysis of esters [10,11] and hydrogenation of dienes [12,13].

The dehydrogenation of methanol to methyl formate, $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$, and the steam reforming of methanol, $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$, occurred selectively over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 catalysts, while over other supported Pd catalysts the decomposition of methanol, $CH_3OH \rightarrow CO + 2H_2$, occurred predominantly [2–8]. No methyl formate was produced in the dehydrogenation of methanol. Such novel catalytic functions of Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 were developed by the formation of Pd–Zn, Pd–Ga and Pd–In alloys in the course of the reactions or previous reduction of the catalysts [4–8]. It was suggested that reactivity of formaldehyde formed in the reactions was markedly modified upon the formation of the alloys [4,7,8].

In the present study, the dehydrogenation of ethanol is carried out over various supported Pd catalysts. We show that the selectivities for the acetaldehyde and ethyl acetate formation are greatly improved upon the formation of Pd alloy phases. The difference in the reactivity of acetaldehyde intermediate species over Pd alloys and metallic Pd is discussed.

2. Experimental

Catalysts used were Pd supported on various metal oxides, i.e., ZnO (Kanto Chemicals Co. Ltd.), Ga_2O_3 (Wako Pure Chemicals Co. Ltd.), In_2O_3 (Wako Pure Chemicals Co. Ltd.), MgO (Kishida Chemical Co. Ltd.), SiO_2 (Nihon Chromato Co. Ltd.) and Al_2O_3 (Catalysis Society of Japan JRC ALO-4). The supported Pd catalysts were prepared by impregnation of the metal oxides with a solution of $Pd(NO_3)_2$ (Tanaka Noble Metals Ind. Co.) at 353 K. Some Pd/ZnO catalysts were prepared by a precipitation method. A solution of sodium carbonate was added to a mixed solution of $Pd(NO_3)_2$ and $Zn(NO_3)_2$ (Wako Pure Chemicals Co. Ltd.) dropwise at 353 K until the pH of the solution was raised to 8.0. The precipitate was filtered out and washed by distilled water. The Pd loadings of the supported Pd catalysts prepared by the impregnation method were 10 wt%, while that of the Pd/ZnO prepared by the precipitation method was 30 wt%. For comparison, Pd black (Wako Pure Chemicals Co. Ltd.) and 10 wt% Cu/ZnO were also used for the experiments. The Cu/ZnO catalyst was prepared by an impregnation method with a solution of $Cu(NO_3)_2$ (Wako Pure Chemicals Co. Ltd.) and ZnO as was Pd/ZnO.

The supported Pd and Cu/ZnO catalysts thus prepared were dried at 383 K overnight and calcined in air at 773 K for 3 h. The catalysts 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 supported Pd and Cu/ZnO catalysts were reduced in a hydrogen stream (4 vol% H_2) diluted with nitrogen under temperature-programmed conditions at a heating rate of

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5 K/min up to 773 and 523 K, respectively. Pd black was used for the reaction without calcination and previous reduction.

Dehydrogenation of ethanol was carried out in a conventional flow reactor at 493 K in a way similar to that in previous work [14]. The inlet partial pressure of ethanol was kept at 20.2 kPa unless otherwise stated. Nitrogen was used as a diluent. For comparison, dehydrogenation of 1-propanol was also conducted at 473 K. The inlet partial pressure of 1-propanol was maintained at 10.1 kPa. Gases in the effluent were analyzed by gas chromatography. The selectivities for the carbon-containing products were evaluated by the carbon basis.

Reactions of acetaldehyde in the absence and the presence of ethanol were conducted at 433 K over the supported Pd catalysts and Pd black. The inlet partial pressures of acetaldehyde and ethanol were kept at 3.0 and 1.5 kPa, respectively.

X-ray diffraction (referred to as XRD) spectra of the catalysts subjected to the reactions were obtained with a Jeol JDX-8020 X-ray diffractometer, using Cu Kα radiation ($\lambda = 0.15405$ nm).

The number of metal surface sites of Pd catalysts was determined by hydrogen chemisorption at 373 K to avoid hydride phase formation [15]. 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. Dehydrogenation of ethanol

When ethanol was fed over the supported Pd catalysts, hydrogen, acetaldehyde, methane, carbon monoxide and C_4 (diethyl ether, ethyl acetate, methyl ethyl ketone and crotonaldehyde) species were produced along with hydrocarbons (ethane, propane and propene). The activities of the catalysts were stable under given conditions. Over ZnO and SiO_2 alone, no reactions occurred under the present experimental conditions, while over Ga_2O_3 and In_2O_3 alone, trace amounts of hydrogen and acetaldehyde were produced. Figure 1 shows the selectivities to carbon-containing products, the conversion of ethanol and the turnover frequency for the hydrogen formation at 493 K over various supported Pd catalysts prepared by the impregnation method along with those over Pd black and Cu/ZnO. The selectivities to the carbon-containing products are greatly affected by the kinds of supports. Over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 acetaldehyde is produced with high selectivity, while over the other supported Pd catalysts and Pd black methane and carbon monoxide are produced. Over Pd/Ga_2O_3 and Pd/In_2O_3 ethyl acetate was formed along with acetaldehyde and a trace amount of methyl ethyl ketone. The selectivities for the ethyl acetate formation were 10.5 and 22.4% over Pd/Ga_2O_3 and Pd/In_2O_3, respectively. Over Pd/SiO_2 and Pd/Al_2O_3, a considerable amount of diethyl ether is produced in addition to small amounts of acetaldehyde and hydrocarbons (ethane and propane), suggesting that the dehydration of ethanol, $2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$, occurs. The turnover frequencies obtained over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 catalysts exceeded those obtained over the other supported Pd catalysts and Pd black. The Cu/ZnO catalyst exhibits high selectivity for the acetaldehyde formation as the Pd/ZnO catalyst.

Experiments were conducted over Pd/ZnO prepared by the precipitation method. The dehydrogenation of ethanol proceeded somewhat faster than that over Pd/ZnO prepared by the impregnation method. For example, the conversion levels of ethanol at 493 K and at space time of 0.76 s^{-1} for the Pd/ZnO catalysts prepared by the precipitation and the impregnation method, were 34.5 and 21.7%, respectively. However, the product distribution over Pd/ZnO prepared by the precipitation method was similar to that over Pd/ZnO

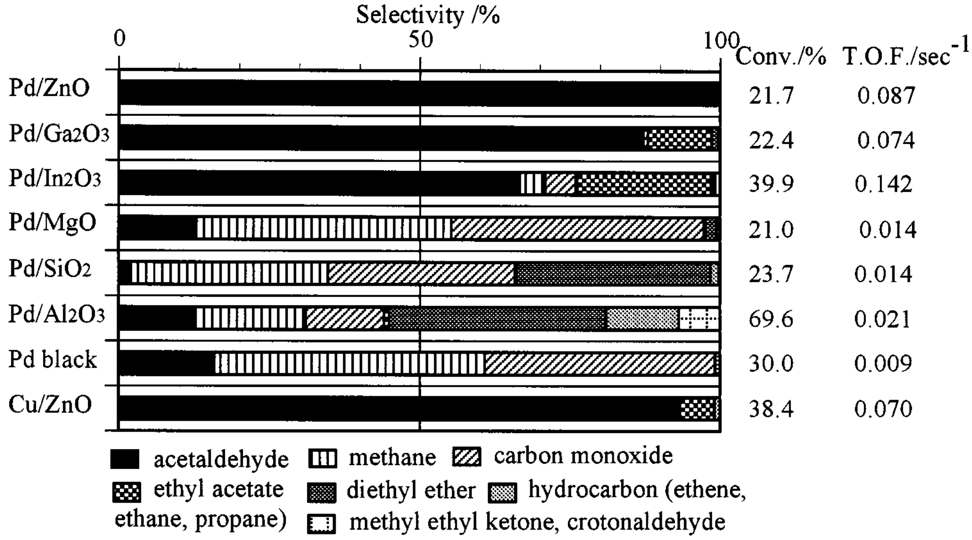

Figure 1. Selectivities to carbon-containing products in the dehydrogenation of ethanol at 493 K.

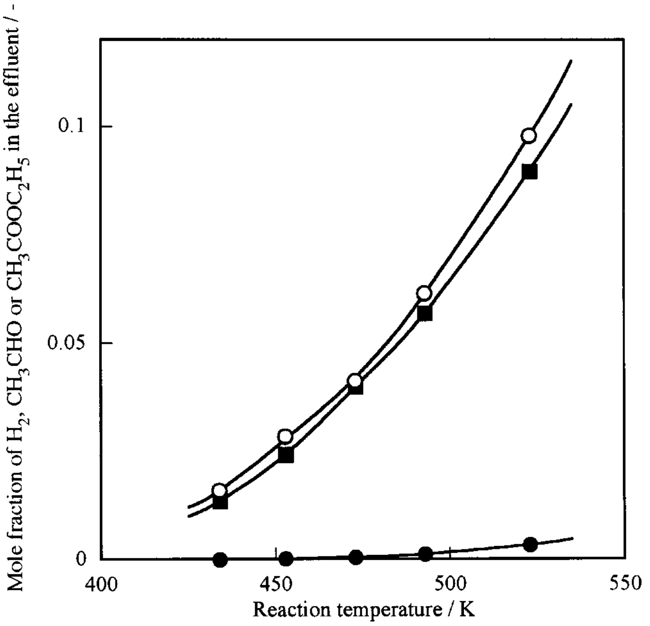

Figure 2. Mole fraction of hydrogen, acetaldehyde and ethyl acetate against reaction temperature over Pd/ZnO catalysts. (○) H_2, (■) CH_3CHO and (●) $CH_3COOC_2H_5$.

prepared by the impregnation method. Figure 2 shows the effect of the reaction temperature upon the dehydrogenation of ethanol over Pd/ZnO prepared by the precipitation method. Hydrogen and acetaldehyde were produced nearly in 1 : 1 molar ratio along with a trace amount of ethyl acetate. No other products were formed. The mole fraction of hydrogen and acetaldehyde increase rapidly with the increased reaction temperature, while that of ethyl acetate increases slowly with reaction temperature.

Figure 3 (A) and (B) illustrate the mole fraction of hydrogen, acetaldehyde, ethyl acetate, methane and carbon monoxide in the effluent against space time over Pd/ZnO prepared by the precipitation method and over Pd black, respectively. For Pd/ZnO, the mole fraction of acetaldehyde in the effluent increases with the increased space time, passes through a maximum and decreases gradually, while that of ethyl acetate increases with space time. These results suggested that ethyl acetate is produced through acetaldehyde. For Pd black, the mole fraction of acetaldehyde increases with space time, showing a maximum, and then decreases. Methane and carbon monoxide are produced nearly in 1 : 1 molar ratio. They increase with increasing space time. No ethyl acetate was produced over Pd black. As observed over Pd(110) or (111) surfaces [16,17], methane and carbon monoxide were most probably produced through the reactions $C_2H_5OH \rightarrow CH_3CHO + H_2$ and $CH_3CHO \rightarrow CH_4 + CO$. The mole fraction of hydrogen increases gradually with the increased space time both over Pd/ZnO and over Pd black. Though the mole fraction of hydrogen was varied from 0.04 to 0.1, the mole fractions of acetaldehyde, ethyl acetate, methane and carbon monoxide increase or decrease monotonously with increasing space time. It was suggested that the dehydrogenation of ethanol was unaffected by the presence of hydrogen.

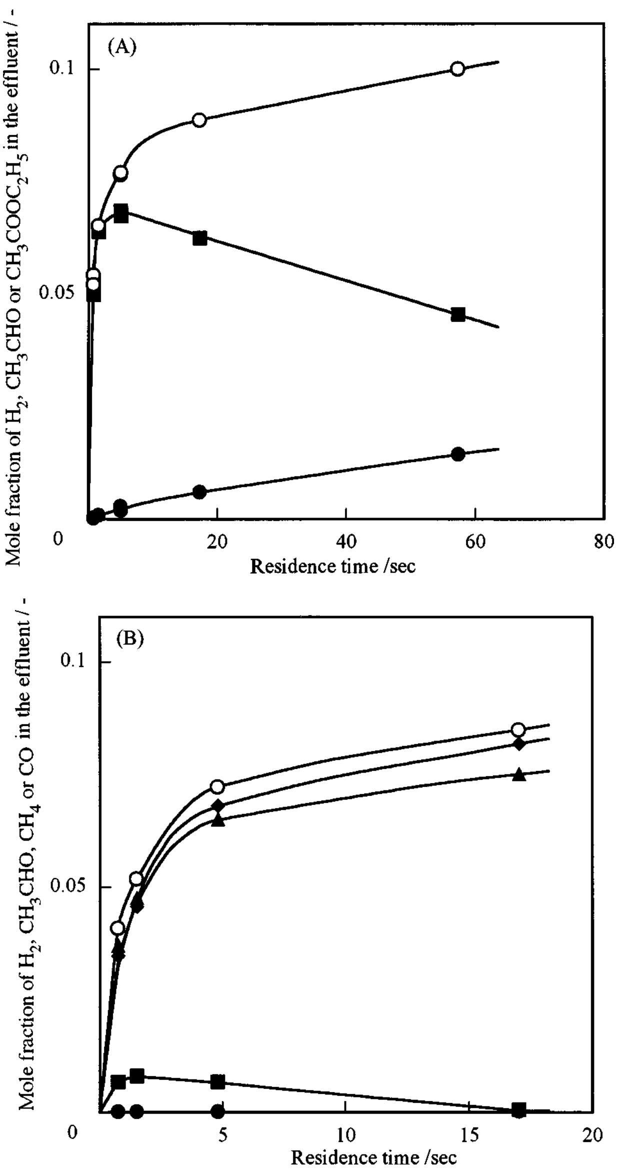

Figure 3. Mole fraction of hydrogen, acetaldehyde, ethyl acetate, methane and carbon monoxide in the effluent against the space time. (A) Pd/ZnO and (B) Pd black. Experiments were carried out at 493 K. (○) H_2, (■) CH_3CHO, (●) $CH_3COOC_2H_5$, (◆) CH_4 and (▲) CO.

Figure 4 compares the selectivity for the ethyl acetate formation at various conversion levels of ethanol over Pd/ZnO prepared by the precipitation method, in addition to those over Pd/Ga_2O_3, Pd/In_2O_3, Pd/SiO_2, Cu/ZnO and Pd black. Over Pd/ZnO, Pd/Ga_2O_3, Pd/In_2O_3 and Cu/ZnO catalysts, the selectivity increases with the increased conversion level. In particular above 40% of the ethanol conversion, the selectivities increase markedly with the increased conversion level. At the same conversion levels, the selectivities over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 catalysts exceed those over Cu/ZnO. In contrast, over Pd/SiO_2 and Pd black, the selectivities to ethyl acetate are lower than 0.9% over all conversion levels studied.

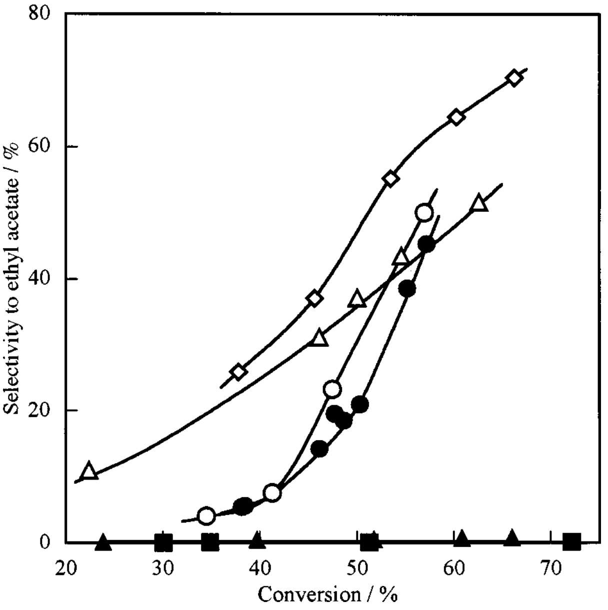

Figure 4. The selectivity for the ethyl acetate formation against the conversion of ethanol at 493 K. (○) Pd/ZnO, (△) Pd/Ga_2O_3, (◇) Pd/In_2O_3, (▲) Pd/SiO_2, (■) Pd black and (●) Cu/ZnO.

The dehydrogenation of 1-propanol was also carried out over Pd/ZnO, Pd/SiO_2 and Pd black. Over Pd/ZnO, propionaldehyde and hydrogen were selectively produced along with a trace amount of propione propionate, whereas over Pd/SiO_2 and Pd black ethane and carbon monoxide were produced in a 1 : 1 molar ratio. The formation of propionaldehyde over Pd/SiO_2 and Pd black was far below that over Pd/ZnO. These results strongly suggest that the decarbonylation of the aldehyde species, $CH_3CH_2CHO \rightarrow C_2H_6 + CO$, formed in the dehydrogenation of 1-propanol is greatly suppressed over Pd/ZnO, while over Pd/SiO_2 and Pd black, the aldehyde species are rapidly decarbonylated.

In previous work [4,7], the dehydrogenation and the steam reforming of methanol were carried out over various supported Pd catalysts (Pd/ZnO, Pd/Ga_2O_3, Pd/In_2O_3, Pd/MgO, Pd/SiO_2, Pd/Al_2O_3, Pd/ZrO_2, Pd/CeO_2, Pd/HfO_2, etc.). The activity and the selectivity for the dehydrogenation of methanol to methyl formate or the steam reforming of methanol were markedly enhanced by previous reduction of Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 at higher temperatures [4–8]. It was found that the catalytic functions of Pd for the dehydrogenation and the steam reforming of methanol were greatly modified upon the formation of Pd–Zn, Pd–Ga and Pd–In alloys by the previous reduction of Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 [4–8].

Figure 5 illustrates XRD patterns for the various supported Pd catalysts and Pd black subjected to the dehydrogenation of ethanol. For Pd/ZnO and Pd/In_2O_3, peaks for PdZn alloys [18] are discerned at $2\theta = 41.2$ and 44.1° and that for $Pd_{0.52}In_{0.48}$ alloy [19] appears at $2\theta = 39.3°$. For Pd/Ga_2O_3, peaks ascribed to Ga_5Pd [20] or Ga_2Pd_5 [21] alloy grow at $2\theta = 39.5$, 41.3 and 45.9° or at $2\theta = 38.2$, 39.9, 40.2 and 47.9°, although some peaks overlapped with those of Ga_2O_3. By contrast, the other supported Pd catalysts and Pd black exhibit peaks ascribed to metallic Pd [22] at $2\theta = 40.1$ and 46.7°. These results suggest that catalytic performances of Pd–Zn, Pd–Ga and Pd–In alloys for the dehydrogenation of ethanol are markedly different from that of metallic Pd formed on SiO_2, MgO, Al_2O_3 or Pd black as those of Pd–Zn, Pd–Ga and Pd–In alloys for the dehydrogenation and the steam reforming of methanol [4–8]. The selectivity to acetaldehyde or ethyl acetate was greatly improved on Pd alloy catalysts.

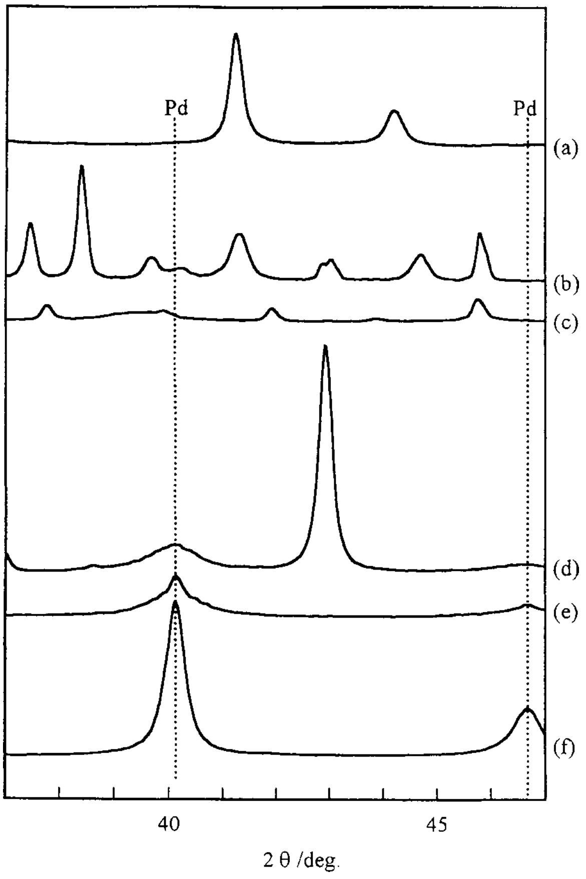

Figure 5. XRD patterns for the supported Pd catalysts and Pd black subjected to the dehydrogenation of ethanol at 493 K. Pd loading 10 wt%, (a) Pd/ZnO reduced to 773 K, (b) Pd/Ga_2O_3, (c) Pd/In_2O_3, (d) Pd/MgO, (e) Pd/SiO_2 and (f) Pd black.

An experiment was carried out over Pd/ZnO previously reduced with H_2 at room temperature. The selectivity for the acetaldehyde formation was dropped to 71%. Methane and carbon monoxide were produced along with acetaldehyde. This catalyst showed a weak broad XRD peak at $2\theta = 40.4°$ slightly higher than that for a peak typical of metallic Pd, i.e., $2\theta = 40.1°$, suggesting that metallic Pd was present along with Pd–Zn alloy. Hence, the formation of methane and carbon monoxide would be enhanced over Pd/ZnO reduced at room temperature, resulting in the decreased selectivity for the acetaldehyde formation.

3.2. Difference in the reactivity of acetaldehyde

The Pd/ZnO catalysts reduced to various temperatures were tested for the decomposition of acetaldehyde at 433 K.

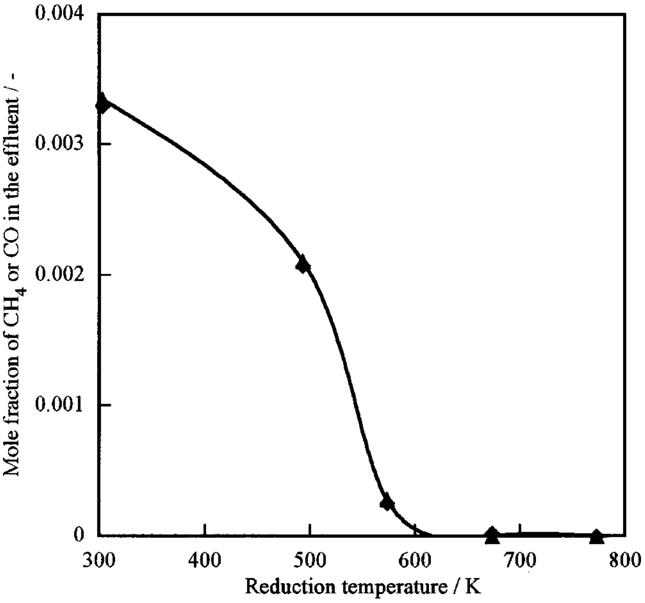

Figure 6. Mole fraction of methane and carbon monoxide in the effluent against the reduction temperature of Pd/ZnO in the decomposition of acetaldehyde. Experiments were carried out at 433 K and inlet partial pressure of acetaldehyde was kept at 3.0 kPa. (♦) CH_4 and (▲) CO.

Figure 6 plots the mole fraction of methane and carbon monoxide in the effluent against the reduction temperature. Over the catalysts reduced to lower temperatures, methane and carbon monoxide were produced in 1 to 1 molar ratio, along with trace amounts of propene, methyl ethyl ketone and crotonaldehyde. The mole fractions of methane and carbon monoxide rapidly decrease with increasing of the reduction temperature. Over Pd/ZnO reduced to 773 K, no reactions occurred.

Similar experiments were carried out over Pd/Ga_2O_3, Pd/In_2O_3, Pd/SiO_2 and Pd/Al_2O_3 catalysts reduced to 773 K and Pd black. Over the Pd/Ga_2O_3 or the Pd/In_2O_3 catalysts where the Pd–Ga or the Pd–In alloy was prevailingly formed, the formation of methane and carbon monoxide was negligible. Only trace amount of crotonaldehyde was produced. By contrast, over the catalysts having metallic Pd phase, such as Pd/SiO_2 and Pd black, acetaldehyde was selectively decomposed to methane and carbon monoxide with a molar ratio of unity along with a small amount of propene. The decarbonylation of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$, occurred selectively. The rates of methane and carbon monoxide formation over Pd/SiO_2 and Pd black were, respectively, seven and three times faster than that over Pd/ZnO reduced at room temperature where metallic Pd predominated. Over Pd/Al_2O_3, considerable amount of crotonaldehyde was produced along with methane and carbon monoxide. Crotonaldehyde was also produced over Al_2O_3 alone. Hence, it was suggested that Al_2O_3 was responsible for the formation of crotonaldehyde over Pd/Al_2O_3, whereas metallic Pd formed on Pd/Al_2O_3 was involved in the formation of methane and carbon monoxide.

Experiments were conducted with ethanol alone and with a mixture of acetaldehyde and ethanol at 433 K over the various supported Pd catalysts reduced to 773 K and Pd black. For ethanol alone, acetaldehyde was selectively produced along with hydrogen over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3. No ethyl acetate was formed at this temperature. However, by addition of acetaldehyde, ethyl acetate was produced along with a trace amount of methyl ethyl ketone. Ethyl acetate was most probably produced through hemiacetal intermediates formed by reaction between acetaldehyde and ethoxide (or ethanol) as methyl formate was formed by reaction of formaldehyde with methanol over copper-based catalysts [7]. Over the other supported Pd catalysts and Pd black, methane and carbon monoxide were formed. No ethyl acetate was produced by the reactions of acetaldehyde in the presence of ethanol. Small amounts of propane and diethyl ether were formed over Pd/SiO_2 in addition to methane and carbon monoxide.

Based on these results, we conclude that acetaldehyde formed in the dehydrogenation of ethanol was stabilized over Pd–Zn, Pd–Ga and Pd–In alloys and, hence, transformed into ethyl acetate through the nucleophilic addition of ethoxide (or ethanol) at higher conversion levels of ethanol as over Cu-based catalysts [14]. These features of the Pd alloys were greatly different from those of the other Pd catalysts having metallic Pd where acetaldehyde formed in the dehydrogenation of ethanol was rapidly decarbonylated to methane and carbon monoxide either in the absence and the presence of ethanol.

4. Conclusion

The dehydrogenation of ethanol proceeded selectively over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 upon the formation of Pd–Zn, Pd–Ga and Pd–In alloys, yielding acetaldehyde and ethyl acetate. The selectivities to acetaldehyde and ethyl acetate were markedly affected by the reaction conditions. At lower space time, acetaldehyde was produced with high selectivity. With increased space time, acetaldehyde decreased and ethyl acetate increased. Over Pd/SiO_2, Pd/MgO and unsupported Pd, ethanol was decomposed to methane and carbon monoxide through the reaction $C_2H_5OH \rightarrow CH_4 + CO + H_2$. The reactivity of aldehyde intermediate species formed in the dehydrogenation of alcohols over Pd–Zn, Pd–Ga and Pd–In alloys were greatly different from those over metallic Pd. Over the Pd alloys, aldehydes formed in the reactions were stabilized and transformed into esters while over metallic Pd, they were decarbonylated to methane and carbon monoxide.

References

[1] G.C. Bond, *Catalysis by Metals* (Academic Press, London, 1962).
[2] N. Iwasa, O. Yamamoto, A. Akazawa, S. Ohyama and N. Takezawa, J. Chem. Soc. Chem. Commun. (1991) 1322.
[3] N. Iwasa, S. Kudo, H. Takahashi, S. Masuda and N. Takezawa, Catal. Lett. 19 (1993) 211.

[4] N. Iwasa, S. Masuda, N. Ogawa and N. Takezawa, Appl. Catal. A 125 (1995) 145.

[5] N. Iwasa, T. Akazawa, S. Ohyama, K. Fujikawa and N. Takezawa, React. Kinet. Catal. Lett. 55 (1995) 245.

[6] N. Iwasa, S. Masuda and N. Takezawa, React. Kinet. Catal. Lett. 55 (1995) 349.

[7] N. Takezawa and N. Iwasa, Catal. Today 36 (1997) 45.

[8] N. Iwasa, T. Mayanagi, N. Ogawa, K. Sakata and N. Takezawa, Catal. Lett. 54 (1998) 119.

[9] M.L. Cubeiro and J.L.G. Fierro, Appl. Catal. A 168 (1998) 307.

[10] P.S. Wehner and B.L. Gustafson, J. Catal. 135 (1992) 420.

[11] B.E. Green, C.S. Sass, L.T. Germinario, P.S. Wehner and B.L. Gustafson, J. Catal. 140 (1993) 406.

[12] A. Sarkany, Z. Zsoldos, B. Furlong, J.W. Hightower and L. Guczi, J. Catal. 141 (1993) 566.

[13] G.D. Zakumbaeva, V.A. Naidin, T.S. Dagirov and E.N. Litvyakova, Russ. J. Phys. Chem. 61 (1987) 801.

[14] N. Iwasa and N. Takezawa, Bull. Chem. Soc. Jpn. 64 (1991) 2619.

[15] P.C. Aben, J. Catal. 10 (1968) 224.

[16] J.L. Davis and M.A. Barteau, Surf. Sci. 187 (1987) 387.

[17] R. Shekhar and M.A. Barteau, Catal. Lett. 31 (1995) 221.

[18] X-ray Powder Data File, ASTM 6-620.

[19] X-ray Powder Data File, ASTM 46-1011.

[20] X-ray Powder Data File, ASTM 15-577.

[21] X-ray Powder Data File, ASTM 27-232.

[22] X-ray Powder Data File, ASTM 46-1043.