Methanol synthesis from CO_2 under atmospheric pressure over supported Pd catalysts

Nobuhiro Iwasa*, Hiroshi Suzuki, MasaoTerashita, Masahiko Arai, and Nobutsune Takezawa

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Received 12 January 2004; accepted 22 April 2004

Pd/ZnO catalyst exhibits high activity and selectivity for methanol synthesis in the hydrogenation of CO_2 under atmospheric pressure. PdZn alloys are formed upon reduction of the Pd/ZnO catalyst at high temperatures. The catalytic activity and selectivity are greatly enhanced upon the formation of such PdZn alloys. The turnover frequency and selectivity of methanol formation are markedly larger than those of a Cu/ZnO type control catalyst.

KEYWORDS: Methanol synthesis; CO_2 hydrogenation; PdZn alloy.

1. Introduction

Methanol is an important feedstock for the production of many chemicals. It is produced from synthesis gas ($CO/CO_2/H_2$) derived from natural gas, and Cu/ZnO-based catalysts have been widely used in industrial methanol production [1–3].

Supported Pd catalysts are also active for methanol synthesis from CO or CO_2 and hydrogen at elevated pressures [4–12]. It has been reported that the activity and the selectivity of supported Pd catalysts depend on the type of support [5,10,11] and on the promoters used [6,7] as well as on the preparation of the catalysts [8,9,12]. However, to our knowledge, there are few reports for hydrogenation of CO_2 at atmospheric pressure.

Previously, we found that the catalytic performance of supported Pd catalysts for the steam reforming of methanol ($CH_3OH + H_2O \rightarrow 3H_2 + CO_2$), the reverse reaction of methanol synthesis from CO_2, is markedly improved in the presence of ZnO. Such novel catalytic function of Pd/ZnO emerges by the formation of PdZn alloys upon the reduction of the Pd/ZnO [13–15].

In the present study, the hydrogenation of CO_2 has been carried out over various supported Pd catalysts under atmospheric pressure. Significant effects of supports upon catalyst activity and selectivity are observed. We show that PdZn alloy catalyst is effective in the synthesis of methonal from CO_2.

2. Experimental

Catalysts used in this study were various supported Pd catalysts. The supported Pd catalysts were prepared by impregnation of an aqueous solution of palladium nitrate on various metal oxides, i.e., ZnO (Kanto Chemicals), Ga_2O_3, In_2O_3 (Wako Pure Chemicals), SiO_2 (Nihon Chromato), MgO (Kishida Chemical), CeO_2 and ZrO_2. The CeO_2 and ZrO_2 were prepared by thermal decomposition of zirconium oxynitrate (Kanto Chemicals) and cerium carbonate (Wako Pure Chemicals), respectively. Palladium loading of the catalysts was kept at 10 wt%. For comparison, Pd black (Wako Pure Chemicals) and Cu/ZnO were also used. The Cu/ZnO catalyst with copper loading of 45 wt.% was prepared by coprecipitation method [16].

The supported Pd 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 a reactor and calcined again at 773 K for 2 h in a stream of O_2 (20 vol%) diluted with nitrogen at a flow rate of 100 cm^3/min.

Prior to the reaction, the supported Pd catalysts were reduced in a hydrogen stream (4 vol%) diluted with nitrogen under temperature-programmed conditions at a heating rate of 5 K/min up to 773 K. Pd black was used for the reaction without calcination and reduction. CO_2 hydrogenation was carried out in a conventional flow reactor with a CO_2/H_2 mixture ($CO_2/H_2 = 1/9$) at atmospheric pressure and at residence time (W; weight of the catalyst, F; total flow rate) of 0.48 s, unless otherwise stated. Reaction temperature was varied from 440 to 493 K. Gases in the effluent were analyzed by gas chromatograph equipped with thermal conductivity detector and flame ionization detector. Hydrogenation of CO was also conducted with a stream of $CO/H_2 = 1/9$. X-ray diffraction (XRD) patterns of the catalysts subjected to the reactions were obtained with a JEOL JDX-8020 X-ray diffractometer, using CuKα radiation ($\lambda = 0.15405$ nm).

The number of Pd surface metal sites on the catalysts was determined by hydrogen chemisorption at 373 K to

---

*To whom correspondence should be addressed.

1011-372X/04/0700–0075/0 © 2004 Plenum Publishing Corporation

avoid hydride phase formation [17]. The turnover frequency for the methanol formation was estimated from the number of surface metal sites and the outflow rate of methanol formation.

3. Results and discussion

3.1. Catalytic activity for CO_2 hydrogenation

When a mixture of CO_2 and H_2 was fed over the catalysts, methanol and CO were produced along with a trace amount of methane. Table 1 lists catalytic activity of the various supported Pd catalysts at 463 K. For comparison, result obtained over Pd black was also listed in table 1. All of the data were measured without thermodynamics limitation though the reaction was carried out at atmospheric pressure. The rate of methanol formation was markedly different with the choice of support used. Over Pd/ZnO, Pd/Ga_2O_3, Pd/In_2O_3, Pd/ZrO_2 and Pd/CeO_2 catalysts, methanol was produced along with CO and methane. The rate of methanol formation decreases in the order Pd/ZnO $\gg$ Pd/In_2O_3, Pd/ZrO_2 $>$ Pd/Ga_2O_3 $>$ Pd/CeO_2. The selectivity to methanol also depends on the choice of support. The Pd/ZnO and Pd/Ga_2O_3 catalysts exhibit higher selectivities compared with the other supported Pd catalysts, which show very low selectivities of 1–2%. In contrast, Pd/SiO_2, Pd/MgO and Pd black produced no methanol. CO was produced by the reverse water gas shift reaction. Thus, Pd/ZnO catalyst exhibits the highest rate and selectivity of methanol formation among the various supported Pd catalysts studied.

The reaction was also conducted using a Cu/ZnO catalyst prepared by coprecipitation method, and result was shown in table 1. Compared with the Cu/ZnO, the rate of methanol formation over Pd/ZnO is somewhat lower; however, the selectivity to methanol and the turnover frequency greatly exceed those of the Cu/ZnO catalyst.

Table 1

CO_2 hydrogenation over various Pd-based catalysts[a]

Catalyst	Rate of formation (μmol min^{-1} g^{-1})			Selectivity[b]	T.O.F.[c] $\times 10^3$
	CH_3OH	CO	CH_4	(%)	(s^{-1})
Pd/ZnO	1.28	0.682	0.01	65.1	1.1
Pd/Ga_2O_3	0.169	0.607	0.01	23.3	0.12
Pd/In_2O_3	0.246	15.4	0.01	1.72	0.21
Pd/SiO_2	0	0.522	0.09	0	0
Pd/MgO	0	2.05	0.07	0	0
Pd/ZrO_2	0.222	13.2	0.54	1.65	0.06
Pd/CeO_2	0.11	9.90	0.16	1.08	0.005
Pd black	0	0.431	0.02	0	0
Cu/ZnO	1.74	3.96	0	30.4	0.075

[a] Reaction temperature; 463 K.

[b] Selectivity for methanol formation.

[c] Turnover frequency for methanol formation.

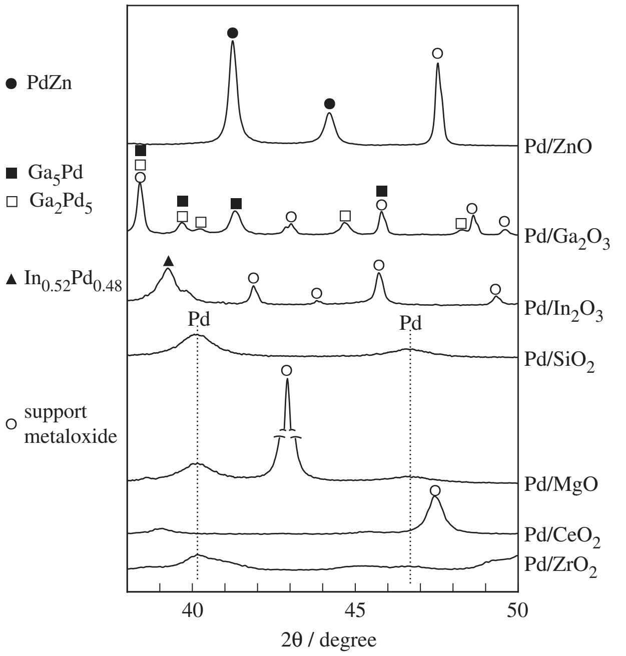

Figure 1. XRD patterns for various supported Pd catalysts after reaction.

3.2. Structure of the catalysts

Figure 1 illustrates XRD patterns for the supported Pd catalysts after the reaction. Those XRD patterns are almost the same as previously reported for the same catalysts after reduction [18]. For Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3, PdZn, Ga_5Pd, Ga_2Pd_5 and $In_{0.52}Pd_{0.48}$ the respective alloys are formed. The other supported Pd catalysts exhibit only the peaks ascribed to metallic Pd, and no alloys were formed. Previously, we found that the catalytic features of supported Pd catalysts for the steam reforming of methanol (reverse reaction of methanol synthesis from CO_2 and hydrogen) were greatly modified in the presence of Pd alloys such as Pd–Zn, Pd–Ga and Pd–In alloys. The activity and the selectivity for the steam reforming of methanol were significantly enhanced upon the formation of such Pd alloys formed by the reduction of Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3. Hence, the high activity and selectivity observed in methanol synthesis with Pd/ZnO catalyst may also be due to the alloying of Pd with Zn.

The reaction was also conducted over Pd/ZnO catalyst samples reduced at different temperatures. In figure 2, the rates of methanol and CO formation are plotted against the reduction temperature. Over the catalyst reduced at a low temperature, 493 K, CO was produced predominantly and the selectivity for methanol formation is only 0.1%. With increasing reduction temperature, the rate of CO formation decreased, while that of methanol increased. The selectivity of methanol was enhanced with increasing reduction temperature. When the catalyst was reduced at 773 K, the selectivity attained 65%.

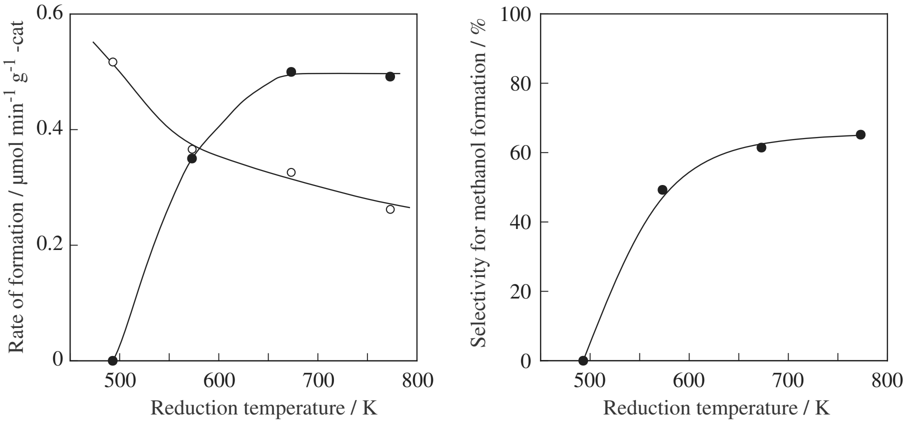

Figure 2. Effect of reduction temperature of Pd/ZnO catalyst upon the hydrogenation of CO_2. (●) (methanol) and (○) (CO). Reaction temperature; 440 K.

The XRD patterns for the Pd/ZnO catalysts reduced at different temperatures after the reaction were shown in figure 3. The catalyst reduced at the lower temperature of 493 K, in which CO was produced predominantly, the peaks appeared around $2\theta = 40.1°$ assigned to metallic Pd. The peak position shifts to higher 2θ value with increasing reduction temperature. The catalysts reduced above 673 K, producing methanol with high selectivity, show peaks of PdZn alloys only with no peak for metallic Pd. These results indicated that the CO was selectively produced on metallic Pd, whereas methanol was produced on PdZn alloy. In our previous work, we found that a metal-support interaction occurs between metallic Pd and ZnO reduced at higher temperatures [15,19]. Here, electron transfer takes place from Pd to Zn upon the formation of PdZn alloys. Ponec *et al.* indicated that cationic Pd species are active in methanol synthesis from CO and hydrogen. They showed a linear relationship between activity of methanol synthesis and the amount of Pd^{n+} species in Pd/SiO_2 modified with Mg or La [6,7]. Recently, Matsumura *et al.* reported that cationic Pd species can be formed in Pd supported CeO_2 prepared by precipitation method [20]. The activity and the selectivity of the Pd/CeO_2 catalyst are high even at a low reaction temperature 443 K [11]. Hence, positively charged Pd species in the PdZn alloys play an important role in methanol synthesis, in the hydrogenation of CO_2.

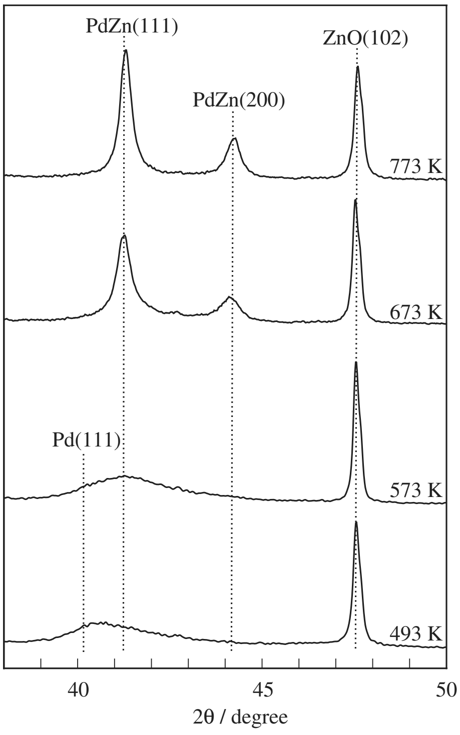

Figure 3. XRD patterns for Pd/ZnO catalysts reduced at different temperatures.

3.3. Reaction pathways

Effect of residence time upon the reaction was investigated over Pd/ZnO catalyst reduced at 773 K. Figure 4 (a) and (b) illustrate the rate of formation and the selectivity for CO and methanol formation, respectively. Both the rates of CO and methanol formation increased monotonously with an increase of residence time, while the selectivity of CO and methanol did not change markedly over the whole residence time range studied. When the selectivity is extrapolated to zero value of residence time (dotted line in Figure 4(b)), it does not go to 0% or 100%. These results indicate that CO and methanol are produced in parallel pathways over Pd/ZnO catalyst.

Hydrogenation of CO was also conducted with the various supported Pd catalysts (table 2). The Pd/SiO_2, Pd/MgO, Pd/CeO_2 and Pd/ZrO_2 catalysts produce methanol along with methane. Pd/CeO_2 and Pd/ZrO_2 catalysts give higher formation rate for methanol, similar to the results of Matsumura *et al.* [11] and Fujitani *et al.* [21]. Over Pd/CeO_2 and Pd/ZrO_2, dispropotionation of CO was also occurred, giving CO_2. By contrast, over Pd/ZnO, Pd/Ga_2O_3 and

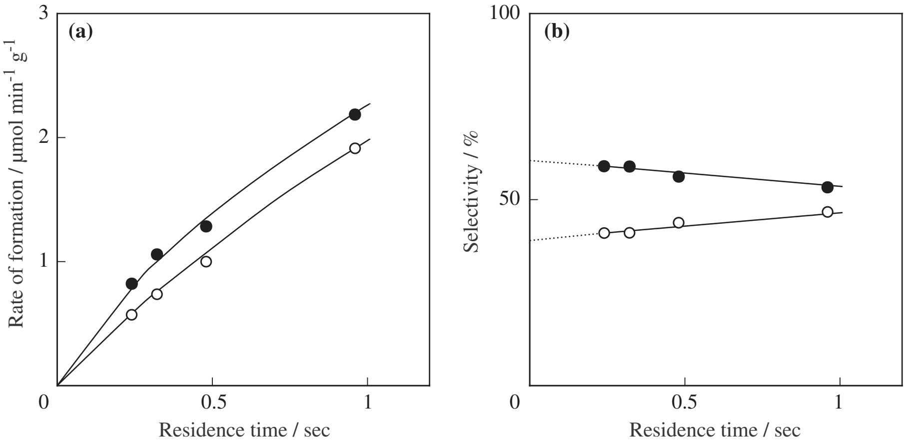

Figure 4. Effect of W/F upon the hydrogenation of CO_2 over Pd/ZnO catalysts. (●) (methanol) and (○) (CO). Reaction temperature: 463 K.

Table 2
CO hydrogenation over various Pd-based catalysts[a].

Catalyst	Rate of formation (μmol min^{-1} g^{-1})			Selectivity[b]	T.O.F.[c] × 10^3
	CH_3OH	CH_4	CO_2	(%)	(s^{-1})
Pd/ZnO	0	0	0	–	0
Pd/Ga_2O_3	0	0	0	–	0
Pd/In_2O_3	0	0	0	–	0
Pd/SiO_2	0.141	0.060	0	70.1	0.03
Pd/MgO	1.21	$<$0.004	0	99.9	0.20
Pd/CeO_2	2.83	0.163	0.239	87.5	0.14
Pd/ZrO_2	1.98	0.528	1.65	72.9	0.54
Pd black	0	0 [d]	0 [d]	–	0

[a] Reaction temperature; 463 K.
[b] Selectivity for methanol formation.
[c] Turnover frequency for methanol formation.
[d] Trace amounts of methane and CO_2 were produced at initial stage of reaction.

Pd/In_2O_3, no reaction took place, although methanol was produced in the hydrogenation of CO_2. It was strongly suggested that reaction pathway of methanol formation in the hydrogenation of CO_2 over Pd/ZrO_2, Pd/CeO_2 is different from that over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3. Over Pd/CeO_2 and Pd/ZrO_2, having metallic Pd present, CO_2 was transformed to CO by the reverse water gas shift reaction and then CO was hydrogenated to methanol, while over Pd/ZnO, Pd/Ga_2O_3, Pd/In_2O_3 having Pd alloys, methanol was produced from CO_2 directly.

4. Conclusion

The activity and the selectivity of supported Pd catalysts for hydrogenation of CO_2 significantly depend on the supports used. Pd/ZnO catalyst shows the highest activity and selectivity for the formation of methanol in the hydrogenation of CO_2. Such novel catalytic function of the Pd/ZnO catalyst is developed by the reduction of the catalyst at higher temperatures, forming PdZn alloys. Such PdZn alloys act as active sites for the synthesis of methanol. The turnover frequency and selectivity for methanol formation obtained over reduced Pd/ZnO catalysts are larger than those over Cu/ZnO catalyst.

References

[1] J.C.J. Bard and R. P. A. Sneeden, Catal. Today 2 (1987) 1.
[2] K. Klier, Adv. Catal. 31 (1982) 243.
[3] H.H. Kung, Catal. Rev. Sci. Eng. 22 (1980) 235.
[4] M.L. Poutsma, L.F.Elek, P.A. Ibarbia, A.P. Risch and J.A. Rabo, J. Catal. 52 (1978) 157.
[5] Yu.A. Ryndin, R.F. Hicks, A.T. Bell and Yu.I. Yermakov, J. Catal. 70 (1981) 287.
[6] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1983) 26.
[7] V. Ponec, Surf. Sci. 272 (1992) 111.
[8] L. Fan and K. Fujimoto, J. Catal. 150 (1994) 217.
[9] L. Fan and K. Fujimoto, J. Catal. 172 (1997) 238.
[10] T. Fujitani, M. Saito, Y. Kanai, T. Watanabe. J. Nakamura and T. Uchijima, Appl. Catal. A 125 (1995) L199.
[11] W.-J. Shen, M. Okumura, Y. Matsumura and M. Haruta, Appl. Catal. A 213 (2001) 225.
[12] C.-H. kim, J. S. Lee and D. L. Trimm, Top Catal. 22 (2003) 319.
[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 and N. Takezawa, Top Catal. 22 (2003) 215.
[16] S. Fujita, Y. Kanamori, A.M. Satriyo, N. Takezawa, Catal. Today 45 (1998) 241.
[17] P.C. Aben, J. Catal. 10 (1968) 224.
[18] N. Iwasa, T. Mayanagi, O. Ogawa, K. Sakata and N. Takezawa, Catal. Lett. 54 (1998) 119.
[19] N. Iwasa, N. Ogawa, S. Masuda and N. Takezawa, Bull. Chem. Soc. Jpn. 71 (1998) 1451.
[20] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai and M. Haruta, Appl. Catal. A 171 (1998) 123.
[21] T. Fujitani and I. Nakamura, Bull. Chem. Soc. Jpn. 75 (2002) 1393.