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Selective PdZn Alloy Formation in the Reduction of Pd/ZnO Catalysts

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Temperature programmed reduction (TPR) experiments were carried out over Pd/ZnO with different Pd loadings. Combined results with an X-ray diffraction method and X-ray photoelectron spectroscopy showed that a Pd–Zn alloy with a structure of PdZn was selectively produced in the course of TPR of Pd/ZnO. It was suggested that hydrogen retained in Pd spilled over to ZnO. The ZnO was reduced to metallic Zn, being converted to PdZn. The molar amounts of the ZnO reduced were practically the same as the those of Pd loaded. Hence, all the Pd loaded was completely transformed to the PdZn alloys upon reduction.

The catalytic functions of Group 8—10 metals are greatly different from those of copper for reactions involving methanol.[1—10] Over Group 8—10 metal catalysts, methanol is decomposed to CO and H_2,[1—3] while over copper catalysts it is dehydrogenated to $HCOOCH_3$.[1] For the steam reforming of methanol, Group 8—10 metal catalysts show poor selectivity.[4,5] Over copper catalysts the reaction occurs with high selectivity.[6—10]

Previously, we found that Pd/ZnO catalysts show anomalously high selectivity for the dehydrogenation of methanol to methyl formate[3] and the steam reforming of methanol, among various supported Pd catalysts.[11] The selectivities for the dehydrogenation and the steam reforming were greatly improved by previously reduced Pd/ZnO catalysts at high temperatures. Involvement of PdZn alloys in the steam reforming was suggested. Over the other ZnO supported Group 8—10 metal catalysts, such as Ni/ZnO and Co/ZnO, the selectivities for the dehydrogenation and the steam reforming were much lower than those over Pd/ZnO.[12,13] No reaction occurred over ZnO or Zn alone. Hence, the original function of Pd was greatly modified upon the formation of PdZn alloys.

In connection with these findings, it should be noted that the formation of PdZn alloys was also reported by other authors for reduced Pd/ZnO[14—16] or Pd deposited on a single crystal of ZnO.[17] Yeh et al.[18] studied temperature programmed reduction (TPR) for 10 wt% Pd/ZnO. With the help of transmission electron microscopy, they concluded that ZnO was reduced to metallic Zn, yielding PdZn alloys.

In this work, TPR experiments were carried out over Pd/ZnO with various Pd loadings. By the use of an X-ray diffraction (XRD) method and X-ray photoelectron spectroscopy (XPS), we show that an alloy having the composition of PdZn is selectively produced in the course of the TPR experiments.

Experimental

Catalysts. Pd/ZnO catalysts (1.0, 2.0, 5.0, 10, 20, 30, and 50 wt% Pd) were prepared by impregnation of ZnO (Kanto Chemicals Co., Ltd., extra pure grade) with a palladium(II) nitrate solution (Tanaka Noble Metals Ind. Co., extra pure) at 353 K. The obtained samples were then dried at 383 K overnight, pressed into granules in sizes of 60—80 meshes (Tyler meshes), and were calcined in air at 773 K for 3 h. The prepared catalyst (1.0 g) was packed in a reactor and calcined again at 773 K for 1 h in a stream of O_2 (20 vol% O_2 diluted with Ar) at a total flow rate of 50 cm^3 STP/min. For comparison, experiments were also conducted over 10 wt% Pd/SiO_2, unsupported Pd (Wako Pure Chemicals Co., Ltd.), and ZnO (Kanto Chemicals Co., Ltd.). Pd/SiO_2 was obtained in a similar manner to that of the preparation of Pd/ZnO. The unsupported Pd catalyst was prepared by decomposition of palladium(II) nitrate at 773 K for 3 h in air. These samples were also calcined in air and treated in O_2 as Pd/ZnO was. The weights of the used samples were 1.0 g for 10 wt% Pd/SiO_2, 20 mg for the unsupported Pd catalyst, and 1.0 g for the ZnO catalyst.

Temperature Programmed Reduction (TPR). TPR runs were carried out in a flow of a hydrogen–argon mixture (4 vol% H_2) at a total flow rate of 50 $cm^3\,min^{-1}$ and at a heating rate of 5 $K\,min^{-1}$ from room temperature to 773 or 1073 K. Before the TPR runs, the hydrogen-argon mixture was fed over the catalyst at room temperature. After completion of the H_2 consumption, TPR experiments were conducted. Hydrogen from the reactor was collected every 2 min in a sampling tube attached to the outlet of the reactor and analyzed by gas chromatography, using a Porapak T column and argon as carrier gas. Reproducibility of the TPR curves was examined through repeated experiments.

Characterization of the Catalysts. XRD spectra of the catalysts were obtained with a Rigaku Denki ADP-301-E X-ray diffractometer, using Cu $K\alpha$ radiation ($\lambda = 0.15405$ nm). XP spectra were recorded on an ESCALAB-Mk2 (V.G. Scientific Co). For XPS measurements, a sample of the catalyst was pressed on a Ni holder coated with gold, placed in a reaction chamber, and reduced in a hydrogen stream to given temperatures at the temperature-programmed condition. The catalyst was then transferred to the analysis chamber without exposure to air and the spectra were recorded.

Results and Discussion

Figure 1 illustrates the variation of the H_2 consumption (expressed as the decreased mol fraction of H_2) with time

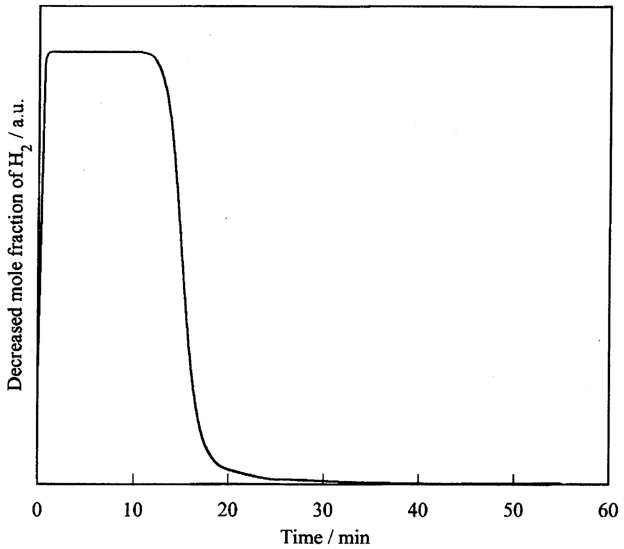

Fig. 1. Time course of the reduction for 10 wt% Pd/ZnO at room temperature.

over 10 wt% Pd/ZnO in a flow of H_2 at room temperature. H_2 is slowly consumed in the first 1—2 min. The H_2 consumption then increases rapidly with time. H_2 supplied was completely consumed at 2—15 min after the exposure to H_2. The H_2 consumption then decreases rapidly, discontinuing at the exposure time of 45 min.

After completion of the H_2 consumption at room temperature, TPR experiments were conducted. Figure 2 depicts TPR profiles for various Pd/ZnO. An inverse peak appeared at 333 K, and was attributed to the desorption of H_2. A small peak of the hydrogen consumption was discernible at 363 K. With further increase in the temperature, the hydrogen uptake occurred appreciably around 400 K and increased, resulting in the growth of the peaks in a temperature range of 573 to 773 K. The positions of the peaks depended upon Pd loading.

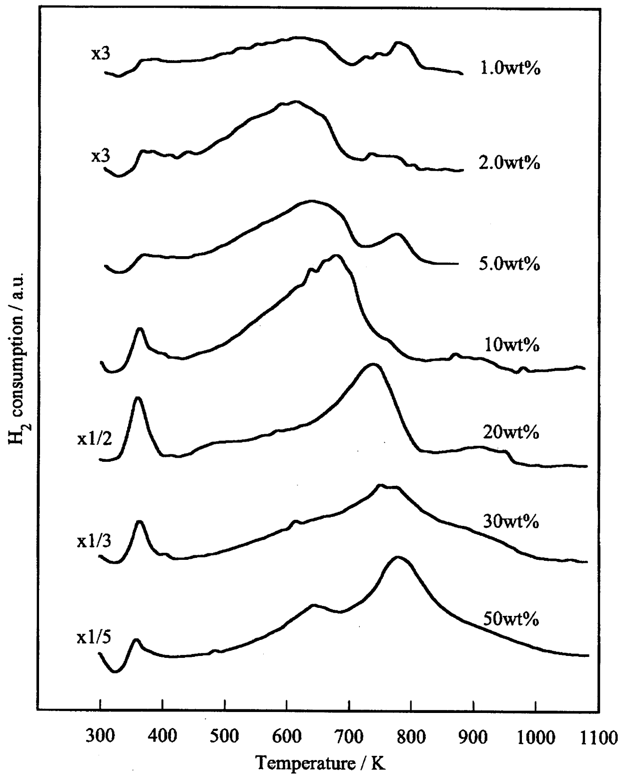

Fig. 2. TPR profiles for different loadings of Pd/ZnO.

Experiments were also carried out over 10 wt% Pd/SiO_2, unsupported Pd, and ZnO alone. For 10 wt% Pd/SiO_2 and unsupported Pd, the hydrogen supplied was rapidly consumed at room temperature. An inverse peak ascribed to the desorption of H_2 appeared at 363 K. At higher temperatures, no hydrogen consumption peak was observed. None of the peaks were discerned in the TPR run over ZnO alone. Hence, the peaks occurring in 573—773 K emerged only in the presence of both Pd and ZnO. On the other hand, the hydrogen consumption at room temperature and the inverse TPR peak always occurred in the presence of Pd.

Figure 3 illustrates XRD spectra of 10 wt% Pd/ZnO re-

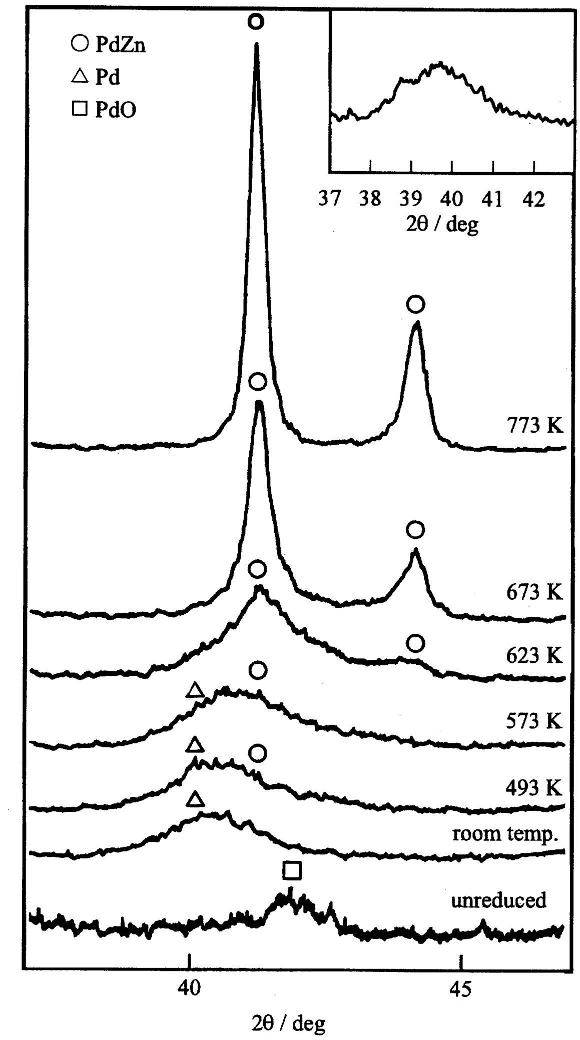

Fig. 3. XRD spectra of 10 wt% Pd/ZnO unreduced and reduced to various temperatures. The reduction temperature of the catalysts is indicated in the figure. XRD spectra obtained in situ measurements were also shown in the inset of the figure.

duced to various temperatures. Unreduced Pd/ZnO produces a broad weak peak ascribed to PdO[19] at $2\theta = 41.9°$. Strong peaks for ZnO[20] are also seen in the range of 2θ values above 47° and below 38°, not shown in the figure. Upon the reduction of the catalyst at room temperature, the peak ascribed to PdO diminished and a new peak grows at $2\theta = 39.7°$ in an XRD spectrum obtained by in situ measurements, shown as an inset of the figure. The position of the peak is located at a 2θ value slightly higher than that for $PdH_{0.7}$, suggesting the formation of PdH_x ($x < 0.7$). Upon flushing H_2 with helium at room temperature or heating to 373 K in a hydrogen flow, a peak for metallic Pd[21] grows at $2\theta = 40.1°$ at the expense of the peak for PdH_x. With further increase in the reduction temperature, the peak for metallic Pd shifts gradually toward higher 2θ values and becomes sharper. Upon the reduction to 623 K, peaks ascribed to PdZn[22] emerge at $2\theta = 41.2°$ and 44.1°. These peaks grow markedly with further increases in the reduction temperatures. No peaks ascribed to metallic Pd and Zn are discerned in the spectra. Similar results were obtained over the other Pd/ZnO catalysts.

The Pd/SiO_2 catalyst also showed peaks ascribed to PdO[19] in X-ray spectra. Upon reduction at room temperature, the peaks ascribed to $PdH_{0.7}$ were observed at $2\theta = 38.8°$ in situ measurements, while those ascribed to PdO disappeared. On flushing H_2 with the helium stream at room temperature or heating to 373 K, the peaks for metallic Pd[20] grew at the expense of the peaks ascribed to $PdH_{0.7}$. Upon the reduction to higher temperatures the peaks for metallic Pd were merely intensified.

Figure 4 illustrates XP spectra of 10 wt% Pd/ZnO reduced to different temperatures. Peaks for Pd $3d_{5/2}$ and Pd $3d_{3/2}$ ascribed to PdO[23—26] are seen for unreduced Pd/ZnO at binding energies of 336.9 and 342.3 eV, respectively. For the catalyst reduced at room temperature, new peaks ascribed to metallic Pd grow at 335.2 and 340.5 eV. At variance with the results of XRD measurements, the peaks for PdO remain to some extent after the reduction at room temperature, suggesting that PdO accumulates on the surface or subsurface of the Pd/ZnO catalysts. For the catalyst reduced to 493 K, the peaks ascribed to PdO diminish. The peaks ascribed to metallic Pd shift slightly to 335.3 and 340.6 eV. With further increases in the reduction temperature, the positions of the peaks for metallic Pd shift to higher binding energy by 0.6 eV, suggesting that the structure of Pd changes. In accord with these findings, peaks ascribed to metallic Zn grow in Auger electron spectra of the catalysts reduced to higher temperatures (Fig. 5). By comparison with the results of XRD measurements, it was concluded that the shift of the XPS peaks for Pd arose from the formation of the PdZn alloy.

On the basis of XRD and XPS measurements, it is evident that the Pd species were primarily present as PdO on unreduced Pd/ZnO, Pd/SiO_2, and unsupported Pd. The PdO species were reduced to Pd in H_2 at room temperature, being transformed to Pd hydrides (PdH_x with the x-values lower than 0.7) for Pd/ZnO and $PdH_{0.7}$ for Pd/SiO_2. For Pd/ZnO, the PdO species remains to some extent at room temperature, but it is completely reduced for Pd/SiO_2 and unsupported Pd.

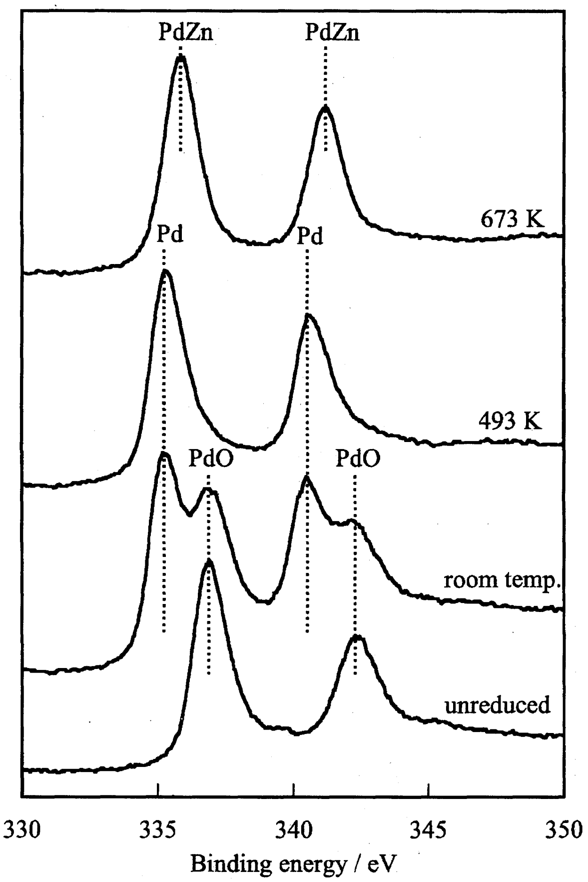

Fig. 4. XPS spectra of 10 wt% Pd/ZnO unreduced and reduced to various temperatures. The reduction temperature of the catalysts is indicated in the figure.

The Pd hydrides, PdH_x ($x < 0.7$) and $PdH_{0.7}$, were decomposed to metallic Pd respectively at 333 and 363 K, giving the inverse TPR peaks. The PdO species partly remaining in Pd/ZnO was reduced at 363 K, showing the weak hydrogen consumption peak. With the elevated temperatures, strong peaks appeared in 573—673 K, attributed to the reduction of ZnO. This resulted in the formation of PdZn alloys.

Table 1 summarizes the amount of H_2 consumed at room temperature over the Pd/ZnO catalysts along with the estimated amount of H_2 for the reduction, $PdO + H_2 \rightarrow Pd + H_2O$, of PdO formed on the catalyst. The amount of H_2 consumed at room temperature always exceeds that required for the reduction of the PdO. For example, on 10 wt% Pd/ZnO the amount of H_2 consumed at room temperature is 1.23 mmol in contrast to that for the reduction of the PdO, 0.93 mmol. Thus, the excess of H_2, $1.23 - 0.93 = 0.30$ mmol, was 0.33 times the amount of Pd loaded, 0.93 mmol, being attributable to the formation of PdH_x. However, the value of excess H_2/Pd increases greatly with the decreased Pd loading as seen from the results in the last column of Table 1. Over 1.0 wt% Pd/ZnO the excess of H_2 reached 0.67 times the amount of Pd loaded. Since the x-value of PdH_x was lower than 0.7 for Pd/ZnO on the basis of the XRD measurements, the excess of H_2 should be lower than 0.35 times that of Pd loaded. Hence, it is highly probable that the excess H_2

Table 1. Amount of H_2 Consumed at Room Temperature over Various Pd/ZnO[a)]

Pd loading wt%	H_2 consumed mmol	H_2 consumed[b)] for PdO→Pd mmol	Excess amount of H_2 consumed[c)] mmol	Excess H_2/Pd[d)]
1.0	0.15	0.09	0.06	0.67
2.0	0.28	0.19	0.09	0.47
5.0	0.64	0.47	0.17	0.36
10.0	1.23	0.93	0.30	0.33
20.0	2.46	1.82	0.64	0.35
30.0	3.66	2.70	0.96	0.36
50.0	6.14	4.36	1.78	0.40

a) The weight of the samples used were 1.0 g in oxidized state, i.e. PdO/ZnO. b) Amount of the H_2 consumption estimated for the reduction, $PdO+H_2 \rightarrow Pd+H_2O$, of PdO formed on the Pd/ZnO catalysts. c) Molar amount of H_2 consumed at room temperature minus molar amount of Pd loaded. d) Excess amount of H_2/amount of Pd loaded.

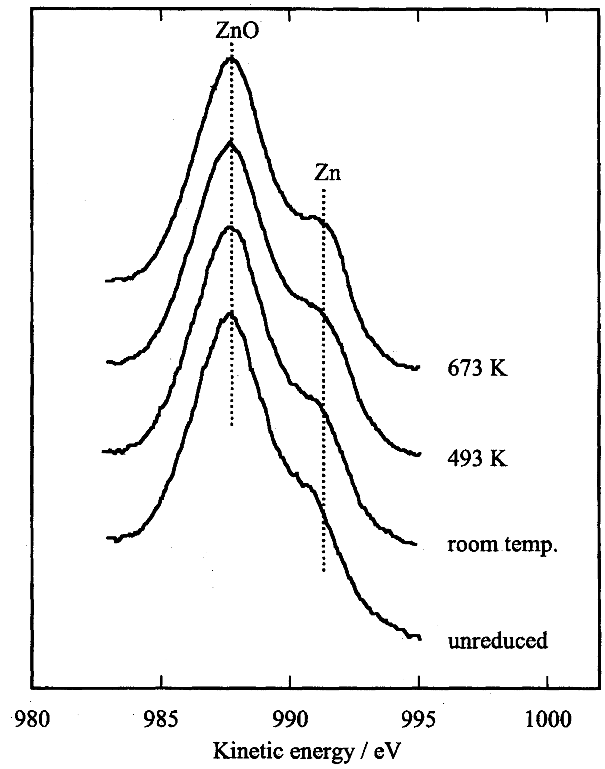

Fig. 5. Zn LMM Auger spectra of 10 wt% Pd/ZnO unreduced and reduced to various temperatures. The reduction temperature of the catalysts is indicated in the figure.

Table 2. Amount of H_2 Desorbed and Consumption in TPR Runs over Various Pd/ZnO

Pd loading wt%	H_2 desorbed for TPR peak at 333 K mmol	H_2 consumed for TPR peak at 363 K mmol	H_2 consumed for TPR peaks at 573—773 K mmol
1.0	—	0.01	0.06
2.0	0.001	0.01	0.11
5.0	0.007	0.02	0.30
10.0	0.005	0.04	0.56
20.0	0.001	0.10	0.92
30.0	0.007	0.08	1.42
50.0	0.07	0.06	3.11

spills partly over the surface of ZnO through Pd in particular over the catalysts with low Pd loadings at room temperature. In contrast, for unsupported Pd, the excess of H_2 was estimated to be 0.36 times the amount of Pd loaded, practically confirming the XRD result for the formation of $PdH_{0.7}$. With the increased temperature, these Pd hydrides were decomposed at 333 and 363 K, respectively for Pd/ZnO and unsupported Pd, giving inverse peaks. In Table 2, is listed the amount of H_2 desorbed at 333 K or consumed in the TPR experiments over Pd/ZnO. By comparison of Tables 1 (column 4), and 2 (column 2), it is evident that only part of the excess H_2 desorbed at 333 K. For instance, over 10 wt% Pd/ZnO the desorbed H_2 was estimated to be 0.005 mmol, being far below the excess of H_2, i.e. 0.30 mmol. Similar results were obtained over the other Pd/ZnO catalysts. This strongly suggests that the excess hydrogen held as PdH_x was primarily spilled over to ZnO in preference to the desorption from the Pd/ZnO catalysts. On the other hand, the excess H_2 was found to desorb completely from 10 wt% Pd/SiO_2 and unsupported Pd.

On the basis of the results in Tables 1 and 2, the amounts of H_2 consumed for the reduction of the ZnO support in Pd/ZnO were evaluated by subtraction of the amounts of H_2 required for the reduction of PdO (Table 1, column 3) and the amounts H_2 desorbed in the TPR at 333 K (Table 2, column 2) from the amount of H_2 consumed at room temperature (Table 1, column 2) and those in the TPR peaks at 363 K and at 573—773 K (Table 2, column 3 and 4, respectively). In Fig. 6, thus evaluated amounts of the H_2 consumption for the reduction of ZnO are plotted against those of Pd loaded on ZnO. It shows that the former value is practically the same as the latter, suggesting that the amount of metallic Zn produced in the reduction of Pd/ZnO is in close agreement with that of Pd loaded. Hence it is highly probable that the spillover of H atoms on Pd to the surface of ZnO is readily quenched once metallic Pd is completely converted into PdZn. Thus, all the Pd loaded are selectively transformed to Pd–Zn alloy having a composition of PdZn in these experiments.

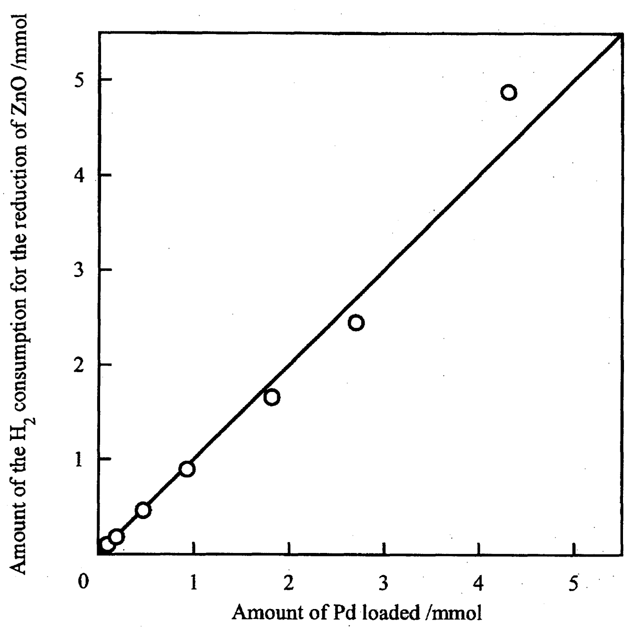

Fig. 6. Relation between the amounts of the H_2 consumption for the reduction of ZnO and the amounts of Pd loaded on ZnO.

In previous work,[3,11] it was found that Pd/ZnO has anomalous catalytic performances for the dehydrogenation of methanol to $HCOOCH_3$ and the steam reforming of methanol. The selectivity as well as the activity for the these reactions increased greatly with the increase in the reduction temperature. In conjunction with these findings, it is highly probable that the increased selectivity and activity for the dehydrogenation to $HCOOCH_3$ and the steam reforming of methanol is ascribed to the formation of PdZn alloy selectively developed in the reduction. On the other hand, for Pd/SiO_2, and unsupported Pd, metallic Pd was formed in the reduction. Over reduced Pd/SiO_2 and Pd, no $HCOOCH_3$ was produced in the dehydrogenation of methanol, and the selectivities for the steam reforming were much lower than that over reduced Pd/ZnO.

Summary

TPR runs were carried out over various Pd/ZnO with different Pd-loadings. In combination with the observations with XRD method, XPS and AES, we showed that the PdZn alloy phase was selectively developed in the reduction. Hydrogen initially retained in Pd spilled rapidly over to ZnO. The ZnO was then reduced to metallic Zn, being transformed to PdZn. Once the alloy was produced, the spillover of hydrogen atoms on the alloys to ZnO was greatly suppressed, resulting in the selective formation of PdZn in the course of the reduction of Pd/ZnO.

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