Highly selective supported Pd catalysts for steam reforming of methanol

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Steam reforming of methanol, $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$, was carried out over various Pd catalysts (Pd/SiO_2, Pd/Al_2O_3, Pd/La_2O_3, Pd/Nb_2O_5, Pd/Nd_2O_3, Pd/ZrO_2, Pd/ZnO and unsupported Pd). The reaction was greatly affected by the kind of support. The selectivity for the steam reforming was anomalously high over Pd/ZnO catalysts.

Keywords: Steam reforming of methanol; Pd/ZnO; supported Pd catalysts

1. Introduction

The steam reforming of methanol has been recently developed for the hydrogen production for various hydrogenation processes for organic compounds and for fuel cells [1,2]. This reaction occurs selectively over copper-based catalysts [2–5]. Over transition metal catalysts carbon monoxide and hydrogen were appreciably produced. Decomposition of methanol, $CH_3OH \rightarrow CO + 2H_2$, occurred predominantly. The selectivities for the steam reforming over transition metal catalysts are much lower than those over copper-based catalysts [6–8]. In the present paper, we show that Pd/ZnO catalysts are highly active and selective for the steam reforming of methanol.

2. Experimental

Supported Pd catalysts were prepared by impregnation of an aqueous solution of palladium nitrate on various metal oxides, i.e. SiO_2 (Nihon Chromato Kogyo Ltd.), Al_2O_3 (Catalysis Society of Japan JRC-ALO4), La_2O_3 (Wako Pure Chemicals Ltd., extra pure grade), Nb_2O_5 (Wako Pure Chemicals Ltd., extra pure grade),

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Nd_2O_3 (Wako Pure Chemicals Ltd., extra pure grade), ZrO_2 which was prepared by thermal decomposition of zirconium oxynitrate (Kanto Chemical Co., Inc., extra pure grade), ZnO (Kanto Chemical Co., Inc., extra pure grade), in a rotary evaporator at 353 K. The catalysts thus prepared were dried at 383 K overnight and calcined in air at 773 K for 3 h. Unless otherwise stated, Pd loading was kept at 1 wt% over these metal oxides. For comparison, and unsupported Pd catalyst derived from palladium black was also used for the reaction. Experiments were carried out at atmospheric pressure in a fashion similar to that in the previous work [4]. A conventional flow reactor was used. The inlet partial pressures of methanol and water were both kept at 24.3 kPa unless otherwise stated. Residence time was varied in a range covering from 0.23 to 3.29 s. Nitrogen was used as a diluent. Gaseous components in the effluent were analyzed by gas chromatography. The selectivity for the steam reforming was evaluated on the carbon basis, i.e. $P_{CO_2}/(P_{CO_2} + P_{CO} + 2P_{CH_3OCH_3})$, where P_{CO_2}, P_{CO} and $P_{CH_3OCH_3}$ represent the partial pressures of CO_2, CO and CH_3OCH_3, respectively. The number of surface Pd atoms was determined by the adsorption of hydrogen at 373 K [9]. The dispersion of Pd was estimated from the ratio of the number of surface Pd atoms to the total number of Pd atoms used for the catalysts.

3. Results and discussion

When a mixture of methanol and water was fed over the catalysts, hydrogen, carbon dioxide and carbon monoxide were produced. Only Pd/Al_2O_3 gave dimethyl ether in addition to these products. Table 1 lists the rate and the turnover frequency for the hydrogen production and the selectivity for the steam reforming at 493 K together with the dispersion of Pd. Kinetic parameters such as the rate, the turn-

Table 1
Steam reforming of methanol over various supported Pd catalysts [a]

Catalyst	Rate of H_2 production ($cm^3 (g cat)^{-1} h^{-1}$)	TOF [b] (s^{-1})	Selectivity [c] for the steam reforming (%)	Dispersion (%)
Pd/SiO_2	10.1	0.0187	0	7.2
Pd/Al_2O_3	151	0.152	1.4	13.1
Pd/La_2O_3	248	0.661	8.0	5.0
Pd/Nd_2O_3	300	0.156	7.0	25.3
Pd/Nb_2O_5	124	0.0835	4.2	19.6
Pd/ZrO_2	324	0.148	20	28.9
Pd/ZnO	672	0.829	97	10.7
Pd	164	0.0103	0.1	2.1

[a] Reaction temperature = 473 K, Pd loading = 1.0 wt%, residence time = 0.47 s.
[b] Turnover frequency for H_2 production.
[c] Defined as $P_{CO_2} / (P_{CO_2} + P_{CO} + 2P_{CH_3OCH_3})$.

over frequency and the selectivity are greatly affected by the kind of support used. The turnover frequency is improved by the use of metal oxide supports. It is noteworthy that Pd/ZnO is highly selective for the steam reforming as compared with other supported Pd catalysts.

Fig. 1 illustrates the relationship between the conversion of methanol and the selectivity for steam reforming over Pd/ZnO, Pd/ZrO_2, Pd/Nb_2O_5 and unsupported Pd catalysts at 493 K. Over Pd/ZnO the selectivity exceeds 96% over all conversion levels studied. Over Pd/ZrO_2 and Pd/Nb_2O_5, the selectivities increase with the increase of conversion level. However, they are still far below that obtained over Pd/ZnO. Over unsupported Pd the selectivity is considerably low. Decomposition of methanol, $CH_3OH \rightarrow CO + 2H_2$, occurs in high selectivity. No reaction took place over ZnO alone. With the increase of Pd loading up to 10 wt% on ZnO, the activity and the selectivity for the steam reforming increased. The rate of the hydrogen production was attained to 967 cm^3 (g cat)$^{-1}$ h^{-1} over 10 wt% Pd/ZnO at 493 K and at a residence time of 0.47 s. The selectivity for the steam reforming was 97%. The rate and the selectivity were comparable to those obtained over 10 wt% Cu/SiO_2 for which the rate of the hydrogen production was recorded at 465 cm^3 (g cat)$^{-1}$ h^{-1} with a selectivity over 99%.

When the reaction was conducted over Pd/ZnO at elevated temperatures, the conversion increased markedly and the selectivity decreased to some extent. At 623 K and residence time of 0.47 s, the conversion exceeded 99% with the selectivity of 92.0%.

Figs. 2A and 2B illustrate the partial pressures of the products in the effluent against residence time (t_r) at 493 and 573 K. In figs. 3A and 3B, a parameter $K = P_{H_2}P_{CO_2}/P_{H_2O}P_{CO}$, which is estimated from the partial pressure of hydrogen, P_{H_2}, etc. in the effluent, compares with the equilibrium constant K_p of the water–gas shift reaction. At 493 K, the partial pressure of all of the products increases

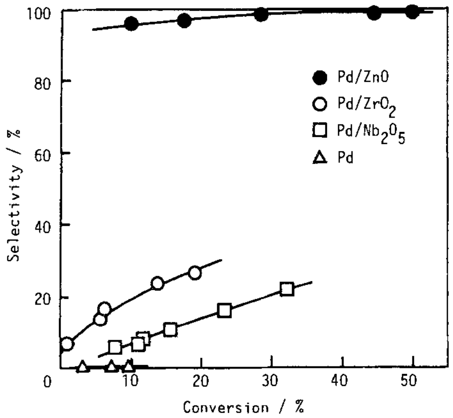


Fig. 1. Conversion of methanol versus selectivity for the steam reforming over various Pd catalysts at 493 K. Pd loading on the supported catalysts, 1 wt%; inlet partial pressure, $P_{CH_3OH} = P_{H_2O} = 24.3$ kPa.

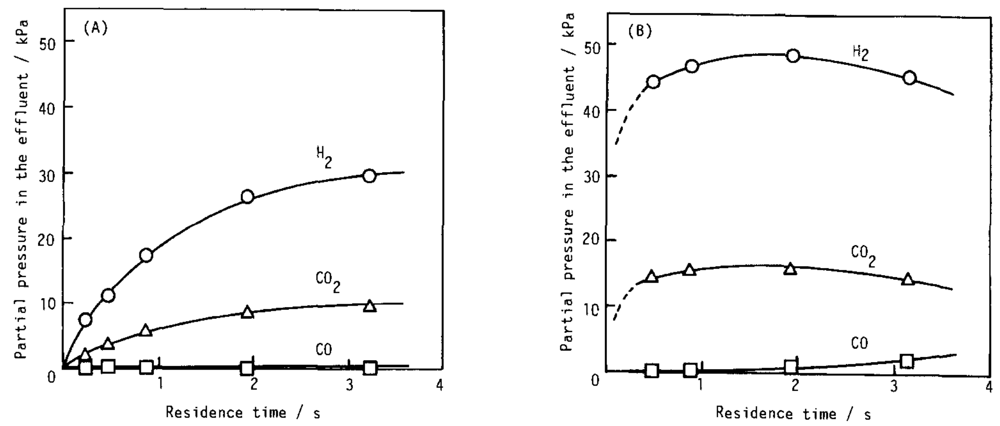


Fig. 2. The outlet partial pressure of the products against residence time over Pd/ZnO. Experiments were carried out at (A) 493 K and (B) 573 K. Pd loading, 1 wt%; inlet partial pressure, $P_{CH_3OH} = P_{H_2O} = 24.3$ kPa.

with increasing t_r. The K-value increases with increasing t_r and exceeds the K_p-value above $t_r = 1.8$ s. On the other hand, at 573 K the partial pressure of hydrogen and carbon dioxide in the effluent increases with the increase of t_r, decreasing gradually through a maximum at $t_r = 1.6$ s. Although considerably low, the partial pressure of carbon monoxide increases slowly with increasing t_r at shorter t_r. At t_r

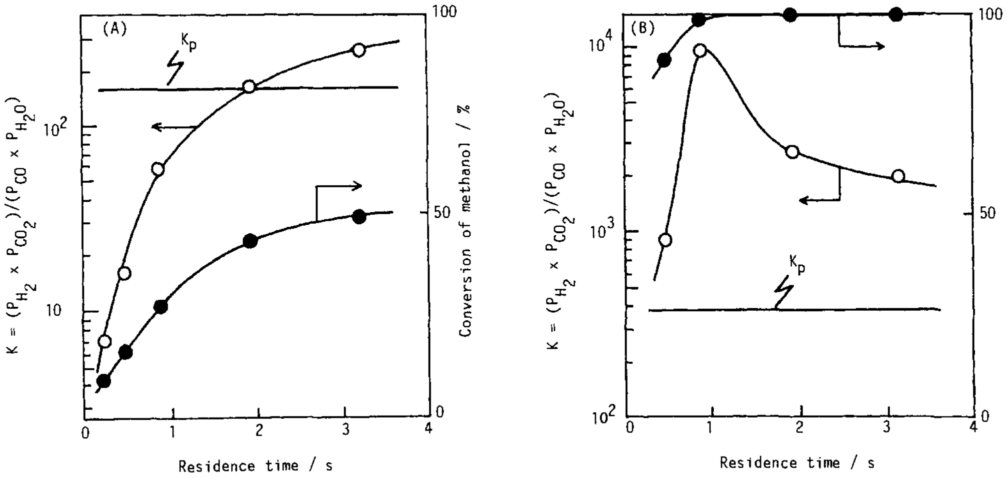


Fig. 3. Parameter $K = P_{H_2}P_{CO_2} / P_{CO}P_{H_2O}$ in the course of the steam reforming of methanol over Pd/ZnO. Experiments were carried out at (A) 493 K and (B) 573 K. Pd loading, 1 wt%; inlet partial pressure, $P_{CH_3OH} = P_{H_2O} = 24.3$ kPa. K_p represents equilibrium constant of the water–gas shift reaction.

longer than 1.6 s the partial pressure of carbon monoxide grows more rapidly. The K-values obtained always exceed the K_p-value over the whole range of t_r studied at 573 K. The K-value increases with the increase of t_r, reaches to a maximum and decreases. At the maximum, the K-value is estimated to be 9.7×10^3, being about 250 times the K_p-value. When carbon monoxide was fed with a mixture of methanol and water, the partial pressure of carbon dioxide and hydrogen in the effluent decreased appreciably. These findings strongly suggested that no water–gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, was involved in the steam reforming of methanol over Pd/ZnO. At higher temperatures and at longer t_r, the carbon dioxide formed was partly transformed into carbon monoxide through the reverse water–gas shift reaction, so that the K-value decreased at longer t_r.

Fig. 4 illustrates the effect of water upon the steam reforming over Pd/ZnO at 493 K. The title reaction occurs in high selectivity at higher partial pressure of water. At lower partial pressure of water, methyl formate is produced along with hydrogen, carbon dioxide and carbon monoxide. The selectivity for the steam reforming decreases considerably. In the absence of water no carbon dioxide is formed. Methyl formate is produced along with carbon monoxide and hydrogen. In the previous work [10], we showed that the reaction $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$ occurred in high selectivity over Pd/ZnO in the decomposition of methanol. No reaction occurred over ZnO alone. Over copper-based catalysts, the formation of methyl formate was highly selective in the decomposition of methanol. In the presence of water, the steam reforming proceeded in high selectivity [4,11]. These findings were therefore quite similar to those obtained over copper-based catalysts.

By contrast, over unsupported and other supported Pd catalysts no methyl formate was produced in the absence of water. The decomposition of methanol,

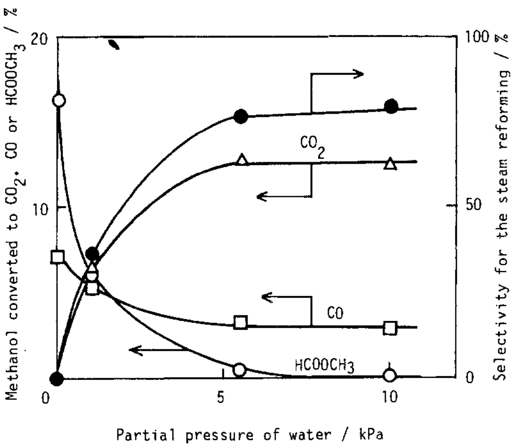
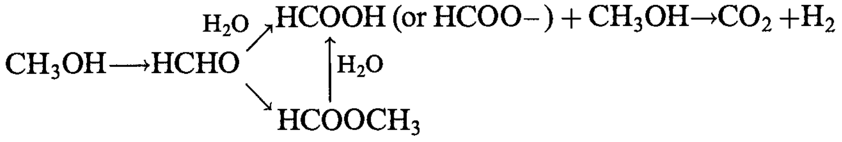


Fig. 4. Effect of the partial pressure of water upon the conversion of methanol to CO_2, CO or $HCOOCH_3$ and upon the selectivity for the steam reforming at 493 K. Inlet partial pressure of methanol was held at 10.1 kPa. Residence time = 0.47 s.

$CH_3OH \rightarrow CO + 2H_2$, occurred exclusively. As the partial pressure of water increased, that of carbon dioxide in the effluent increased to some degree. When carbon monoxide was fed with the mixture of methanol and water, the partial pressure of carbon dioxide in the effluent increased, as observed on Pt/SiO_2 [7].

These findings strongly suggest that the steam reforming over Pd/ZnO catalysts proceeds in a different way from that over unsupported and other supported Pd catalysts. It is highly probable that over Pd/ZnO the reaction occurs primarily through the steps



$$\begin{tikzcd}
 & & HCOOH\ (\text{or } HCOO-) + CH_3OH \rightarrow CO_2 + H_2 \\
CH_3OH \arrow[r] & HCHO \arrow[ur, "H_2O"] \arrow[dr] & \\
 & & HCOOCH_3 \arrow[uu, "H_2O"']
\end{tikzcd}$$

involving the reaction between formaldehyde and water or/and methyl formate and water, as observed over copper-based catalysts [7]. At lower temperatures or/and shorter t_r, carbon monoxide would be produced via the decomposition of formaldehyde or methyl formate [7,10]. At higher temperatures and longer t_r, the carbon dioxide formed was further transformed to carbon monoxide probably through the reverse water–gas shift reaction.

Further study of the effect of ZnO upon the steam reforming of methanol over Pd catalysts is currently under way.

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