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Steam reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and group VIII metals

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Abstract

HCHO species were effectively involved in the steam reforming and the dehydrogenation of methanol over supported copper and Group VIII metal (Ni, Rh, Pd, and Pt) catalysts. It was suggested that the difference in the catalytic performances of copper and Group VIII metals was ascribed to the difference in the reactivity of HCHO species formed in the course of the reactions. On the basis of the mechanisms proposed, novel functions of Pd/ZnO catalysts recently developed were discussed.

Keywords: Methanol steam reforming; Methanol dehydrogenation; Copper; PdZn alloys

1. Introduction

Catalytic functions of copper are markedly different from those of Group VIII metals in the conversions of alcohols, the hydrogenation of unsaturated aldehydes/ketones and of esters or carboxylic acids [1–10]. Methanol is dehydrogenated to $HCOOCH_3$ over copper catalysts through the reaction $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$, while over Group VIII metal catalysts it decomposes to CO and H_2 via the reaction $CH_3OH \rightarrow CO + 2H_2$ [1,2,5,10–13]. In the steam reforming of methanol, $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$, copper catalysts exhibit high selectivity [14–22]. Over Group VIII metal catalysts, CO is predominantly produced along with CO_2 and H_2 [23–25]. The selectivities for the steam reforming over Group VIII metal catalysts are much lower than those over copper catalysts. In the hydrogenation of unsaturated aldehydes or ketones [6,26], the $C = O$ bond is often reduced in preference to the $C = C$ bond on copper-based catalysts. Unsaturated alcohols are produced in high selectivity. On the other hand, over Group VIII metal catalysts the $C = C$ bond undergoes hydrogenation, and saturated aldehydes or ketones are frequently produced [7,8]. In the hydrogenation of esters or carboxylic acids, copper catalysts show high performances for the production of alcohols as compared with Group VIII metal catalysts [9,10].

Recently, we found that the steam reforming and the dehydrogenation of methanol to $HCOOCH_3$ selectively occurred over Pd/ZnO catalysts [27–31] as observed over copper-based catalysts. In these connections, it is to be noted that Pd/ZnO exhibits high catalytic performances in the hydrogenation of unsaturated aldehydes to unsaturated alcohols and esters of carboxylic acids to alcohols [32–34].

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The present work is focused on the elucidation of the difference in the catalytic functions of copper and Group VIII metals in the steam reforming and the dehydrogenation of methanol on the basis of the mechanisms of these reactions. On the same basis, the novel catalytic functions of Pd/ZnO catalysts are discussed.

2. Experimental

Copper and Group VIII metals (Ni, Rh, Pd and Pt) were supported on various metal oxides (MgO, La_2O_3, Nd_2O_3, MnO_2, Cr_2O_3, HfO_2, Nb_2O_5, Al_2O_3, SiO_2, and ZnO) by impregnation of solutions of corresponding metal salts. The resulting samples were then dried at 383 K overnight and calcined at 773 K for 3 h.

The reactions were carried out in a conventional flow reactor at 101.3 kPa. In the steam reforming of methanol, both the inlet partial pressures of methanol and water were 24.3 or 10.1 kPa. In the dehydrogenation of methanol, the inlet partial pressure of methanol was kept at 24.3 or 10.1 kPa. The residence time was maintained at 0.47 s unless otherwise stated. Nitrogen was used as a diluent. Gases in the effluent were analyzed by gas chromatography. The selectivity, S(SRM), for the steam reforming or, S(MF), for the dehydrogenation to $HCOOCH_3$ was evaluated on the carbon basis, i.e., $S(\mathrm{SRM}) = P(\mathrm{CO_2})/\{P(\mathrm{CO_2}) + P(\mathrm{CO})\}$ or $S(\mathrm{MF}) = 2P(\mathrm{MF})/\{2P(\mathrm{MF}) + P(\mathrm{CO})\}$, where $P(\mathrm{CO_2})$, P(CO) and P(MF) represent the partial pressures of CO_2, CO and $HCOOCH_3$ in the effluent, respectively. In a similar fashion, steam reforming or dehydrogenation of ethanol was conducted in a flow of a mixture of ethanol and water at respective inlet partial pressures of 10.1 and 20.2 kPa or in a flow of ethanol at an inlet partial pressure of 20.5 kPa. Experiments were also carried out in a stream containing HCHO or a mixture of $HCHO/H_2O$, $HCHO/CH_3OH$, $HCHO/CD_3OH$ or CH_3CHO/H_2O. For comparison, some experiments were carried out over unsupported Cu and Pd catalysts.

The isotope distributions in the reactants and the products in the reactions in the mixture of $HCHO/CD_3OH$ were determined by means of GC-MS(JEOL-D-300, Nihon Denshi Co.). X-ray diffraction (referred to as XRD) spectra of the catalysts were obtained with a Rigaku Denki ADP-301E X-ray diffractometer. X-ray photoelectron (referred to as XP) spectra were recorded on an ESCALAB-Mk2 (V.G. Scientific Co.). Temperature programmed reduction (referred to as TPR) of the catalyst was carried out at a heating rate of 5/K · min to 1073 K in a stream of hydrogen (4 vol.%) diluted with Ar at a total flow rate of 50 cm^3/min. The number of the surface sites of metallic copper was determined by titration with N_2O at 333 K [35]. The numbers of the surface sites of Group VIII metals other than Pd were determined by adsorption of H_2 at room temperature [36]. For Pd catalysts, the H_2 adsorption was conducted at 373 K for avoidance of the Pd hydride forma-

Table 1
Steam reforming of methanol over copper and Group VIII metals supported on SiO_2 [a]

Catalyst [b]	Rate of H_2 production (μmol (min g-cat)$^{-1}$)	Selectivity (%)	TOF [c] (s^{-1})	Dispersion (%)
Ni/SiO_2	122	1.1	0.011	10.6
Pt/SiO_2	25	25.6	0.039	2.1
Pd/SiO_2	22	0.0	0.028	1.4
Cu/SiO_2	345	99	0.037	9.9

[a] Reaction temperature 493 K: $P(\mathrm{CH_3OH}) = P(\mathrm{H_2O}) = 24.3$ kPa.
[b] Metal loading, 10 wt.%.
[c] Turnover frequency for H_2 production.

tion [37]. The metal dispersions were evaluated on the basis of the numbers of the surface sites and the total numbers of metal atoms (Cu, Ni, Rh, Pd and Pt) loaded on the supports.

3. Results and discussion

3.1. Catalytic performances of copper and Group VIII metals supported on SiO_2 in the steam reforming and the dehydrogenation of methanol

When a mixture of methanol and water was fed over the catalysts, H_2 and CO_2 were produced along with CO. Table 1 summarizes the catalytic performances of copper and several Group VIII metals supported on SiO_2 in the steam reforming along with the dispersions of metals used. Cu/SiO_2 shows high activity and selectivity in the steam reforming among the catalysts used. The selectivities for Group VIII metal catalysts are much lower than that for Cu/SiO_2. CO and H_2 are predominantly produced, appearing that the methanol decomposition, $CH_3OH \rightarrow CO + 2H_2$, takes place in preference to the steam reforming over Group VIII metal catalysts.

Table 2 lists the results of the dehydrogenation of methanol over copper and several Group VIII metals supported on SiO_2 with the metal dispersions. Cu/SiO_2 exhibits anomalously high selectivity for the $HCOOCH_3$ formation. Over Group VIII metal catalysts methanol was exclusively decomposed to CO and H_2. No $HCOOCH_3$ was detected in the effluent. These results agreed with the previous report by Yasumori and Miyazaki on the methanol dehydrogenation over unsupported Cu and Ni catalysts [1].

3.2. Reaction pathways of the steam reforming and the dehydrogenation of methanol over copper and Group VIII metal catalysts.

It has been frequently proposed that the steam reforming of methanol occurs through the water gas shift reaction coupled with the methanol decomposition over copper-based catalysts [22,38], i.e.,

$$CH_3OH \rightarrow CO + 2H_2 \xrightarrow{H_2O} CO_2 + H_2. \quad (1)$$

However, the water gas shift reaction was found to be blocked in the presence of methanol on Cu/SiO_2 [39]. No changes in the rates of the CO_2 and H_2 formation were observed upon the addition of CO to the inflow of a mixture of methanol and water. Furthermore, it was found that the values of a parameter, $K'_p = \{P(CO_2) \times P(H_2)\}/\{P(CO) \times P(H_2O)\}$, for the effluent in the course of the steam reforming greatly exceeded those of the equilibrium constant K_p for the water gas shift reaction. For example, the K'_p-value reached to 7.0×10^2 for the experiment at 523 K as compared with the K_p-

Table 2
Dehydrogenation of methanol over copper and Group VIII metals supported on SiO_2 [a]

Catalyst [b]	Rate of H_2 production (μmol (min g-cat)$^{-1}$)	Selectivity CO	Selectivity $HCOOCH_3$	TOF [c] (s^{-1})	Dispersion (%)
Ni/SiO_2	1.8	100	0	0.0024	8.1
Rh/SiO_2	20.9	100	0	0.0059	67
Pt/SiO_2	21.2	100	0	0.022	31
Pd/SiO_2	17.6	100	0	0.076	4.1
Cu/SiO_2	83.4	6	94	0.13	10.2

[a] Reaction temperature 473 K: $P(CH_3OH) = 10.1$ kPa.
[b] Metal loading, 1.0 wt.%.
[c] Turnover frequency of the H_2 production.

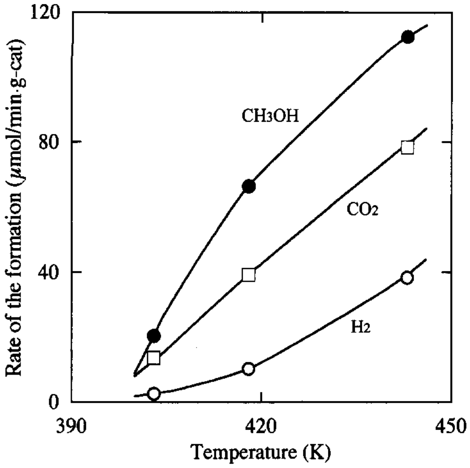


Fig. 1. Rates of the formation of the products formed in the reaction of HCHO in the presence of H_2O over 10 wt.% Cu/SiO_2. $P(HCHO) = 1.22$ kPa, $P(H_2O) = 12.2$ kPa.

value of 1.24×10^2. Thus, pathway (1) involving the water gas shift reaction was infeasible for the steam reforming over copper-based catalysts. In contrast, when HCHO was added to the inflow at 493 K, it completely converted to CO_2 and H_2. This suggests that HCHO is involved in the steam reforming.

Fig. 1 illustrates the rate of the products formed in the reaction of HCHO with H_2O over 10 wt.% Cu/SiO_2. CO_2 and H_2 were produced along with CH_3OH, suggesting that the reactions $HCHO + H_2O \rightarrow 2H_2 + CO_2$ and $HCHO + H_2 \rightarrow CH_3OH$, take place in the mixture of HCHO and H_2O [23]. These reactions occurred rapidly as compared with the steam reforming of methanol. For example, the rate of the CO_2 formation in the mixture of HCHO and H_2O at $P(HCHO) = 1.22$ kPa and $P(H_2O) = 12.2$ kPa at 403 K was estimated to be more than 20 times that in the steam reforming of methanol at $P(CH_3OH) = P(H_2O) = 10.1$ kPa. The reactions in the mixture of HCHO and H_2O also occurred over the unsupported Cu catalyst. For the reaction at 403 K, the turnover frequency (1.7×10^{-3} s^{-1}) of the CO_2 formation over unsupported Cu catalyst was found to be practically the same as that (1.3×10^{-3} s^{-1}) over the 10 wt % Cu/SiO_2 catalyst at 403 K. No reaction occurred over SiO_2 support alone. Hence, the reactions for the mixture of HCHO and H_2O primarily proceeds on the surface of copper. SiO_2 support plays a minor role in the reactions over the Cu/SiO_2 catalyst.

Experiments were also conducted with a mixture of ethanol and water over 10 wt.% Cu/SiO_2 catalyst in place of a mixture of methanol and water. CH_3COOH was produced with the selectivity of 43% (carbon basis) along with CH_3CHO, H_2, and C_4-species at an ethanol conversion of 80% at 523 K [40]. When mix-

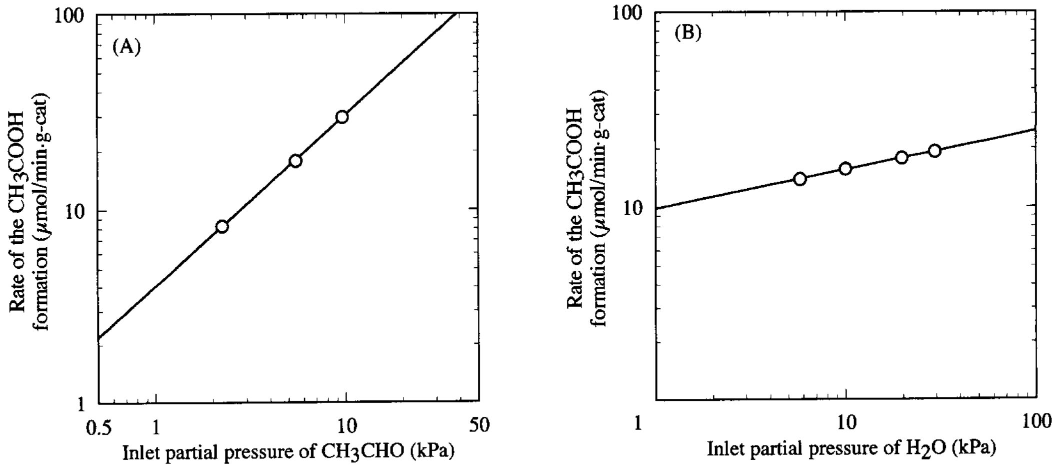


Fig. 2. Effect of the partial pressures of (A) H_2O and (B) CH_3CHO upon the reaction in the mixtures of CH_3CHO and H_2O over 30 wt.% Cu/SiO_2 at 523. (A) $P(CH_3CHO) = 5.57$ kPa. (B) $P(H_2O) = 20.2$ kPa.

tures of CH_3CHO and H_2O were fed over the catalyst, CH_3COOH and H_2 were produced along with butyraldehyde and ethanol. For example, at $P(CH_3CHO) = 2.2$ kPa and $P(H_2O) = 20.2$ kPa CH_3COOH, H_2, butyraldehyde, and ethanol were produced at rates of 8.3, 6.7, 0.76, and 0.48 μmol/min · g-cat at 523 K, respectively. The formation of CH_3COOH was fairly selective. Fig. 2A and Fig. 2B, respectively, illustrate the rate, r(AcOH) of the CH_3COOH formation against the partial pressures of CH_3CHO and H_2O. They show that the rate can be expressed as $r(\mathrm{AcOH}) = k_A P(CH_3CHO)^{0.9} \times P(H_2O)^{0.2}$, where $P(CH_3CHO)$ and $P(H_2O)$ represent the partial pressures of CH_3CHO and H_2O, respectively. These results suggest that CH_3COOH and C_2H_5OH are produced via the reactions $CH_3CHO + H_2O \rightarrow CH_3COOH + H_2$ and $CH_3CHO + H_2 \rightarrow C_2H_5OH$. Because of selective formation of CH_3COOH, occurrence of a Cannizzaro-type reaction, $2CH_3CHO + H_2O$ $CH_3COOH + C_2H_5OH$, seems to be impracticable.

On the basis of these results, we can conclude that the steam reforming of methanol proceeds over copper-based catalysts through a pathway

$$CH_3OH \xrightarrow{-H_2} HCHO \xrightarrow{H_2O(\text{or } HO-)} HCOOH(\text{or } HCOO-) \rightarrow CO_2 + H_2, \qquad (2)$$

involving the reaction, $HCHO + H_2O$ (or HO −) HCOOH (or HCOO −) + H_2, which probably initiated by nucleophilic addition of H_2O (or HO −) to HCHO species.

As opposed to these findings, when CO was added to the inflow in the course of the steam reforming over 1 wt.% Pt/SiO_2 [23] and 1 wt.% Pd/SiO_2, CO_2 in the effluent increased. When a mixture of HCHO and H_2O was fed over the catalysts at varied residence time, CO and H_2 were produced in 1 to 1 molar ratio at shorter residence time. With increase in the residence time, the yield of CO decreased and that of CO_2 increased. This suggests involvement of the water gas shift reaction. Mizuno et al. [24] also studied the steam reforming of methanol over nickel-based catalysts at different residence time. They confirmed that CO was responsible for the steam reforming. Hence, we conclude that the steam reforming occurs through pathway (1) over Group VIII metal catalysts.

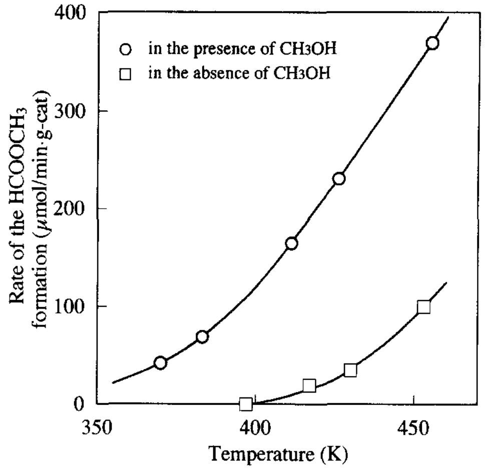


Fig. 3. Reaction of HCHO in the absence and in the presence of methanol over 10 wt.% Cu/SiO_2. □, in the absence of methanol; ○, in the presence of methanol. $P(HCHO) = 1.11$ kPa, $P(CH_3OH) = 12.2$ kPa.

When HCHO or a mixture of HCHO and CH_3OH was fed over 10 wt.% Cu/SiO_2 catalyst, $HCOOCH_3$ was produced in high selectivity. The rate of the $HCOOCH_3$ production was greatly enhanced in the presence of CH_3OH (Fig. 3). At 393 K, the rate in the presence of CH_3OH was estimated to be 20 times that in the absence of CH_3OH. The $HCOOCH_3$ formation in the mixture of HCHO and CH_3OH was much more rapid than the dehydrogenation of methanol to $HCOOCH_3$. The HCOOCH3 formation at $P(HCHO) = 1.11$ kPa and $P(CH_3OH) = 12.2$ kPa proceeded at a rate more than 20 times the HCOOCH3 formation in the dehydrogenation of methanol at $P(CH_3OH) = 10.1$ kPa. Similar results were obtained over the unsupported Cu catalyst. For the reaction with

HCHO and CH_3OH at $P(HCHO) = 1.11$ kPa and $P(CH_3OH) = 12.2$ kPa, the turnover frequency (8.0×10^{-3} s^{-1}) of the $HCOOCH_3$ formation over the unsupported Cu was 1.8 times that (4.4×10^{-3} s^{-1}) over 10 wt.% Cu/SiO_2 at 373 K. Hence, SiO_2 produced no enhancing effect upon the $HCOOCH_3$ formation over the Cu/SiO_2 catalyst.

Experiments were also conducted at various inlet partial pressures HCHO and CH_3OH over 10 wt.% Cu/SiO_2. Fig. 4 plots the conversion of HCHO to $HCOOCH_3$ against the inlet partial pressure of HCHO at a given inlet partial pressure of CH_3OH. It shows that the conversion levels of HCHO are practically constant irrespective of the inlet partial pressure of HCHO, suggesting that the reaction is of the first order in the partial pressure of HCHO. Since the inlet partial pressure of CH_3OH was greatly in excess of that of HCHO under the present experimental conditions, the following equation can be derived for the reaction with the mixtures of HCHO and CH_3OH; $k\tau = -\ln(1-x)$, where k can be expressed as $k = k_{MF}P(CH_3OH)^n$, (k_{MF} = rate constant; n = reaction order). Parameters τ and x designate residence time, and the conversion of HCHO, respectively. Fig. 5 presents the k-values obtained at various inlet partial pressures of CH_3OH, showing that the reaction order is approximated to be 0.4 with respect to the partial pressure of CH_3OH. Hence, the rate, $r(MF)$, of the formation of $HCOOCH_3$ can be expressed as $r(MF) = k_{MF}P(HCHO) \times P(CH_3OH)^{0.4}$, suggesting that CH_3OH (CH_3O^-) is involved in the $HCOOCH_3$ formation from HCHO in the presence of CH_3OH.

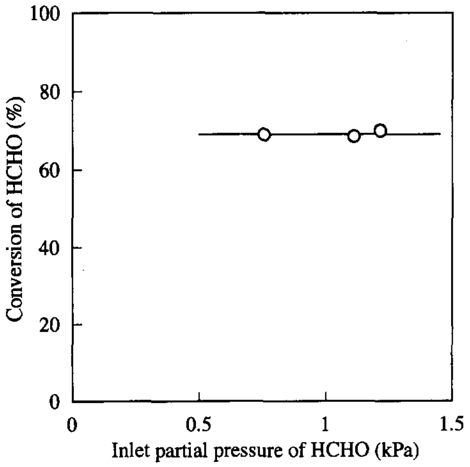


Fig. 4. Conversion of HCHO in a mixture of HCHO and CH_3OH at different partial pressures of HCHO over 10 wt.% Cu/SiO_2. Reaction temperature, 410 K. $P(CH_3OH) = 12.2$ kPa.

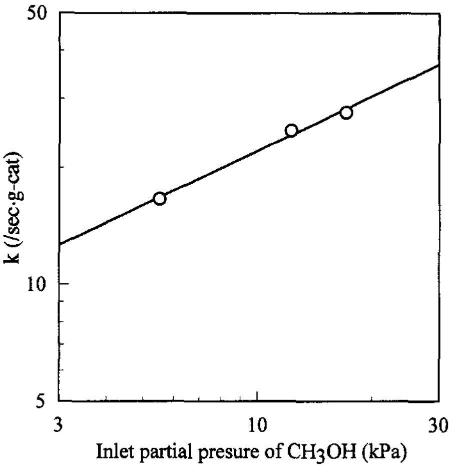


Fig. 5. k-Value for the $HCOOCH_3$ formation from HCHO in the presence of CH_3OH versus inlet partial pressure of CH_3OH. Reaction temperature, 410 K.

When experiments were carried out with a mixture of HCHO and CD_3OH, $HCOOCD_3$ was solely produced, while transesterification $HCOOCH_3 + CD_3OH \rightarrow HCOOCD_3 + CH_3OH$ was practically negligible [41]. Hence, we conclude that the $HCOOCH_3$ formation over copper-based catalysts occurs through a pathway

$$CH_3OH \rightarrow HCHO \xrightarrow{CH_3OH(\text{or } CH_3O-)} HCOOCH_3, \tag{3}$$

in which the reaction of CH_3OH (or CH_3O^-) with HCHO is initiated by nucleophilic addition of CH_3OH (or CH_3O^-) to HCHO species as Tischenko reaction occurs [42,43]. Similar reaction pathways were also recently proposed for the dehydrogenation of methanol over Cu/ZnO [44–47] and CrO_3/SiO_2 [48], and for the oxidation of methanol over Ag [49,50] and Au [51].

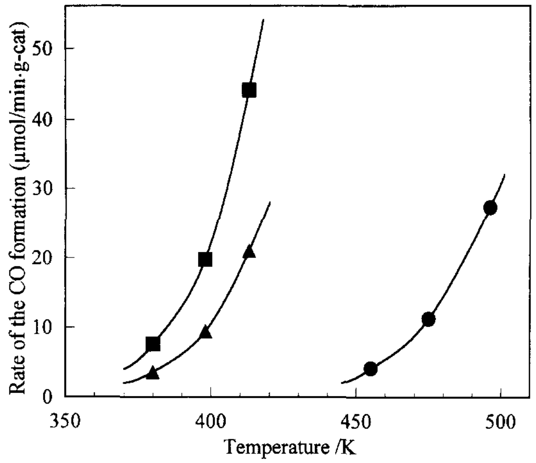
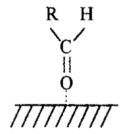


Fig. 6. Reaction of HCHO in the absence and in the presence of methanol, and the decomposition of methanol over 1 wt.% Pt/SiO_2. ■, reaction of HCHO in the absence of methanol; ▲, reaction of HCHO in the presence of methanol. $P(HCHO) = 1.11$ kPa, $P(CH_3OH) = 12.2$ kPa. ●, the decomposition of methanol.

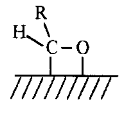
In great contrast to these observations, HCHO was readily decomposed to CO and H_2 either in the absence or the presence of CH_3OH over 1 wt.% Pt/SiO_2 and 1 wt.% Pd/SiO_2. No other products were detected in the effluent. As Fig. 6 illustrates, the rate of the HCHO decomposition in the absence and the presence of CH_3OH is estimated to be more than 50 times as fast as that of the CH_3OH decomposition over the Pt/SiO_2 catalyst. Similar results were obtained over the Pd/SiO_2 catalyst. When ethanol alone ($P(C_2H_5OH) = 20.5$ kPa) was fed over unsupported Pd catalyst, CH_4 and CO were produced together with H_2 and CH_3CHO. For example, at 523 K and at residence time of 0.75s the partial pressures of CH_4, CO, H_2, and CH_3CHO in the effluent were 3.7, 3.6, 4.1 and 0.66 kPa, respectively. This suggests that CH_3CHO species formed undergo rapid C–C and C–H bond disruption through the reactions, $C_2H_5OH \rightarrow CH_3CHO + H_2$ and $CH_3CHO \rightarrow CH_4 + CO$, in conformity with the results obtained by Madix et al. [52], Barteau et al. [53,54] and Gates et al. [55] on single crystals of Pt, Pd, and Ni, respectively.

Based on these findings, we conclude that HCHO formed in the reactions maintains its structure on the surface of copper, and is rapidly attacked by nucleophiles (H_2O or HO^-, or CH_3OH or CH_3O^-), being finally transformed to CO_2 and H_2 or $HCOOCH_3$. On the other hand, HCHO species formed on Group VIII metals is readily decomposed to CO and H_2. Hence, no reaction occurred between HCHO and nucleophiles.

Recent studies in surface science revealed that the structures of aldehydes adsorbed on IB metals (Cu and Ag) were greatly different from those on Group VIII metals (Rh, Ru, Pt, Pd) [52,56–64]. They adsorbed preferentially in η^1(O)-structure



on IB metals, while on Group VIII metals (Rh, Ru, Pt, Pd) they existed as η^2(C,O)-aldehydes



The η^1(O)–HCHO species preserve the molecular identity of HCHO and simply desorb without decomposition in the temperature desorption experiments. In contrast, the C–C and C–H bonds are rapidly ruptured for η^2(CO)–aldehyde species [52–55]. Hence, it is highly probable that the difference in the original catalytic functions of copper and Group VIII metals for the steam reforming and the dehydrogenation of methanol is ascribed to the difference in the structures of HCHO intermediates formed on these metals. This suggests that η^1(O)–HCHO species formed in the course of the reactions are attacked by nucleophiles such as CH_3OH (CH_3O^-) and H_2O (HO^-) and, thus, the reactions take place through pathways (2) and (3) on copper catalysts. As opposed to this, η^2(C,O)–HCHO species formed on Group

Table 3
Steam reforming of methanol over various Pd catalysts [a]

Catalyst [b]	Rate of H_2 production μmol (min g-cat)$^{-1}$	TOF [c] (s^{-1})	Selectivity (%)	Dispersion (%)
Pd	120	0.010	0.1	2.1
Pd/SiO_2	7.6	0.019	0	7.2
Pd/Al_2O_3	112	0.15	1.4	13
Pd/Nb_2O_5	93.7	0.084	4.2	20
Pd/Nd_2O_3	223	0.16	7.0	25
Pd/La_2O_3	183	0.66	8.0	5.0
Pd/ZrO_2	241	0.15	20	29
Pd/ZnO	500	0.83	97	11

[a] Reaction temperature 493 K: $P(CH_3OH) = P(H_2O) = 24.3$ kPa.
[b] Metalloading, 1.0 wt.%.
[c] Turnover frequency for the H_2 production.

VIII metals rapidly decompose because of the strong back donation of electrons from the metals into π_{co}^* antibonding orbital of the aldehyde [60,62,63,65–70]. Thus, CO and H_2 were primarily produced in the course of the steam reforming and the dehydrogenation of methanol on Group VIII metal catalysts.

3.3. Highly selective Pd/ZnO catalysts for the steam reforming and the dehydrogenation of methanol

Table 3 shows the catalytic performance of various supported and unsupported Pd for the steam reforming of methanol. Pd/ZnO produced anomalously high selectivity for the steam reforming among Pd catalysts. Over the other Pd catalysts, CO and H_2 were produced in high selectivity. No reaction occurred over ZnO alone. Hence, the catalytic function of Pd is greatly modified in the presence of ZnO.

Fig. 7A and Fig. 7B compare the conversion of methanol and the selectivity for the steam reforming against the temperature of the previous reduction of 10 wt.% Pd/ZnO, 10 wt.% Pd/SiO_2 and 10 wt.% Pd/ZrO_2. Catalytic performance of 10 wt.% Pd/ZnO is greatly improved upon the previous reduction at high temperatures. The selectivity reached to 98% upon the previous reduction at 773 K. On the

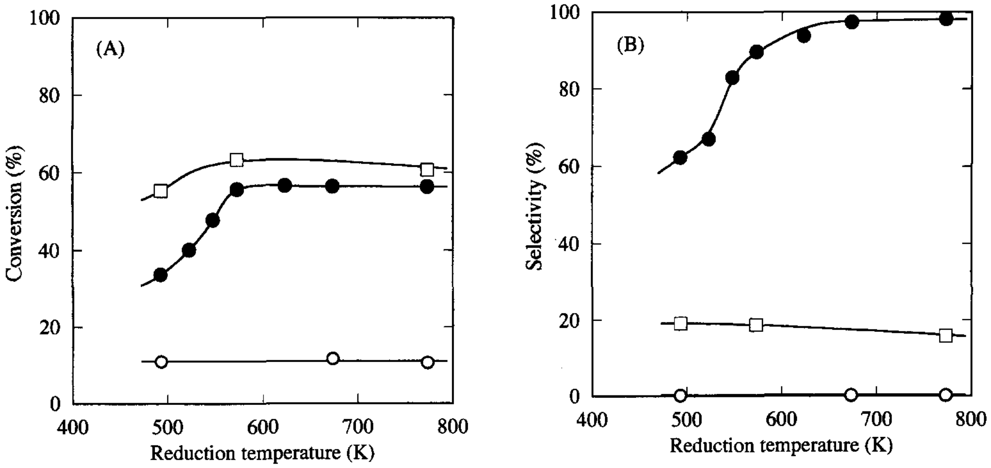


Fig. 7. (A) Methanol conversion and (B) selectivity for the steam reforming over 10 wt.% Pd/ZnO, 10 wt.% $PdSiO_2$ and 10 wt.% Pd/ZrO_2 reduced at various temperatures. ●, 10 wt.% Pd/ZnO; ○, 10 wt.% $PdSiO_2$; □, 10 wt.% Pd/ZrO_2. The reaction was carried out at 493 K. $P(CH_3OH) = P(H_2O) = 10.1$ kPa. Residence time was 0.47 s.

other hand, the selectivities for the other Pd catalysts are kept at lower levels irrespective of the reduction temperature.

Experiments were also carried out over Pd/ZnO having various amounts of Pd loaded. It was found that 30 wt.% Pd/ZnO exhibited best performance for the steam reforming so far studied at inlet partial pressures of both CH_3OH and H_2O of 24.3 kPa. The reaction occurred at the rate of the H_2 production of 990 μmol/g-cat · min with the selectivity of 99%. In contrast, over 30 wt.% Cu/SiO_2 previously studied [16], the rate of the H_2 production and the selectivity were respectively estimated to be 684 μmol/g-cat · min and 97%. The catalytic performance of the Pd/ZnO exceeded that of the Cu/SiO_2.

Fig. 8 shows XRD spectra for 10 wt.% Pd/ZnO reduced at various reduction temperatures. It is seen that PdZn alloy phases are developed under the reduction of the catalyst at high temperatures. On the other hand, only metallic Pd phase emerged in XRD spectra upon the reduction of other Pd catalysts. No alloy phase or reduction of supports was detected. These results were also supported by TPR of the catalysts [10]. The formation of PdZn was confirmed by means of XPS (Fig. 9). In XP spectra of 10 wt.% Pd/ZnO reduced at higher temperatures, peaks for $Pd_{5/2}$ and $Pd_{3/2}$ levels appeared at 335.9 and 341.2 eV, respectively, attributed to PdZn alloy. Zn LMM Auger spectra for the Pd/ZnO catalyst exhibited a shoulder peak at 992 eV attributed to metallic Zn on a peak at 987.7 eV due to ZnO upon the reduction of the catalyst (Fig. 10). The positions of the XPS peaks for Pd of the alloy are located at higher binding energy by 0.6 eV than those of metallic Pd, while located at lower binding energy by 1.1 eV than those of Pd(II). Although the AES peaks for Zn are somewhat ill-defined, these results suggest that electron transfer take place from Pd to Zn in the formation of PdZn alloy as Rodorigues found in the formation of Pd_xZn_y alloys on Ru (001) [71].

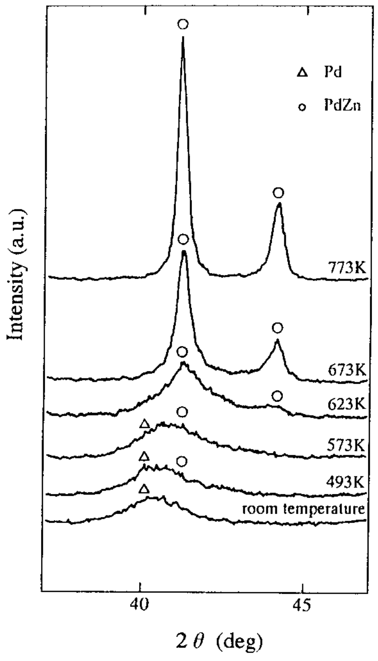


Fig. 8. XRD spectra of 10 wt.% Pd/ZnO reduced at various temperatures.

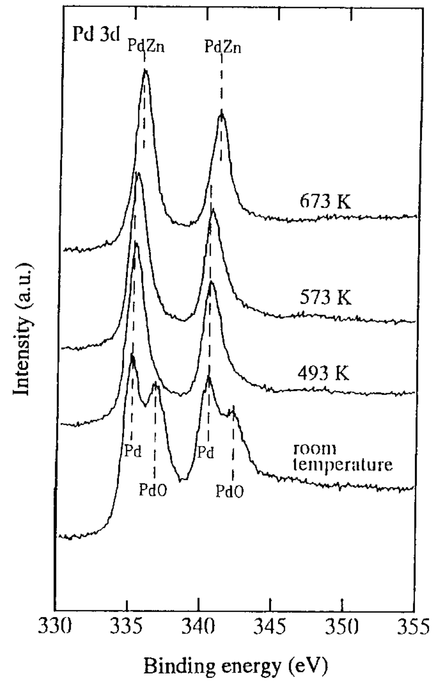


Fig. 9. XPS spectra of 10 wt.% Pd/ZnO reduced at various temperatures. The temperatures at which the catalysts were reduced are indicated in the figure.

The parameter of K_p' for the water gas shift was compared with the equilibrium constant of the water gas shift over 1 wt.% Pd/ZnO reduced at 773 K. It was found that the K'_p-values greatly exceed the equilibrium constant of the water gas shift at longer residence time. For example, the K'_p-value reached to 1.0×10^4 for the experiment at 573 K at residence time of 0.94s as compared with the K_p-value of 40.8. Thus, pathway (1) involving the water gas shift reaction was excluded for the steam reforming over Pd/ZnO catalysts.

HCHO species were found to react readily with H_2O at temperature as low as 373 K over Pd/ZnO reduced at higher temperatures, giving CO_2 and H_2 in high selectivity. No reaction occurred over ZnO free from Pd under the reaction conditions studied. Over unsupported Pd, CO and H_2 were stoichiometrically produced. These findings strongly suggest that the steam reforming occur through pathway (2) over Pd/ZnO reduced at high temperatures. Consistent with the proposed mechanism of the reaction, CH_3COOH was produced over 10 wt.% Pd/ZnO when experiments were conducted with a mixture of ethanol and water. The selectivity for the CH_3COOH formation achieved 50% at 493 K at a conversion level of 50%.

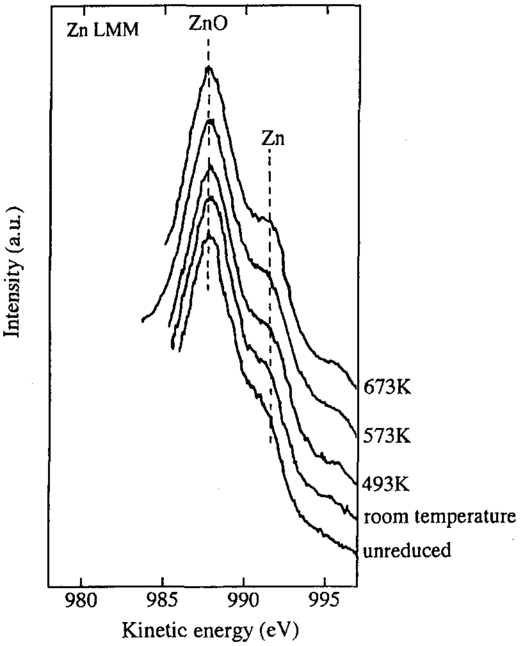


Fig. 10. Zn LMM Auger spectra for 10 wt.% Pd/ZnO reduced at different temperatures. The temperatures at which the catalysts were reduced are indicated in the figure.

Table 4
Dehydrogenation of methanol over various supported Pd catalysts [a]

Catalyst [b]	Rate of H_2 production (μmol (min g-cat)$^{-1}$)	Selectivity (%)	
		CO	$HCOOCH_3$
Pd	192	100	0
Pd/SiO_2	17.6	100	0
Pd/MnO_2	74.5	100	0
Pd/MgO	101	100	0
Pd/Cr_2O_3	83.8	100	0
Pd/TiO_2	106	100	0
Pd/ZrO_2	188	100	0
Pd/HfO_2	59.3	100	0
Pd/La_2O_3	50	100	0
Pd/Nd_2O_3	142	100	0
Pd/ZnO	110	20	80

[a] Reaction temperature 473 K: $P(CH_3OH) = 10.1$ kPa.
[b] Metal loading, 1.0 wt.%.

The dehydrogenation of methanol was also carried out over various supported Pd catalysts. Only Pd/ZnO exhibits high catalytic performance for the formation of $HCOOCH_3$ (Table 4). Over other Pd catalysts, CO and H_2 are stoichiometrically produced.

These findings strongly suggest that the original catalytic function of Pd is greatly suppressed upon the formation of PdZn alloys, and novel catalytic function typical of copper emerges. For the reactions over Pd/ZnO, the extent of back donation of electrons to C = O bond of HCHO intermediate species probably decreases because of the formation of PdZn alloy as Rodoriguez showed in the adsorption of CO on Pd_xZn_x alloys formed on Ru(001) surface [71]. Since the electron transfer occurs from Pd to Zn in the formation of the alloys, it is highly probable that η^1(O)–HCHO species are stabilized on positively charged Pd sites of the PdZn alloy in preference to η^2(C,O)–HCHO species. Hence, we conclude that high catalytic performance of PdZn alloys in the steam reforming of methanol and the dehydrogenation of methanol to $HCOOCH_3$ is ascribed to the preferential formation of HCHO intermediates in η^1(O)-form.

4. Conclusion

The steam reforming and the dehydrogenation of methanol were carried out over supported copper and Group VIII metal (Ni, Rh, Pd, and Pt) catalysts. Copper-based catalysts and Pd/ZnO exhibited high performance in the steam reforming and the dehydrogenation to $HCOOCH_3$. Over the other VIII Group metal catalysts, the selectivity for the steam reforming was much lower than those over copper and Pd/ZnO. CO and H_2 were predominantly produced. In the dehydrogenation of methanol, methanol was exclusively decomposed to CO and H_2. No $HCOOCH_3$ was produced. It was suggested that the difference in the catalytic performances of these catalysts were ascribed to the difference in the reactivity of HCHO intermediate species formed in the course of the reactions. In these connections, involvement of η^1(O) – and η^2(C,O) – HCHO species in the reactions were discussed on the basis of the recent surface studies of the adsorption of aldehyde species. It was shown that the catalytic functions of Pd were greatly modified upon the formation PdZn alloys over Pd/ZnO. Modification of the structure of adsorbed HCHO species were suggested upon the formation of the alloys.

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