Dehydrogenation of Methanol to Methyl Formate over Palladium/Zinc Oxide Catalysts

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Methyl formate is selectively produced in the dehydrogenation of methanol over Pd/ZnO; the reaction is suggested to proceed through the same steps as over copper-based catalysts.

Methanol is selectively dehyrogenated to methyl formate over copper-based catalysts.[1–7] However, over other transition metal catalysts, carbon monoxide and hydrogen are produced exclusively.[8,9] Miyazaki *et al.*[10] and J. S. Lee *et al.*[11] recently showed that methyl formate was selectively produced over tungsten carbide catalyst. However, to our knowledge no work has been published for the selective formation of methyl formate over supported transition metal catalysts. In the present communication, we show that Pd/ZnO is highly effective for the formation of methyl formate in the dehydrogenation of methanol.

Supported and unsupported Pd catalysts were used for the title reaction. For comparison, Cu/SiO_2 and ZnO were also used for the reaction. The supported Pd catalysts were mostly prepared by impregnation of a solution of palladium nitrate on various metal oxides (ZnO, SiO_2, Al_2O_3, MnO_2, MgO, Cr_2O_3, TiO_2, ZrO_2, HfO_2, La_2O_3 and Nd_2O_3) in a rotary evaporator at 343 K. Some Pd/ZnO catalysts were prepared by the precipitation method. A solution of sodium carbonate was added to a mixed solution of palladium nitrate and zinc nitrate dropwise at 353 K until the pH of the solution was raised to 8.0. Thereafter, the precipitate formed stood in the solution for 1 h. Support-free Pd was derived from Pd black commercially available. Cu/SiO_2 was prepared by impregnation of a solution of copper nitrate on SiO_2. Commercially available ZnO was used. The prepared catalysts were then dried at 383 K overnight and calcined in air at 773 K for 3 h. The reaction was carried out in a conventional flow reactor at atmospheric pressure. A nitrogen stream was bubbled through a solution of methanol kept at a given temperature. A gaseous mixture of nitrogen and methanol thus prepared was fed over the catalyst. The inlet partial pressure of methanol was always kept at 10.1 kPa. Gaseous components in the effluent were analysed by gas chromatography.

Table 1 lists the rate of the hydrogen formation and the selectivities to carbon-containing products (on the carbon basis) obtained at 473 K over various supported Pd (prepared by the impregnation method, Pd loading = 1 wt%) and unsupported Pd catalysts at a steady state of the reaction. The results for Cu/SiO_2 are also listed for comparison. The rate of the hydrogen formation, r_{H_2}, and the selectivities are greatly affected by the kinds of supports used. It is to be noted that

Table 1 Kinetic parameters obtained over various supported and unsupported Pd catalysts

Catalyst[a]	r_{H_2}[b]	Conversion (%)	Selectivity[c] (%) CO	HCO$_2$Me	(Me)$_2$O
Pd black	4.32	21.6	100	0	0
Pd/ZnO	246	20.5	20	80	0
Pd/SiO$_2$	39.5	2.0	100	0	0
Pd/Al$_2$O$_3$	266	70.9	10	0	90
Pd/MnO$_2$	167	8.4	100	0	0
Pd/MgO	227	11.4	100	0	0
Pd/Cr$_2$O$_3$	188	9.4	100	0	0
Pd/TiO$_2$	237	11.9	100	0	0
Pd/ZrO$_2$	422	21.1	100	0	0
Pd/HfO$_2$	133	6.7	100	0	0
Pd/La$_2$O$_3$	112	5.6	100	0	0
Pd/Nd$_2$O$_3$	318	15.9	100	0	0
Cu/SiO$_2$	233	17.6	6	94	0

[a] Supported Pd catalysts: Pd loading = 1.0 wt%. Cu/SiO$_2$: Cu loading = 0.8 wt%. These catalysts were prepared by the impregnation method. *Reaction conditions*: T = 473 K, Inlet partial pressure of methanol = 10.1 kPa, residence time = 0.471 s. [b] r_{H_2} = Rate of the hydrogen formation in cm^3 min^{-1} g^{-1}-metal. [c] Selectivity to carbon-containing products.

Pd/ZnO is highly selective for the formation of methyl formate. The activity for the hydrogen formation is comparable to that over Cu/SiO$_2$. Over other Pd catalysts no methyl formate is produced. Carbon monoxide and diethyl ether are produced over Pd/Al$_2$O$_3$. Other supported Pd and support-free Pd catalysts give carbon monoxide selectively. Over ZnO alone no reaction occurred at the present experimental conditions. Thus, the anomalous catalytic function of Pd/ZnO observed in the present experiments probably resulted from the synergic effect of ZnO upon the reaction.

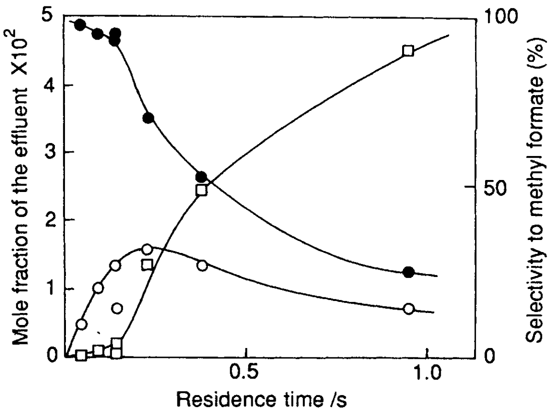

Fig. 1 Mole fraction of the carbon-containing products in the effluent and selectivity to methyl formate against residence time over 30 wt% Pd/ZnO prepared by the precipitation method. T = 493 K; inlet partial pressure of MeOH = 10.1 kPa. (○) HCO$_2$Me, (□) CO, (●) selectivity to HCO$_2$Me.

The dehydrogenation of methanol over Pd/ZnO prepared by the precipitation method proceeded somewhat faster than that over Pd/ZnO prepared by the impregnation method. The selectivity to methyl formate was improved to some extent. Fig. 1 illustrates the mole fraction of the carbon-containing products in the effluent and the selectivity to methyl formate against residence time over 30 wt% Pd/ZnO prepared by the precipitation method. The mole fraction of methyl formate increases with the increase of residence time and then decreases through a maximum. The mole fraction of carbon monoxide increases slowly with the increase of residence time at low residence time. However, when the mole fraction of methyl formate approaches the maximum, it starts to grow rapidly. In accordance with these observations, the selectivity to methyl formate approaches 100% at low residence time whereas it decreases with the increase of residence time. At higher residence time methyl formate is suggested to decompose to methanol and carbon monoxide. These findings were almost the same as those observed over copper-based catalysts.[1,2] Hence, it is highly probable that over Pd/ZnO the formation of methyl formate proceeds through a sequence, as shown in eqn. (1), in which formaldehyde is involved.

$$\mathrm{MeOH} \rightarrow \mathrm{HCHO} \rightarrow \mathrm{HCO_2Me} \rightarrow \mathrm{CO} \qquad (1)$$

Further details of the role of ZnO in the methyl formate formation will be discussed elsewhere.

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