CHEMISTRY LETTERS, pp. 1249-1252, 1981.

SELECTIVE METHANOL FORMATION FROM ATMOSPHERIC CO AND H_2 OVER NOVEL PALLADIUM CATALYSTS

Yasuo KIKUZONO[†], Setsuko KAGAMI, Shuichi NAITO, Takaharu ONISHI
and Kenzi TAMARU
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
† Present address: Sumitomo Chemical Company, Limited, Niihama, Ehime 792

Novel palladium catalysts prepared from M_2PdCl_4(M=alkali metals) type complexes have been studied, which produce methanol selectively from CO-H_2 mixture below atmospheric pressure.

It was reported that supported palladium catalysts are effective for selective methanol synthesis from CO and H_2 under high pressure.1) On the other hand, only methane was detected from CO-H_2 reaction in the flow system under atmospheric pressure.2,3) Recently some interesting interactions between group VIII noble metals and support oxides have been recognized4), which was studied in connection with CO-H_2 reaction.5,6) Palladium metals supported on some basic oxides such as MgO and La_2O_3, exhibited high activity for the methanol formation from CO-H_2 mixture under atmospheric pressure.7) But the details of this reaction and the nature of the active sites have not been clarified yet.

In this communication, novel palladium catalysts have been studied, which produced methanol and dimethyl ether selectively from CO-H_2 mixture below atmospheric pressure. The catalysts were prepared by impregnating aqueous solutions of M_2PdCl_4 (M=Li, Na) type complexes onto various acidic oxides such as silica (Aerosil), alumina(Aluminium Oxide C, Aerosil), silica-alumina(Shokubai Kasei) and NaY-zeolite(Linde). After the impregnation, these catalysts (5 - 5.9 wt% Pd) were dried by air circulation at room temperature with a liquid nitrogen cold trap for 15 - 20 hours prior to the reduction by hydrogen (66.5 kPa) at 573 - 773 K for several hours. The hydrogenation of CO was carried out at 453 K in the circulation system with liquid nitrogen cold traps, and the reaction products were analyzed by gas chromatography and quadrupole mass spectrometer.

Table 1 shows the rates of the product formation from CO-H_2 reaction (CO : 20 kPa, H_2 : 40 kPa) at 453 K over Na_2PdCl_4 derived catalysts supported on various oxides. As shown in the table methanol was mainly produced over silica, alumina and zeolite supported catalysts. However, in the case of silica-alumina supported catalyst, main product changed to dimethyl ether, which was produced by the dehydration of methanol on the acidic sites of the support.

Table 1. CO-H_2 reaction$^{a)}$ over Na_2PdCl_4 derived supported catalysts at 453 K

Supports	Loaded Pd wt %	H_2 redn. temp. (K)	h.	Product formation rates$^{b)}$ MeOH	DME$^{c)}$	CH_4	$C_2^{+d)}$	CO_2	MeOH+2DME select. (%)
silica	5.0	773	5	5.39	0.00	0.11	0.02	0.53	89.0
silica-alumina	5.9	573	2	17.4	34.2	2.9	0.02	0.14	96.6
alumina	5.0	673	2	45.2	0.60	2.4	0.14	0.56	93.7
NaY-zeolite	5.9	723	5	9.1	1.00	0.20	0.00	0.00	98.2

a) P_{H_2} = 40 kPa, P_{CO} = 20 kPa, in the closed circulating system (ca. 250 ml) with liquid nitrogen cold traps

b) x 10^{-2} ml-STP/g-catal.hour

c) dimethyl ether

d) total amounts of hydrocarbons which have more than two carbon atoms.

Figure 1 shows the effects of various alkali metal cations upon the activity of the CO-H_2 reaction at 453 K over M_2PdCl_4 derived silica supported catalysts (M = alkali metals and NH_4). Lithium doped catalyst exhibited a high activity for methanol formation, comparable to sodium doped one, whereas the activities of non-doped (M = MH_4) and K, Rb and Cs doped catalysts decreased drastically in the order. As shown in the same figure, the amounts of CO adsorbed were also decreased to almost half of those of the lithium and sodium doped catalysts, although those changes in surface areas are not enough to explain the decrease in the catalytic activities by one or two orders of magnitude. Accordingly, lithium and sodium cations may modify the structure of the reaction sites favourable to the methanol formation and stabilize the reaction intermediate.

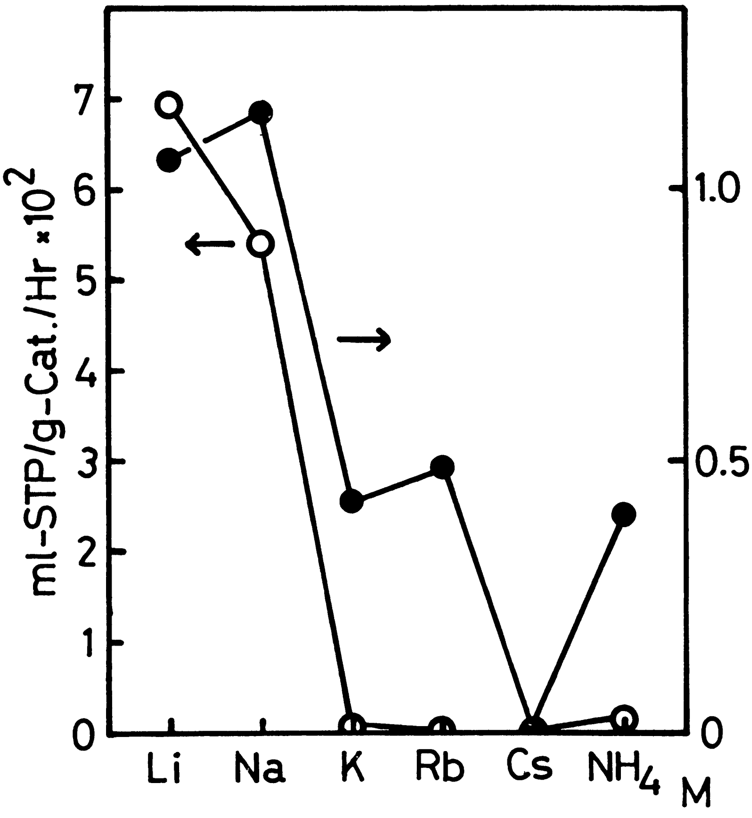

Fig.1 The effects of various alkaline cations on the CO-H_2 reactions over M_2PdCl_4/SiO_2 catalysts (5wt%Pd)

Pretreatment: H_2-reduction

P_{H_2}= 65 kPa, 773 K 5 Hr

—○—: Methanol production rate

CO-H_2 reaction

P_{H_2}= 40 kPa, P_{CO}= 20 kPa

react.temp.= 453 K

—●—: CO adsorption at room temp.

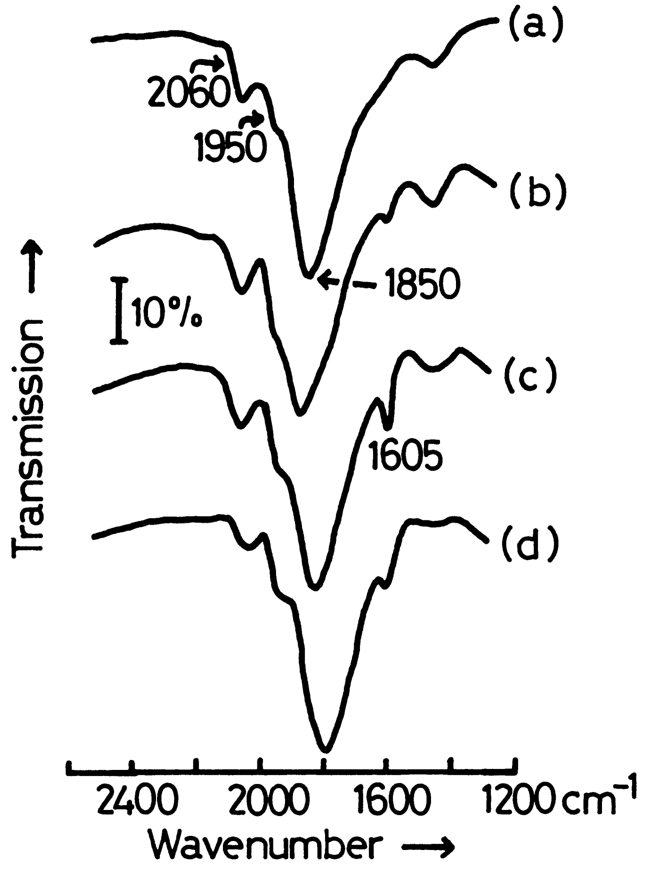

Fig.2 FT-IR spectra of adsorbed species during CO-D_2 reaction over Pd-Na/SiO_2

(a) Only CO gas(2.7 kPa) was introduced at room temp.

(b) CO and D_2 mixture at room temp. for 20 min.
(total pressure = 9.3 kPa, CO:D_2= 1:2)

(c) CO-D_2 at 373 K for 20 min.

(d) CO-D_2 at 423 K for 20 min.

To obtain the detailed informations about the reaction sites and the reaction intermediates, infrared spectroscopic technique was applied to these systems. In the cases of lithium and sodium doped catalysts during the CO-H_2 reaction, new infrared absorption band at 1605 cm^{-1} was observed in addition to the adsorbed CO bands. This band can be assigned to an adsorbed formate ion produced by the hydrogenation of CO on the surface, as shown in fig. 2. The same band was observed when formic acid, formaldehyde, or methanol was introduced on these catalysts at room temperature. On the other hand, no infrared absorption band at 1605 cm^{-1} was obtained during CO-H_2 reaction over potassium doped or non-doped catalyst, nor by the introduction of formaldehyde or methanol at room temperature. These results suggest that it is important to have such surface structure promoted by Li and Na cations which can stabilize the reaction intermediate as a surface formate ion, for the selective methanol formation under mild conditions.

References

1) M.L.Poutsma, L.F.Eleck, P.A.Pisch, and J.A.Rabo, J.Catal., 1978, 52, 157.
2) M.A.Vannice, J.Catal., 1975, 37, 449 : 1977, 50, 228.
3) M.A.Vannice and R.L.Garten, Ind.Eng.Chem.Prod.Res.Dev., 1979, 18, 186.
4) S.J.Tauster, S.C.Fung, and R.L.Garten, J.Amer.Chem.Soc., 1978, 100, 170.
5) M.A.Vannice and R.L.Garten, J.Catal., 1979, 56, 236.
6) A.Bossi, F.Garbassi, and G.Petrini, Proc.VII Inter.Cong.Catal., Tokyo, 1980, E4.
7) M.Ichikawa and K.Shikakura, Proc.VII Inter.Cong.Catal., Tokyo, 1980, B17.

(Received June 12, 1981)