CHEMISTRY LETTERS, pp. 981-984, 1983.

THE EFFECTS OF OXYGEN TREATMENT ON THE CO-H_2 REACTION OVER VARIOUS PALLADIUM CATALYSTS SUPPORTED ON TiO_2 AND ZrO_2

Hiroshi YOSHIOKA, Shuichi NAITO,* and Kenzi TAMARU
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

The effects of oxygen pretreatment on the activity and selectivity of CO-H_2 reaction over sodium-doped and none-doped palladium catalysts supported on TiO_2 and ZrO_2 have been investigated. Large enhancement effect of methanol and C_2 hydrocarbon product formations was observed after the oxygen treatment followed by low temperature reduction.

Supported palladium metal has been accepted to be a good catalyst for selective formation of methanol from CO and H_2 under high pressures.[1] On the other hand, only methane was observed from CO-H_2 reaction in the flow system under atmospheric pressure.[2,3] Recently we have found that methanol formation was enhanced by the addition of alkali metal cations (Li^+ and Na^+) to the supported palladium catalysts even below atmospheric pressure.[4] In this communication, the effect of oxygen treatments of palladium metal on various supports have been studied, which demonstrated remarkable effects on the activity and selectivity in CO-H_2 reaction below atmospheric pressure.

The catalysts were prepared by impregnating aqueous solution of M_2PdCl_4 (M = NH_4 and Na) type complexes onto various oxides such as SiO_2(Aerosil), ZrO_2(Nakarai Chemicals Ltd.) and TiO_2(99% rutile). After the impregnation, these catalysts (5 wt% Pd) were dried by air at room temperature in a closed circulation system with a liquid nitrogen cold trap for 20 hours. Then the catalyst was reduced by hydrogen (26.6 kPa) at 473 ∿ 773 K for several hours (473 K: 5 h , 573 K: 2 h , 673 K: 2 h , 773 K: 3 h). The CO-H_2 reaction (P_{H_2} = 40 kPa, P_{CO} = 20 kPa) was carried out at 453 K in the system with a liquid nitrogen cold traps. The products were analyzed by gas chromatography (molecular sieve 5A for H_2, CO and CH_4; Porapak Q for hydrocarbons and methanol). The oxygen treatment (21.5 kPa of O_2) was

Table. Effects of O_2 treatment on the CO-H_2 reaction over sodium-doped and non-doped palladium (5 wt%) supported catalysts

Catalysts	Exp. No.	H_2 redn. temp (K)	Product formation rates($\times 10^{-2}$ cm^3 /g-cat.h)					Dispersion CO/Pd (at room temp)
			CH_3OH	CH_4	C_2	C_3^+	CO_2	
Pd/SiO_2	(I)	773	0.15	0.11	0	0	0.04	0.046
	(II)	473	0.10	0.12	0.01	0	0.04	0.049
	(III)	773	0.11	0.12	0.01	0	0.04	0.065
Pd-Na/SiO_2	(I)	773	4.12	0.43	0.01	0.02	0.34	0.052
	(II)	473	3.39	0.45	0.01	0.02	0.24	0.058
	(III)	773	1.65	0.52	0.01	0.01	0.58	0.046
Pd/ZrO_2	(I)	773	0.91	0.68	0.01	0.03	0.03	0.057
	(II)	473	3.62	1.21	0.53	0	0.44	0.047
	(III)	773	1.57	0.53	0.02	0.04	0.10	0.064
Pd-Na/ZrO_2	(I)	773	3.59	4.40	0.09	0.20	0.08	0.077
	(II)	473	3.37	4.98	1.67	0	0.78	0.067
	(III)	773	2.94	4.54	0.34	0.08	0.14	0.058
Pd/TiO_2	(I)	773	0.88	0.60	0.01	0.03	0.04	0.061
	(II)	473	4.30	1.71	0.60	0	0.50	0.058
	(III)	773	1.03	0.35	0.03	0.04	0.05	0.066
Pd-Na/TiO_2	(I)	773	3.41	2.02	0.10	0.27	0.11	0.059
	(II)	473	0.66	4.71	2.27	0	2.12	0.049
	(III)	773	0.33	0.76	0.04	0.02	0.31	0.046

Exp.(I); The catalyst was reduced at 773 K before the reaction at 453 K.

Exp.(II); After exp.(I), the catalyst was oxidized at 723K, followed by reduction at 473 K, then the reaction was carried out at 453 K.

Exp.(III); After exp.(II), the catalyst was reduced at 773 K, before the reaction at 453 K (P_{H_2}=40 kPa,P_{CO}= 20 kPa, in a closed circulation system (ca.250 ml) with liquid nitrogen cold trap).

C_3^+ = total amount of hydrocarbons which have more than three carbon atoms.

carried out at 723 K with a liquid nitrogen cold trap for three hours. After the oxidation the catalyst was reduced by hydrogen at 473 K first of all, and the activity and selectivity changes in CO-H_2 reaction were investigated. Then the reduction temperature was raised to 773 K and again CO-H_2 reaction was carried out at 453 K.

The table shows the rates of the product formation from the CO-H_2 reaction over various supported Pd catalysts before and after the oxygen treatment. No change was observed in the rates of the product formation over SiO_2 supported Pd catalyst before and after the oxygen treatment. On the other hand, the rate of methanol and hydrocarbon formations increased considerably in the case of TiO_2 and ZrO_2 supported catalysts after oxygen treatment, followed by the reduction at 473 K. Fig. 1 shows the changes on the distribution of hydrocarbon products in CO-H_2 reaction over Pd/ZrO_2. Before the oxygen treatment, main product was methane with a small amount of higher hydrocarbons. After the oxygen treatment, the rate of formation of ethylene and ethane was accelerated remarkably, and moreover, higher hydrocarbons which have more than three carbon atoms were not detected at all. It is noteworthy that ethylene and ethane were formed selectively on Pd catalyst. This characteristic enhancements brought about by oxygen treatment stayed unchanged during the prolonged reaction period investigated (more than a hundred hours; several turnover numbers based on the Pd metal on the surface), but disappeared completely by further reduction at higher temperature (773 K). These effects could be reproduced for two or three times by repeating oxidation and reduction.

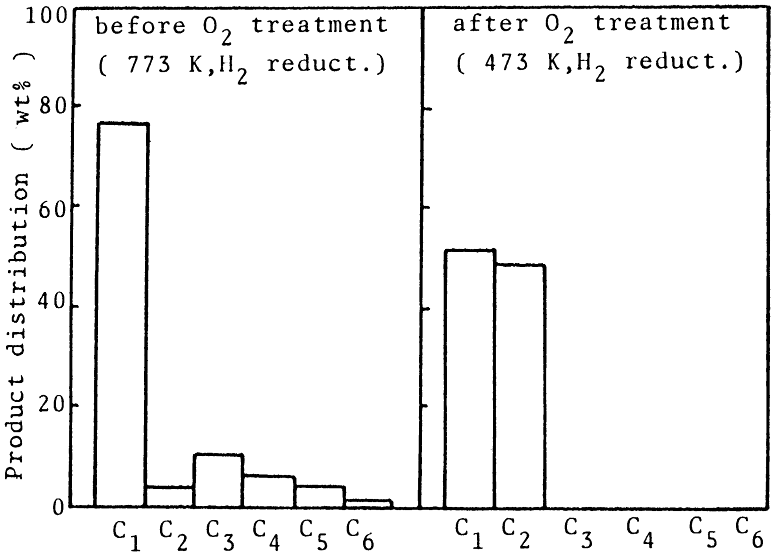

Fig. 1.
Effects of oxygen treatment on the product distribution of CO-H_2 reaction over Pd/ZrO_2 at 453 K.

The results of the CO-H_2 reaction with the same treatments over sodium doped supported Pd catalysts are summarized in the table, which have high activity and selectivity for methanol formation. Similar to the non-doped catalysts, the selectivity for C_2 hydrocarbon formation increased considerably after the oxygen treatment, followed by low temperature reduction over TiO_2 and ZrO_2 supported catalysts. But the effect for methanol formation was not pronounced on these catalysts. Vannice et al. have reported the effect of SMSI in CO adsorption on Pd/TiO_2.[5] In this study, however, Pd/TiO_2 did not show any SMSI effects for CO adsorption when reduced at 773 K, as shown in the table. This is probably due to the higher loading of Pd metals on the supports.

To obtain the detailed information about the active sites, which exhibit characteristic behavior by oxygen treatment, XPS and infrared spectroscopic studies were applied to Pd/TiO_2 catalyst. After the oxygen treatment, Pd metal was oxidised to +1 or +2 valence state (binding energey of XPS: Pd $3d_{3/2}$= 342.9 eV, $3d_{5/2}$= 337.6 eV), but subsequent reduction with hydrogen at 473 K, most of the Pd cations were reduced to zero valent (Pd $3d_{3/2}$ = 340.2 eV, $3d_{5/2}$ = 334.8 eV). However, the existence of the trace amount of Pd^+ could not be excluded because of the broadness of the XPS peaks. Fig.2(a) shows the infrared spectrum of adsorbed CO on 5 wt% Pd/TiO_2 after the reduction at 773 K. A relatively sharp band at 2081 cm^{-1} can be assigned to a linearly adsorbed CO, and a much broader one at 1985 cm^{-1}, to bridged adsorbed CO. After the treatment by O_2, new bands appeared at 2150 and 2098 cm^{-1} which can be assigned to adsorbed CO on cationic Pd sites (spectrum (b)).6) In subsequent reduction by H_2 at 473 K, these bands still remained although their intensity decreased considerably(spectrum (c)), which disappeared completely by reduction at 773 K. These results suggest that cationic site of Pd and /or trace amount of oxygen atoms play an important role in the formation of active sites for methanol formation, as has been suggested by Ponec previously.6) This is seemingly consistent with our previous observations that on sodium doped Pd catalyst, there exists some surface oxygen which can stabilize a reaction intermediate for methanol formation as surface formate ions. Moreover, this might be the reason why no effect of oxygen treatment was observed in the case of sodium doped catalyst in this study. The increase of the selectivity for C_2 hydrocarbons may also be correlated to this cationic palladium.

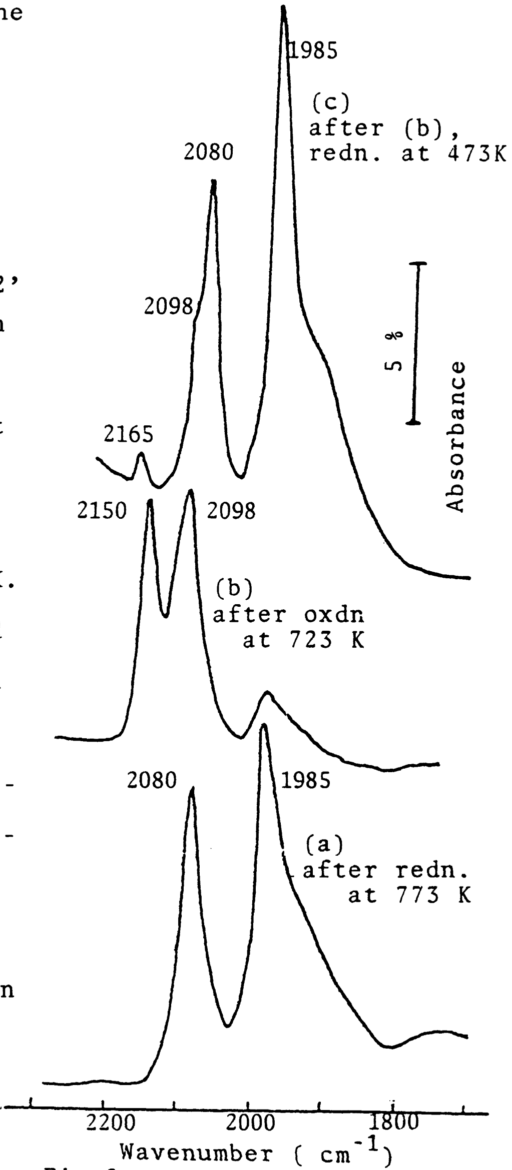

Fig.2.
Infrared spectra of adsorbed CO on Pd/TiO_2 at room temp.

References

1) M. L. Poutsma, L. F. Eleck, P.A.Pish, and J. R. Rabo, J. Catal., 52, 157 (1978).
2) M.A.Vannice, J.Catal., 37, 449 (1975); 50, 228 (1977).
3) M.A.Vannice and R.L.Garten, Ind.Eng.Chem.Prod.Res.Dev., 18, 186 (1979).
4) Y.Kikuzono, S.Kagami, S.Naito, T.Onishi, and K.Tamaru, Chem.Lett., 1981, 1249 : Faraday Discuss.Chem.Soc., 72, 135 (1981).
5) M.A.Vannice, S-Y.Wang, and S.H.Moon, J.Catal., 71, 152 (1981).
6) E.K.Poels, W.A.A.van Barneveld, E.van Broekhoven, V.Ponec, Reac.Kin. and Catal. Lett., 18, 223 (1981).

(Received April 12, 1983)