Noble Selectivity Change in the Hydrogenation of CO over Palladium Membrane Catalysts

Shuichi Naito* and Noriyuki Amemiya
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221

(Received June 21, 1996)

Higher selectivity for oxygenated products was observed in CO-H_2 reaction when hydrogen was supplied separately by the permeation through Pd membrane, than that when both CO and H_2 were supplied on Pd surface from the gas phase, indicating the direct participation of bulk hydrogen for oxygenated product formation.

Poustma et al. first reported that silica supported palladium catalysts catalyze the synthesis of methanol from CO and H_2 with high activity and selectivity under high pressures.[1] On the contrary, Vannice et al. showed that at atmospheric pressure and similar temperatures, palladium is an active and selective catalyst for methanation when supported on alumina.[2] Since then, many studies have been reported demonstrating the controlling factors of the selectivity in CO-H_2 reaction on Pd, such as particle sizes of the metal,[3,4] the composition of the supports[5,6] and the addition of promoters.[7-9]

Since adsorbed CO is well known to inhibit the activation of hydrogen in CO-H_2 reaction over group VIII metal catalysts, it is interesting to study the changes in activity and selectivity when applying different methods of supplying hydrogen to the surface. In this study, we employed a Pd membrane catalyst and carried out the reaction of CO with bulk hydrogen H(b) permeated through Pd bulk from outside the membrane reactor, and compared the results with the CO-H_2 reaction inside the membrane reactor. We found a drastic change in selectivity between these two reactions.

A palladium thimble type membrane (0.2 mm thickness, 2 mm diameter, 60 mm length) jointed with glass was used as a reaction cell, which was connected to a closed gas circulation system. Before each run, the catalyst was oxidized with 20 kPa of oxygen at 473 K for 1 h, and then reduced with 26.7 kPa of hydrogen at 573 K for 2 h. The reaction was carried out in the closed gas circulation system under atmospheric pressures. To gather the primary products, a liquid nitrogen cold trap was employed in the circulation system. The products were analyzed by gas chromatography with flame ionization detection (FID: porapak N column). Two kinds of reactions were carried out as follows: Mixed mode(M); both CO and H_2 were introduced inside the circulation system, and Permeation mode(P); only CO was introduced inside the circulation system and hydrogen was supplied through the Pd membrane.

Product distributions of mixed and permeation mode reactions at 513 K are summarized in Figure 1. When both CO(4.0 kPa) and H_2(8.0 kPa) were introduced in the circulation system (mixed mode), the main products were methane and higher hydrocarbons with less than ten percent of oxygenated products. On the other hand, when only CO(4.0 kPa) was introduced in the circulation system and H(b) was supplied through Pd membrane (H_2 = 4.0 kPa: permeation mode), the amounts of formed methane and hydrocarbons were reduced drastically, with the slight decrease of oxygenated products (see TOF in Table 1). Consequently, the selectivity for oxygenated products was improved markedly by changing the method of supplying hydrogen to the Pd surface.

The characteristic feature of the product distribution in Pd membrane catalyst is that C_2 hydrocarbon and oxygenated products such as ethylene and acetaldehyde are the relatively abundant products, although it is well known that methane and methanol are the main products over supported Pd catalysts. To make this point clearer, we investigated the CO-H_2 reaction over Pd foil (0.2 mm thickness, 5 g) and obtained similar product distribution to the membrane catalyst. It is interesting to note that XRD pattern of this Pd foil exhibited abnormally strong intensity of (200) peak compared to Pd black.

Pressure dependencies of the reaction rates were investigated for these two kinds of reactions over Pd membrane catalyst. The reaction orders in the mixed mode reaction were similar to those of silica supported Pd catalysts: 1~1.5 order for the partial pressure of hydrogen and almost zero-th order for the partial pressure of CO. However, the reaction orders in the permeation mode reaction were quite different: about 0.5 order for the partial pressure of H_2 and -0.3~-0.5 order for the partial pressure of CO. These results suggest that the supply of H(b) to the surface is inhibited by the presence of CO(a), which may be the rate determining step in the permeation mode reaction.

The temperature dependencies of mixed and permeation mode reactions were also investigated between the temperature range from 453 K to 573 K. The results are summarized as Arrhenius plots in Figure 2. The activation energies in the

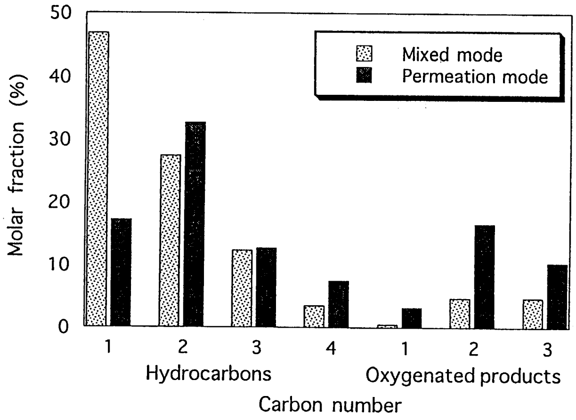

Figure 1. Product distributions of mixed and permeation mode reaction at 513 K.

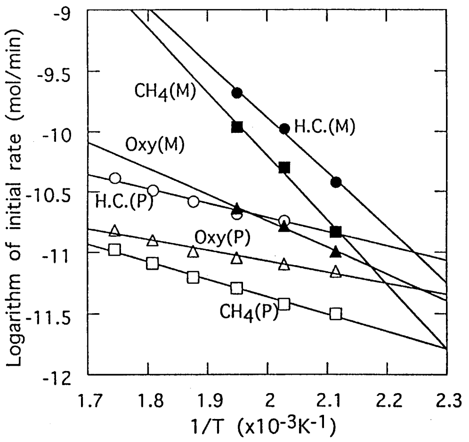

Figure 2. Temperature dependencies of the initial rates of methane, higher hydrocarbons(H.C.) and oxygenated products(Oxy) formations in the mixed mode (M, closed symbols) and permeation mode (P, open symbols).

Table 1. TOF and activation energies of CO-H2 reaction

Mode	products	TOF (s^{-1}x10^5, 493K)	Ea (kJ/mol)
Permeation	Methane	0.60	30.7
	Hydrocarbons	2.86	24.3
	Oxygenates	1.26	15.6
Mixed	Methane	7.85	101
	Hydrocarbons	16.5	86.4
	Oxygenates	2.59	54.5

mixed mode reaction obtained from the slopes of these plots are similar to those of supported Pd catalysts. On the other hand, the activation energies in permeation mode are similar to the activation energy of hydrogen permeation through the Pd membrane employed(16 kJ/mol). These results also suggest that the rate determining step of the permeation mode is the diffusion of hydrogen through Pd bulk.

The most interesting result in the present study is a drastic improvement in selectivity for oxygenated products in the permeation mode reaction. Since the supply of H(b) through the Pd bulk is the rate determining step in the permeation mode, the concentration of adsorbed hydrogen H(a) on Pd surface may be much less than that in the mixed mode reaction, which causes the drastic decrease of the overall reaction rates. If we assume that oxygenated compounds may be formed by CO insertion into alkyl adsorbed species, the number of hydrogen atoms required for oxygenated product formation should not so different from those of corresponding hydrocarbon formation. Since the decrease of the TOF for oxygenated product formation was much less than that for hydrocarbon formation, we have to suppose the participation of other kind of hydrogen for oxygenated product formation. The most plausible explanation would be the possibility of a direct participation of bulk hydrogen.

It is known that H(b) in the Pd bulk is less stable than H(a) on the Pd surface[10] and the presence of subsurface hydrogen H(sub) was reported by Rieder et al.[11] and Behm et al.,[12]which possesses a much lower heat of desorption (29 kJ/mol) than H(a). Accordingly it is reasonable to suppose that supplied H(b) from the bulk may have different reactivity from H(a) and quickly form oxygenated products before it settles on the surface as H(a). It is known that bulk hydrogen in Pd possesses protonic character, which may react preferentially with oxygenated intermediates on the surface.

In the case of supported Pd catalysts, it is reported that the turnover frequency of methanol formation increases with increasing the particle size of Pd metal.[4] Since larger Pd particles absorb more hydrogen in the bulk,[10] it is consistent with our conclusion that bulk hydrogen exhibits higher activity for oxygenated product formation. We also studied the CO-H_2 reaction over Pd black catalysts under the same condition as the mixed mode over Pd membrane catalysts, and found more than 90% of the products was methanol. Consequently, different reactivities of the surface and bulk hydrogen would be another controlling factors of the selectivity in CO-H_2 reaction over Pd catalysts.

References

1 M. Potsma, L. F. Elect, P. A.. Ibarbia, A..P. Risch, and J.A.. Rabo, *J. Catal.*, **52**, 157 (1978).
2 M.A. Vannice and R. L. Garten, *Ind. Eng. Chem., Prod. Res. Dev.*, **18**, 186 (1979).
3 S. Ichikawa, H. Poppa, and M. Boudart, *J. Catal.*, **91**, 1 (1985).
4 K. P. Kelly, T. Tatsumi, T. Uematsu, D.J. Driscoll, and J.H. Lunsford, *J. Catal.*, **101**, 396 (1986).
5 Y. A. Ryndin, R. F. Hicks, A.. T. Bell, and Y.I. Yermakov, *J. Catal.*, **70**, 287 (1981).
6 C. Sudhakar and M. A. Vannice, *J. Catal.*, **95**, 227 (1985).
7 M. Ichikawa and K. Shikakura, 7th Int. Congr. Catal., (1980) p925.
8 Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, *Faraday Discuss.*, **72**, 135 (1981).
9 J.M. Driessen, E.K. Poels, J.P. Hindermann, and V. Ponec, *J. Catal.*, **82**, 26 (1983).
10 M. Boudart and H.S. Hwang, *J. Catal.*, **39**, 44 (1975).
11 K. H. Rieder, M. Baumberger, and W. Stocker, *Phys. Rev. Lett.*, **51**, 1799 (1983).
12 R. J. Behm, V. Penka, M. G. Cattania, and G. Ertl, *J. Chem. Phys.*, **78**, 7486 (1983).