

Effect of SMSI (Strong Metal–Support Interaction) Behaviour on CO–H₂ Reaction over Supported Rh Catalysts

Hideo Orita, Shuichi Naito,* and Kenzi Tamaru

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

The catalytic activity and selectivity in the CO–H₂ reaction over supported Rh catalysts were investigated by changing reduction temperatures, supports, and doping alkali metal cations; the reduction at 723 K of TiO₂-supported catalysts decreased not only the amounts of hydrogen adsorption but also the CO conversion.

Recently, Tauster *et al.*¹ have reported that strong metal–support interactions (SMSI) occur between Group 8 noble metals and transition metal oxide supports when the catalysts are reduced by hydrogen at high temperatures (700–800 K). The SMSI effect renders noble metals inactive for H₂ and CO adsorption. Vannice *et al.*² have found that TiO₂-supported Ni exhibited turnover frequencies which were one to two orders of magnitude higher than for other Ni catalysts, and the characteristic selectivities to produce higher-molecular weight paraffins.

In the present study, we have investigated the catalytic properties of supported Rh metals in the CO–H₂ reaction by changing hydrogen reduction temperatures, metal precursors, and supports. We have found that the specific activity and selectivity of supported Rh metal in the CO–H₂ reaction can show a remarkable variation depending on these three factors. The catalysts were prepared by impregnating aqueous solutions of metal chlorides [RhCl₃, Na₃RhCl₆, (NH₄)₃RhCl₆, or a mixture of RhCl₃ and alkaline chloride] onto oxide supports such as TiO₂ (P-25, Aerosil), Al₂O₃ (Sumitomo Chemical Co. Ltd.), and MgO (Merck). After the impregnation, the catalysts (5 wt% Rh) were dried in air at 383 K for *ca.* 12 h and treated in air in a closed circulation system at room temperature with a liquid nitrogen cold trap for *ca.* 15 h prior to the reduction by hydrogen at 473–723 K for several hours. The hydrogenation of CO was carried out at 453 K in the circulation system with a liquid nitrogen cold trap, and the reaction products were analysed by g.c. and quadrupole mass spectrometry. Electron microscopic measurements were conducted using a Hitachi H-500 electron microscope.

Table 1 shows the effects of reduction temperatures, metal precursors, and supports upon the activity and selectivity in the CO–H₂ reaction at 453 K over supported Rh catalysts. The conversion of CO over TiO₂-supported catalysts showed about 70-fold variation depending on the doping alkali metal cation, whereas the H/Rh value (the ratio of the amount of adsorbed hydrogen atoms to rhodium metal atoms on the support) changed only 4-fold. This fact indicates that the

variation of activity is not due to the change in metal surface area but occurs because the electronic state of the rhodium is modified by the doping alkali metal cations. Such doping effects caused a decrease in CO conversion and an increase in the selectivity for formation of C₂-oxygenated compounds. An improvement in the selectivity for formation of oxygenated compounds by doping alkali metal cations has been reported recently for Pd³ and Rh.^{4,5} As the reduction temperature was raised from 473 to 723 K, H/Rh values for all the TiO₂-supported Rh catalysts decreased drastically and the ratio of ethylene to ethane increased. Treatment under an O₂ atmosphere restored the initial properties of the TiO₂-supported Rh catalysts.

The Fourier-transform i.r. spectra of the Na₃RhCl₆-TiO₂ catalyst under the reaction conditions were examined (JEOR JIR-03F spectrometer). After the reduction at 473 K, the absorption bands characteristic of the surface acetate ion and adsorbed hydrocarbon species were identified in addition to linear and bridged forms of adsorbed CO. As the reduction temperature was increased to 723 K, no band for adsorbed species was observed, as may be expected from SMSI. It was confirmed that these phenomena were not due to the lack of sufficient transmittance for i.r. measurements. On the other hand, the properties of the catalysts supported on Al₂O₃ or MgO remained almost unchanged after H₂ reduction or O₂ treatment at 723 K.

RhCl₃-TiO₂ reduced at 473 K is much more active than RhCl₃-Al₂O₃ and produces a larger amount of higher-molecular weight hydrocarbons. Vannice *et al.*² reported similar support effects for Ni–TiO₂, and suggested that these effects were due to SMSI. However, in our case, the catalysts reduced at 473 K still have the capacity to adsorb hydrogen and therefore are not in the SMSI state. Consequently, H₂ reduction at higher temperatures is necessary for SMSI, where not only the amount of adsorption of H₂ or CO but also the CO conversion in the CO–H₂ reaction decreased considerably. In order to confirm that the decrease in H/Rh value and CO conversion was not due to the sintering effect, RhCl₃-TiO₂

Table 1. Effect of SMSI behaviour on the CO–H₂ reaction over supported Rh catalysts.

Catalysts	H/Rh ^a (%)			CO conversion ^b			Selectivity for C ₂ oxygenated compounds (%)		
	(i) ^c	(ii)	(iii)	(i) ^c	(ii)	(iii)	(i) ^c	(ii)	(iii)
RhCl ₃ -TiO ₂	52	0.7	31	67.7	3.4	90.9	0.7	0.9	1.1
(NH ₄) ₃ RhCl ₆ -TiO ₂	14	<i>ca.</i> 0	6.3	16.2	1.2	24.8	1.5	0.8	1.2
RhCl ₃ + 3LiCl-TiO ₂	22	1.5	42	13.8	1.9	7.4	15	9	19
Na ₃ RhCl ₆ -TiO ₂	26	0.2	24	6.2	2.0	3.0	17	16	20
RhCl ₃ + 3KCl-TiO ₂	27	<i>ca.</i> 0	27	3.8	1.5	4.2	16	17	11
RhCl ₃ + 3CsCl-TiO ₂	14	<i>ca.</i> 0	26	1.0	0.8	3.1	8	10	6
RhCl ₃ -Al ₂ O ₃	66	73	— ^d	4.0	7.6	—	0	0.9	—
Na ₃ RhCl ₆ -MgO	28	27	—	0.6	0.9	0.3	25	24	27

^a Based on H₂ adsorption at room temperature. ^b ml S.T.P. h⁻¹ g-cat⁻¹. Reaction temperature = 453 K, P^o(H₂) = 24 kPa, P^o(CO) = 12 kPa. ^c After H₂ reduction at 473 K for 4 h; (ii) after (i), the catalyst was reduced at 723 K for 2.5 h prior to the reaction; (iii) after (ii), the catalyst was reduced by H₂ at 473 K for 2 h, treated with O₂ at 723 K for 2 h, and again reduced by H₂ at 473 K for 2.5 h prior to the reaction. ^d Not measured.

reduced at 723 K was examined by electron microscopy. A mean particle size for Rh metal of *ca.* 4 nm was observed, which is in good agreement with that calculated from H₂ adsorption (H/Rh = 0.31). Therefore, we conclude that the phenomena shown in Table 1 are due to SMSI.

We thank Mr. M. Kakugo, Sumitomo Chemical Co. Ltd., for electron microscopy examinations.

Received, 12th April 1983; Com. 459

References

- 1 S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170; S. J. Tauster and S. C. Fung, *J. Catal.*, 1978, **55**, 29.
 - 2 M. A. Vannice and R. L. Garten, *J. Catal.*, 1979, **56**, 236.
 - 3 Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, 1981, 1249; *Faraday Discuss. Chem. Soc.*, 1981, **72**, 135.
 - 4 S. Kagami, S. Naito, Y. Kikuzono, and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1983, 256.
 - 5 H. A. Dirkse, P. W. Lednor, and P. C. Versloot, *J. Chem. Soc., Chem. Commun.*, 1982, 814.
-