Effects of Reduction Conditions on the Catalytic Activity of Rhodium Supported on TiO2 for the Hydrogenation of Carbon Monoxide: Favorable Metal-Support Interaction

Hiroshi Fujitsu,* Nobuhide Ikeyama,† Yasunobu Shigaki,† and Isao Mochida

Research Institute of Industrial Science,

†*Department of Molecular Technology Graduate School of Engineering Sciences, Kyushu University 86, Kasuga 816*

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Synopsis.   Catalytic activity of Rh/TiO2 was influenced significantly by reduction conditions, the maximum activity per weight being obtained by reduction at 400°C for 2 h, in spite of limited adsorption abilities against reactant gases. The nature of Rh/TiO2 is sensitively modified to develop the most favorable metal-support interaction.

Designs of novel catalysts for CO–H2 reaction have been extensively investigated for these years.[1] The roles of support and additive may be one of the most influential factors to be considered for this purpose. Titania is one of the most interesting supports to modify the catalytic activity and selectivity,[2-5] since Tauster et al.[6] reported SMSI as for the reduced adsorption abilities of group VIII metals supported on the oxide after the reduction at higher temperatures (above 500°C). Vannice et al.[7] claimed that the turnover frequency on such catalysts was enhanced by the higher reduction temperatures because of SMSI, however the activity per weight was rather similar to that reduced at lower temperature.[8] It has been scarecely attempted yet to find catalysts of better practical performance in spite of a number of studies on SMSI concept.[5,7] Kikuchi et al.[9] reported recently that Ru supported on rutile of large surface area showed the larger activity per weight at the SMSI than that at the non-SMSI state.

The present authors are going to report significant effects of the reduction temperature and time on the catalytic activity of Rh on TiO2 for the CO–H2 reaction to find the most active catalyst.

The most favorable extent of the reduction for the highest catalytic activity per weight must exist, since electron transfer from the support is profoundly influenced by the reductive heat-treatment.[10]

Experimental

Rh/TiO2 was prepared by the impregnation of RhCl3–3H2O on TiO2 (Aerosil Inc, P-25, 50 m²/g) using a methanol solution (Rh: 4.6 wt%). The catalytic reaction was carried out at 200 and 250°C, using a circulating reactor (vol. 800 ml) with a fixed catalyst bed (0.5 g cat, diluted with 5 g SiC), through which a reactant gas of CO and H2 (their partial pressures were 26.7 and 53.3 KPa, respectively) flowed. Before the reaction, the catalyst was reduced in situ, and evacuated at 200°C for 1 h. During the reaction, products except for methane were trapped at liquid nitrogen temperature. The reactant gases and methane were analyzed with a gas chromatograph (Molecular Sieve 13 X, 1m) by the sampling at proper intervals during the reaction. Other trapped products were analyzed after the reaction with a gas chromatograph (Porapack Q, 1m, for CO2; VZ-10, 2m, for hydrocarbons).

Reaction rates were calculated from the conversion of CO. The catalytic reacation was repeated three time at least giving
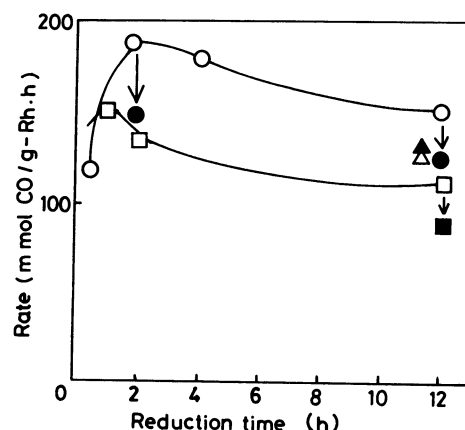

Fig. 1. Effects of reduction conditions and oxygen preadsorption on the catalytic activity of Rh/TiO2. cat: 0.5 g/5 g SiC, P_{H2}/P_{co}=26.7/53.3(KPa), reaction temp: 200°C, reduction temp: 200°C (△,▲), 400°C (○,●), 500°C (□,■), open: without oxygen preadsorption, colsed: after the oxygen pre-adsorption.

well-reproduced rates and product distributions.

Adsorption of CO, H2 and O2 on the catalyst was measured volumetrically using the same reactor.

Results and Discussion

Catalytic activities at 200°C depended very much on the reduction conditions, both temperature and time, as shown in Fig. 1. The reduction at 400°C for 2 h (catalyst-400) provided the highest activity per weight among the reduction conditions examined. Longer time at the same temperature decreased the rate considerably. The catalyst reduced at 500°C (catalyst-500) showed the maximum activity by the reduction for 1 h and gradual decreases of activity with longer times to give the lowest activity by 12 h. In contrast, the reduction at 200°C (catalyst-200) provided constant activities independent on the reduction time. Such activity differences due to the reduction conditions were more marked in the reaction at 250°C (Table 1).

More long-chain hydrocarbons ($>C_5$) were obtained over the catalysts reduced at both 400 and 500°C when the product distributions were compared.

Table 2 summarized the effects of reduction conditions on the adsorption abilities against H2, CO and O2 at room temperature. The reduction at 200°C provided ca. 0.5 of both H/Rh and CO/Rh atomic ratios regardless the reduction time. These ratios decreased markedly by increasing the reduction temperature. The smallest values on the catalyst-500 indicate the definite SMSI as reported in the literature.[6] In contrast, adsorption ability of the catalyst against O2

TABLE 1. EFFECTS OF THE REDUCTION TEMPERATURE AND OXYGEN ADSORPTION ON THE CATALYTIC ACTIVITY OF Rh/TiO_2 AT 250°C[a]

Redn. temp	Reaction rate	
°C	m mol CO/g-Rh·h	
	Virgin	After O_2 adsorption[b]
200	1180	1200
400	1350	900
500	970	680

a) cat.(4.6 wt % Rh): 0.5 g/5 g SiC, reduction time: 2h $P_{H_2}/P_{CO}=26.7/53.3$ KPa. b) 20.0 KPa O_2 was pre-adsorbed at room temperature, followed by evacuation at 200°C-1 h.

TABLE 2. ADSORPTION ABILITIES OF THE CATALYSTS AGAINST H_2, CO AND O_2

Redn. temp	Adsorption		
°C-h	H/Rh[a]	CO/Rh[b]	O/Rh[c]
200- 2	0.54	0.52	0.48
-12	0.54	0.51	—
400- 2	0.23	0.32	0.53
-12	0.11	0.23	—
500- 2	0.05	0.08	0.50
-12	0.02	0.06	—

a) Room temp, $P_{H_2}=1.3—93.3$ KPa. b) Room temp, $P_{CO}=26.7$ KPa. c) Room temp, $P_{O_2}=20.0$ KPa.

was not influenced by the reduction conditions to show almost constant values of O/Rh ratio as reported by Meriaudeau et al.[11]

The oxygen adsorption at room temperature provided remarkable effects on the catalytic activity, depending strongly on the reduction temperatures of the catalysts as shown in Fig. 1 and Table 1. The reaction rates over the catalysts-400 and -500 at 200 and 250°C were decreased by the oxygen adsorption by ca. 20 and 30%, respectively, whereas no retardation was observable with the catalyst-200. The product distribution was not effected by the oxygen adsorption.

It may be the most significant observation in the present study that the catalyst reduced at 400°C for 2 h exhibited the highest catalytic activity per g-Rh. The interaction between Rh and TiO_2 which allowed the maximum activity per g-Rh can be defined as FMSI (Favorable Metal Support Interaction), its search being a practical target in the catalyst design. The reduction

at 400°C for 2 h may compromise most favorably the extents of reduction and dispersion of Rh as well as electron-donating ability of supporting TiO_2.[10] The hydrogenation activity of such a catalyst was rather low to increase the yields of longchain hydrocarbons.

The activity per g-catalyst is the product of the activity of an active site and its number on the catalyst surface. The latter has been proposed to be estimated from the amounts of hydrogen adsorption (H/Rh ratio).[5,7,8] However, it is suspicious that the ratio reflects its accurate number. The nature of the metal catalyst is suggested to be modified significantly by the support according to the pretreatment conditions.

The balanced activation abilities against H_2 and CO of Rh modified through FMSI may provide the maximum activity where the number of the active sites is rather unchanged. Such a FMSI may be possible between Rh metal and properly reduced titania by dehydration and hydrotreatment.

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