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Remarkable Activity Enhancement of Rh/Al_2O_3 Prepared from $RhCl_3$ for $CO-H_2$ Reaction by the Pretreatment of High Temperature Evacuation

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Catalytic activity of Rh/Al_2O_3 prepared from $RhCl_3$ for the $CO-H_2$ reaction at 473 and 523 K was found to be remarkably enhanced by the evacuation after the reduction of catalyst. Evacuation at 773 K after the reduction with hydrogen at 673 K exhibited the maximum activity of 1200 mmol CO/g-Rh h, which is comparable to that of Rh/TiO_2. Significant increases in H_2 and CO adsorption, especially the irreversible adsorption of CO, as well as the enhanced reactivity of the adsorbed CO by the evacuation treatment may cause the activity enhancement.

For these few years, effects of the support have been recognized to be one of the most important factors to prepare better catalysts, especially for the $CO-H_2$ reaction.[1)] It is well known that the catalytic activity of Rh supported on SiO_2, Al_2O_3 and TiO_2 increases in the following order when the reduction temperature was fixed around 673 K:$Rh/SiO_2 < Rh/Al_2O_3 < Rh/TiO_2$.[2-4)] Solymosi et al.[2)] reported that the different reactivity of surface carbon species caused such an activity order, whereas Murakami et al.[3)] pointed both the different rate of dissociative adsorption of CO and the different reactivity of surface CH_x species. Present authors found that the reactivity of irreversibly adsorbed CO on these catalysts with H_2 at 473 K depended very much on the nature of support.[4)] Interestingly, Rh/Al_2O_3 exhibited a higher catalytic acitivity when the reduction temperature was raised up to 773 K, whereas Rh/SiO_2 did not show any increase in the activity. More adequate conditions for the reduction and evacuation of Rh/Al_2O_3 was suggested to exhibit a better activity.

The authors are going to discribe in the present letter that the evacuation at 773 K after the reduction at 673 K increased the activity of Rh/Al_2O_3 comparable to that of Rh/TiO_2.

Rh/Al_2O_3 was prepared by the impregnation of $RhCl_3 \cdot 3H_2O$ on Al_2O_3 (Aerosil Inc., C type, 100 m^2g^{-1}) from its methanol solution. The catalyst was reduced with

H_2 (26.7 kPa) for 2 h at a temperature range of 473-773 K in situ and then evacuated at a temperature range of 473-973 K for 1 h before the reaction. CO-H_2 reaction was carried out at 473 and 523 K in a closed circulating reactor (900 ml) with a fixed catalyst bed. Analyses of the reactants and the products (gas chromatograph) and IR measurements of adsorbed CO (FT-IR) were described in previous papers.[4-7] Adsorption of H_2 and CO was measured volumetrically at 293, 473 and 523 K for H_2 and at 473 K for CO, respectively, because the Boudouard reaction proceeded above 473 K. The adsorption of CO in the second run after the evacuation for 1 h and the difference between the adsorption amounts of the first and the second runs were defined as reversible and irreversible adsorption, respectively.

Figure 1 summarizes the effects of reduction and evacuation temperature on the catalytic activity of Rh/Al_2O_3 at 523 K. When the evacuation temperature was fixed at 473 K, the catalytic activity increased with increasing reduction temperature to achieve a maximum value (550 mmol CO/g-Rh h) by the reduction at 773 K. When the reduction temperature was fixed at 673 K, the rise in the temperature of evacuation from 473 to 773 K increased the activity from 270 to 1200 mmol CO/g-Rh h which is comparable to the maximum rate on Rh/TiO_2 (1350 mmol CO/g-Rh·h).[5,6] Further increase in evacuation temperature decreased the activity. Evacuation at 773 K of the catalyst reduced at 773 K showed a fairly high activity of 1000 mmol CO/g-Rh·h.

Similar effects of the evacuation temperature on the catalytic activity were observed in the reaction at 473 K. The product distributions were slightly affected by the present preparative conditions, affording more C_2-C_4 hydrocarbons with a major production of methane.

Adsorption abilities of Rh/Al_2O_3 against H_2 and CO are summarized in Table 1. At all adsorption temperatures, the adsorption ability of the catalyst reduced at 673 K for H_2 increased with the rise in the evacuation temperature to show the maximum by the evacuation at 773 K, however further increase in the temperature decreased the ability. Total CO adsorption ability at 473 K was less influenced by the evacuation and reduction temperatures compared to the H_2 adsorption abilities. However, the amount of irreversibly adsorbed CO at 473 K increased by the higher evacuation temperature to show the maximum after the reduction and evacuation at 673 and 773 K, respectively.

IR spectrum of irreversibly adsorbed CO on Rh/Al_2O_3 reduced and evacuated at 673 and 773 K, respectively, exhibited a rather strong band at 2100 cm^{-1} (one robe of twin type), in addition to the band at 2050 (linear) and $\approx$1850 cm^{-1} (bridging), which were observed on catalysts regardless of the reduction and evacuation temperature. A preliminary IR study suggests that the evacuation at higher temperatures increased the reactivity of the irreversibly adsorbed CO against H_2 at 473 K.

At the present stage, the effects of evacuation temperature on the surface chemistry of the catalyst are not clear. The remarkable increases in the adsorption abilities, especially for the irreversible adsorption of CO, and the reactivity of the irreversibly adsorbed CO suggest significant changes in the chemical nature as well as numbers of the active Rh sites on Al_2O_3 by the evacuation.

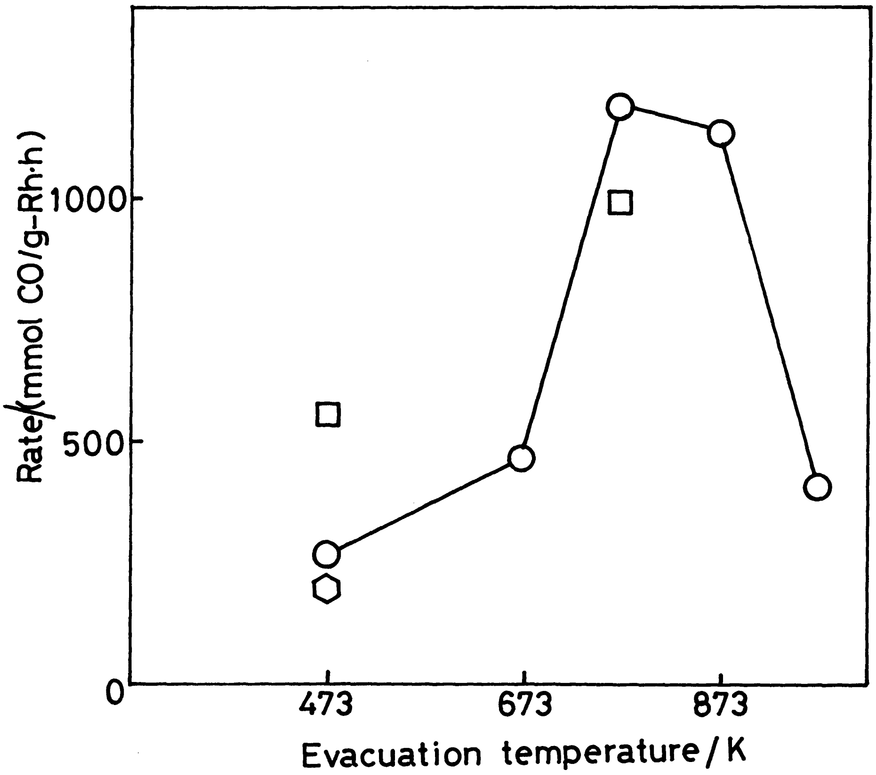

Fig. 1. Effects of evacuation temperature on the catalytic activity of Rh/Al$_2$O$_3$.
CO=26.7 kPa, H$_2$=53.3 kPa, at 523 K
reduction temp: 473 K(⬡), 673 K(○), 773 K(□)

Table 1. Adsorption abilities of Rh/Al$_2$O$_3$ against H$_2$ and CO

		Adsorption amount			
Redn temp	Evac temp	H/Rh			CO/Rh
K	K	293 K	473 K	523 K	473 K(rev./irrev.)
473	473	0.25	0.08	-	0.27(0.16/0.11)
673	473	0.18	0.15	0.12	0.24(0.13/0.11)
	673	0.36	0.24	0.16	0.31(0.15/0.16)
	773	0.40	0.30	0.20	0.34(0.12/0.22)
	873	0.36	0.26	0.20	0.29(0.08/0.21)
	973	0.26	0.18	0.12	0.19(0.06/0.13)
773	773	0.32	0.27	0.20	0.19(0.11/0.18)

Chloride ion may play an important role to define the catalytic activity. Miura et al.$^{8-10)}$ reported that a considerable amount of chloride ion remained after the reduction at 600 K on Ru/SiO_2 which was prepared from $RuCl_3$, although its catalytic activity was not so much affected by the remaining chloride ions. They also reported no chloride ion remaining on Rh/SiO_2 and Pd/SiO_2. In contrast, considerable amount of chloride is suspected to remain on Rh/Al_2O_3 when the reduction and/or evacuation temperatures are low. It may be suggested that liberation of chloride ion by the evacuation at higher temperatures may induce some structural change in supported rhodium and/or some change in the interaction of Rh with the support to enhance its catalytic activity as well as adsorption abilities.

Such a remarkable effect of the evacuation temperature may provide a clue to elucidate roles of Al_2O_3 as a unique catalyst support.

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