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Evacuation at elevated temperatures to enhance the catalytic activity of Rh/TiO₂ for the hydrogenation of CO

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Effects of the evacuation treatment at elevated temperature was investigated to enhance the catalytic activity of Rh/TiO₂ in the early stage of the hydrogenation of CO (CO/H₂ = 26.7/53.3kp) at 523K. The evacuation at 773K after the reduction of RhCl₃/TiO₂ at 673K provided the highest initial activity of 1810mmol CO/g-Rh·h at 523K, both higher or lower evacuation temperatures decreasing the activity to two thirds. The extensive removal of the chlorine involved in the catalyst may allow the most favorable influences of TiO₂ on Rh catalyst through better dispersion and electronic interaction since Rh/TiO₂ prepared from Rh(NO₃)₃ exhibited much inferior activity by the same evacuation treatment.

Introduction

Better supports have been extensively explored to find higher activity and selectivity of the noble metal catalysts in the CO-H₂ reaction^{1~22)} since the SMSI²³⁾ was positively evaluated in the design of the catalyst²⁾. It is well-documented that supporting titania, alumina and silica allow this order of catalytic activity of various metal catalysts,^{13,17,18,22)} the relative activities of Rh on titania and silica ranging several orders of magnitude in the hydrogenation of carbon monoxide. Delicate design of supports is expected to further improve the catalytic activity of supported metals.

The present authors have reported that the evacuation treatment markedly enhanced the catalytic activity of RhCl₃/Al₂O₃ after the reduction.²⁴⁾

In the present study, catalytic activity of Rh/TiO₂ was studied in the hydrogenation of CO at 523K to find the favorable influences of the evacuation treatment in the temperature range of 473 to 823K. The extensive removal of the chlorine of the catalyst precursor is expected to increase the activity of the catalyst on the best support when RhCl₃ was used as the catalyst precursor.

EXPERIMENTAL

Catalysts

Rh/TiO₂ was prepared by the impregnation of RhCl₃·3H₂O and Rh(NO₃)₃ on TiO₂ (P-25,50m²/g) from the methanol solution (Rh:4.6wt%). The catalyst was reduced with hydrogen (26.7kp) for 2h at 673K in a gas-circulating reactor and then evacuated at a temperature range of 473-823K for 1h before the catalytic reaction.

Catalytic reaction

The catalytic reaction was carried out at 523K, using a circulating reactor (volume: 400ml) with a fixed catalyst bed, through which the reactant gas-mixture flowed (Total pressure 80.0kpa; 26.7/53.3(kpa) = CO/H₂ mole ratio). During the reaction, products except for methane were trapped at liquid nitrogen temperature. The reactant gases and products were analyzed with a gas-chromatograph. Reaction rates were calculated from the conversion of CO. Hydrocarbons longer than C₇ were not analyzed. Detail procedures were described in previous papers¹⁹⁻²¹.

RESULTS

Catalytic Activity and Product Distribution on Rh/TiO₂ by the Circulating Reaction.

Table 1 summarizes the initial activities of Rh/TiO₂ catalysts reduced at 673K and

Table 1. Effects of reduction and evacuation conditions on the catalytic activity of Rh supported on TiO₂^{a)}

Cat.	Evact. Temp. (K)	Rate ^{b)}	Selectivity (C.T.%)				O.C. ^{c)}	C.B. ^{d)}	Cl/Rh ^{e)}
			C ₁	C ₂ ~C ₄	C ₅ ~C ₇	CO ₂			
RhCl ₃ /TiO ₂	473	1,360	38	40	15	2	63	95	0.36
	673	1,390	35	42	15	2	62	94	0.06
	773	1,810	21	64	12	1	55	98	0.02
	823	1,580	25	62	8	1	56	96	—
Rh(NO ₃) ₃ /TiO ₂	473	200	32	42	14	1	65	89	
	673	210	32	42	14	1	65	89	
	773	220	32	42	14	1	65	89	

a) catalysts were reduced at 673K for 2h

b) mmolCO/g·Rh·h

c) olefin content

d) carbon balance

e) atomic ratio

evacuated at a temperature range from 473 to 823K. The rate and product distribution were measured at CO conversion levels of about 10%. Higher temperature of evacuation up to

773K increased the initial rate of the reaction at 523K on the catalysts reduced at 673K to as high as 1810mmolCO/g-Rh·h.

In a marked contrast, Rh(NO₃)₃ on TiO₂ showed a slight influence of the evacuation temperature, similar activities around 200mmolCO/g-Rh·h being obtained by the evacuation at 473 to 773K after the reduction at 673K for 2h.

Product distributions on the catalysts are also summarized in Table 1. Although methane was the principal product in every cases, there were observed some changes of product distributions due to the evacuation temperature. The content of olefinic hydrocarbons was as low as 55% over the catalyst of the highest activity prepared from RhCl₃/TiO₂, indicating a high activity for hydrogenation, however the selectivity for methane was least on the catalyst. The higher evacuation temperature decreased slightly the content of C₅~C₇ hydrocarbons, but increased the content of C₂~C₄ hydrocarbons markedly. It should be noted that better carbon balance was obtained on the catalyst. Thus the most active catalyst to provide C₂~C₇ parafins most selectively is very suitable.

Discussion

The evacuation around 773K after the reduction at 673K was found to enhance remarkably the initial catalytic activity of RhCl₃ on TiO₂.

The evacuation should modify the natures as well as number of active sites on Rh/TiO₂. Although the electronic natures of Rh on TiO₂ are not directly revealed yet in the present study, behaviors of the chlorine derived from RhCl₃ are one of the key factors for the activity enhancement by the evacuation. The remaining chlorine (Cl/Rh = 0.36) after the reduction in hydrogen atmosphere at 673K followed by the evacuation at 473K may hinder the favorable influences of TiO₂ on supported Rh to exhibit the highest activity. The evacuation above 673K decreased the level of Cl/Rh to be 0.02, providing the highest activity. Its complete liberation was achieved by the evacuation above 823K where the catalytic activities were decreased. Thus, the less content of chlorine is not directly connected to the high activity since Rh(NO₃)₃/TiO₂ certainly free from chlorine failed to exhibit very high activity. The liberation of chlorine may allow the full activation of metal catalyst by the support.

Too high evacuation temperature may sinter the support as well as the supported metal to decrease the activity.

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