CHEMISTRY LETTERS, pp. 913-914, 1986.

MORPHOLOGY OF Ru PARTICLES ON Al_2O_3 AND ITS EFFECT ON SELECTIVITY IN CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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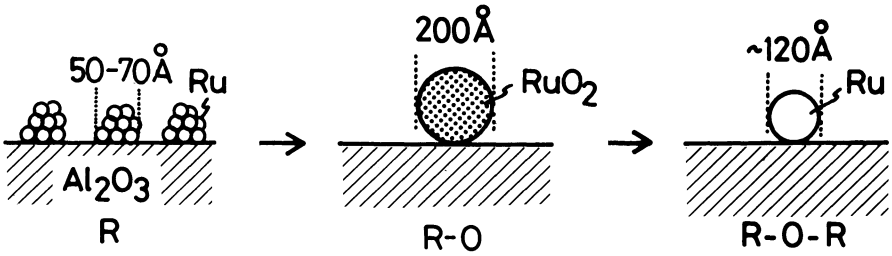
Ru particles dispersed on Al_2O_3 were characterized by TEM, XRD, and H_2 adsorption. It was shown that, after reduction by H_2, Ru particles were aggregates of fine particles, and by oxidation and subsequent reduction they changed to large single crystallites of Ru. This change affected significantly the selectivity of CO hydrogenation in contrast to previous reports obtained for Ru/Al_2O_3 pretreated only by H_2.

Several investigators reported that the carbon number distribution of Fischer-Tropsch synthesis over Ru/Al_2O_3 was independent of the Ru particle size.$^{1-3)}$ But we found that oxidation-reduction treatment changed the selectivity of Ru/Al_2O_3 very much. Characterization of the metal particles by TEM (transmission electron microscopy), XRD (X-ray diffraction) and H_2 adsorption showed that this difference was due to the change in the morphology of metal particles.

Ru/Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 with an aqueous solution of $RuCl_3$ as described previously.$^{3)}$ The contents of Ru were changed from 0.5 to 10 wt%. The catalysts were reduced by 101 kPa of H_2 at 450 °C for 2 h (this treatment is abbreviated as *R*). Some of them were further oxidized at 500 °C with 13 kPa of O_2 and subsequently reduced by H_2 at 450 °C (abbreviated as *R-O-R*). TEM and H_2 adsorption were carried out as described previously.$^{4)}$ XRD patterns were measured in air, and the particle size was estimated from the line width of the XRD peaks.$^{5)}$ CO hydrogenation was performed in a flow reactor at 260 °C under 1 atm ($H_2/CO = 2$) as described previously.$^{4)}$ Hydrogenolysis of butane was carried out in a closed circulation system under 5.45 kPa of butane and 10.9 kPa of H_2 at 100 °C.

Some of the Ru particle sizes determined are given in Table 1. The Ru particle size on 2.5%Ru/Al_2O_3 after *R* was estimated to be 50-70 Å from the data of H_2 adsorption and TEM, but the XRD peaks due to Ru metal were not detected. If these Ru particles are single crystallites, XRD peaks of Ru should be observed.$^{6,7)}$ Therefore, Ru on 2.5%Ru/Al_2O_3 is likely to be aggregates (50-70 Å) consisting of fine particles. After oxidation at 500 °C, these particles changed to RuO_2 crystallites (2θ = 28.1, 35.2, 54.4°) having diameters of 200 Å. By the subsequent reduction (*R-O-R*), RuO_2 was reduced to Ru metal (120 Å (TEM, H_2 adsorption) and 160 Å(XRD)).

The changes in the morphology of Ru by these treatments may be illustrated as below.



Turnover frequency (TOF) and selectivity for the CO hydrogenation and the butane hydrogenolysis are also given in Table 1. The trends in TOF of both reactions were consistent with those reported previously.[8,9] It is remarkable that the selectivities were greatly different between the two series of catalysts (*R* and *R-O-R*), although the similar selectivity was obtained for each series. That is, the higher hydrocarbons were significantly formed after *R* and mostly methane for *R-O-R*. This is in marked contrast to previous reports which claimed that the selectivity over Ru/Al_2O_3 little changed in the range of particle size from 10 Å to about 50 Å.[1,2] Present result for Ru with 20-80 Å (after *R*) is consistent with these previous data. In the literature, Ru/Al_2O_3 having large Ru particle sizes were all prepared from $RuCl_3$ and only treated with H_2, as *R* in the present work. Therefore, the particles may be polycrystallites and this is probably the reason why the selectivity was little dependent on the particle size. The selectivity of the hydrogenolysis of butane was also dependent on the morphology as shown in Table 1. The present result may be the first example to show that the morphology of metal is an important factor determining the selectivity of supported metals.

Table 1. Size of Ru Supported on Al_2O_3, and TOF and Selectivity of the Reactions

wt% of Ru	Treat-ment	Size of Ru/Å			CO + H_2		C_4H_{10} + H_2	
		H_2 a)	EM	XRD	TOF b)	$C_1/C_2(+)$ c)	TOF b)	$C_1/(C_2+C_3)$ c)
0.5	*R*	20	n.d. d)	n.d. d)	1.3	0.7	42.0	0.7
2.5	*R*	46	71	n.d. d)	4.0	0.9	19.0	0.4
10.0	*R*	76	85	(96) e)	6.6	1.1	6.6	0.6
0.5	*R-O-R*	83	- f)	- f)	2.3	3.3	12.5	1.2
2.5	*R-O-R*	119	120	160	1.7	4.8	14.0	2.0
10.0	*R-O-R*	415	181	210	3.5	4.0	20.4	1.3

a) H_2 adsorption. b) $10^{-2}s^{-1}$. c) Ratio of methane to ethane and higher hydrocarbons in weight percentage. d) Not detected. e) Weak. f) Not measured.

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(Received March 10,1986)