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EFFECT OF METAL DISPERSION ON THE ACTIVITY AND SELECTIVITY OF Rh/SiO_2 CATALYST FOR HIGH PRESSURE CO HYDROGENATION

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Metal dispersion has a striking influence on the activity and selectivity of Rh/SiO_2 for high pressure CO hydrogenation. Decreasing dispersion, turnover frequency of CO conversion does not change significantly with dispersion up to 0.5 but increases abruptly at dispersion of 0.45. CH_3OH is produced selectively at high dispersion. C_2-oxygenated compounds are produced favorably for dispersion of 0.25-0.45. CH_4 formation increases monotonously with decrease of dispersion.

Metal dispersion is supposed to be one of main factors of controling the activity and selectivity for a catalytic reaction. For CO hydrogenation, the influence of metal dispersion of supported transition metal catalyst such as Pt,1) pd,1) Ni,2) and Ru3) has been studied. But it is not known clearly about supported Rh catalyst yet, especially for the high pressure CO hydrogenation. Rh catalyst has been known as a good catalyst for the formation of C_2-oxygenated compounds at high pressure.4)

The present study was performed to determine the metal dispersion effects of Rh/SiO_2 catalyst for high pressure CO hydrogenation with special interest in C_2-oxygenated compounds formation. We will report here the first observation of striking influence of metal dispersion on the activity and selectivity of Rh/SiO_2 catalyst.

Eight Rh/SiO_2 catalysts were prepared by impregnation of SiO_2(Davison grade #57, 16-32 mesh) with a methanol or an aqueous solution of $RhCl_3 3H_2O$. Before impregnation process, SiO_2 was evacuated at 200 °C for 2 h. Catalyst were dried up at 120 °C for 3 h finally by rotary evaporator and reduced with hydrogen at 400 °C for 4 h. High pressure reaction was conducted in a flow type fixed-bed stainless steel microreactor. The reactant gas and all the products from the reactor were kept hot and directly introduced gas chromatograph. Four GC columns such as PEG1500 for alcohols and esters, PEG6000 for acids, VZ10 for hydrocarbons, and squalane for inert gases were used for products analysis.

Table 1. Rh dispersion and Rh average particle size of prepared Rh/SiO_2 catalysts

Catalyst	Adsorbed H_2 (mlSTP/g-cat.)	Rh dispersion (H/Rh)	Average particle[b] size of Rh/ Å	Average particle[c] size of Rh/ Å
1.0%Rh/SiO_2	0.89	0.82	14	
2.0%Rh/SiO_2	1.08	0.50	23	
4.7%Rh/SiO_2	2.26	0.44	26	28
4.7%Rh/SiO_2 a)	1.84	0.36	31	
9.0%Rh/SiO_2	3.14	0.32	35	39
14.2%Rh/SiO_2	3.57	0.23	48	
23.0%Rh/SiO_2	6.47	0.26	43	46
30.0%Rh/SiO_2	6.61	0.20	55	

a) Water was used as a impregnation solution.
b) Estimated from dispersion.
C) Estimated from X-ray diffraction line broadening.

Table 2. Reaction behavior of prepared Rh/SiO_2 catalysts

Catalyst	CO conversion	Product selectivity in carbon efficiency / %					
	%	MeOH[b]	AcH	EtOH[b]	AcOH[b]	C_2-oxy.	CH_4
1.0%Rh/SiO_2	0.36	69.1	0.0	18.5	4.4	22.8	2.5
2.0%Rh/SiO_2	0.45	39.6	3.0	22.8	16.7	42.5	10.1
4.7%Rh/SiO_2 a)	1.18	11.4	14.0	19.3	30.2	63.5	20.9
4.7%Rh/SiO_2	4.00	3.4	33.9	17.6	23.8	75.3	16.0
9.0%Rh/SiO_2	11.55	1.2	36.6	11.6	21.6	69.7	23.1
14.2%Rh/SiO_2	16.37	1.9	39.7	9.0	16.7	65.4	25.7
23.0%Rh/SiO_2	30.22	2.0	36.7	7.4	14.3	58.3	31.3
30.0%Rh/SiO_2	27.85	2.8	28.2	5.7	17.6	51.6	31.6

Reaction conditions:

Catalyst charge:1.0 g, reaction temperature: 280 °C, reaction pressure:50 kg/cm^2, flow rate:100 ml/min, syngas ratio(H_2/CO):1, data were obtained at a time-on-stream of 20 h.

a) Water was used as a impregnation solution.
b) Sum of neat product and ester.
MeOH:CH_3OH, AcH:CH_3CHO, EtOH:C_2H_5OH, AcOH:CH_3COOH, C_2-oxy.:C_2-oxygenated products.

Table 1 shows Rh dispersion and average Rh particle size of prepared Rh/SiO_2 catalysts. The Rh particle size estimated from dispersion is in good accordance with that estimated from X-ray diffraction line broadening. Rh dispersion varies from 0.2 to 0.8 with decrease of Rh loading. It has been proved taht it is possible to control Rh dispersion of Rh/SiO_2 catalyst by changing Rh loading.

Table 2 lists the reaction data on these Rh/SiO_2 catalysts which denote the stationary conversions and selectivities obtained at 20 h after the feed was initiated. CO conversion increases with increase of Rh loading of the catalysts. Product selectivities are obviously much different among the catalysts.

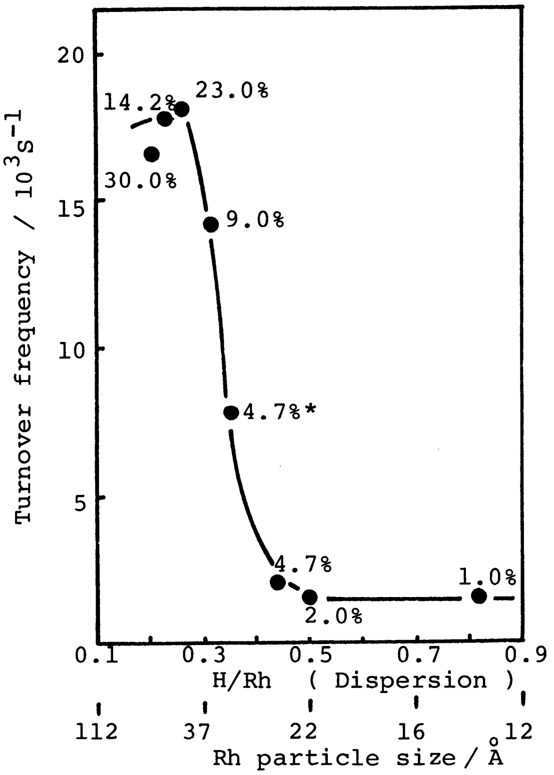

Fig.1. Relationship between dispersion and activity.

*: Water was used as a impregnation solution of catalyst preparation.

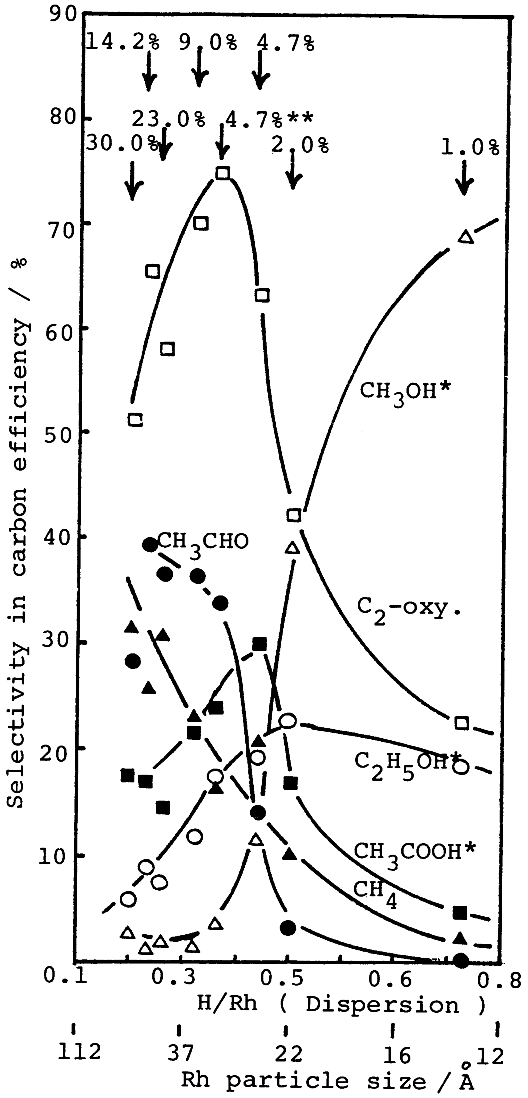

Fig.2. Relationship between dispersion and selectivity.

Footnotes of Fig.2.

*: Sum of neat product and ester.

**: Water was used as a impregnation solution of catalyst preparation.

C_2-oxy.:C_2-oxygenated compounds.

The relationship between turnover frequency of CO conversion and Rh dispersion of each catalyst is shown in Fig. 1, which shows clearly that Rh dispersion affects the activity greatly. Decreasing dispersion, turnover frequency of CO conversion does not change remarkably until 0.5 but increases abruptly ai about 0.45 and attains a maximum at dispersion around 0.25.

Figure 2 shows the relationship between product selectivity and Rh dispersion of each catalyst. The striking influence of Rh dispersion on the selectivity has been proved. CH_3OH formation proceeds selectively at high dispersion such as 0.8 but decreases dramatically with decrease of Rh dispersion. On the other hand, CH_3CHO formation increases abruptly at about 0.5 with decrease of dispersion. CH_3COOH and C_2H_5OH formations become a maximum at dispersion range of 0.4-0.5. CH_4 formation increases monotonously with decrease of Rh dispersion. As a result, it has been clarified that the dispersion range of 0.3-0.5 is favorable for the C_2-oxygenated compounds formation for high pressure CO hydrogenation over Rh/SiO_2 catalyst.

The reason of this striking influence of Rh dispersion on the activity and selectivity for CO hydrogenation is now being investigated and will be discussed in future.

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