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THE SMSI EFFECT ON THE ACTIVITY OF CO HYDROGENATION OVER Nb_2O_5-SUPPORTED Rh CATALYSTS

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In contrast to the case of the TiO_2-supported systems, the activities of CO hydrogenation on Rh/Nb_2O_5 catalysts in the SMSI state were two orders of magnitude lower than in the normal state. The product selectivity appeared to be similar between the normal and SMSI states, but to depend on the metal particle size.

Since Tauster et al.[1)] reported that TiO_2-supported Group VIII metal catalysts exhibited the SMSI (Strong metal-support interaction) behavior, a number of papers have shown that the catalytic activity and selectivity of the TiO_2-supported metals could be influenced by the SMSI.[2)] Especially, extensive works by Vannice et al.[3)] showed that the TiO_2-supported metal catalysts exhibit a very high activity for the CO + H_2 reaction, and they suggested that these enhancements are due to the SMSI effect.[4)] On the other hand, little attention has been paid to the Nb_2O_5-supported system, which was also reported to exhibit the SMSI behavior (i.e., the suppression of hydrogen chemisorption after the high-temperature H_2 treatment).[5)] This paper first reports the effect of SMSI on CO hydrogenation over Rh/Nb_2O_5 catalysts.

The Nb_2O_5 support (BET, 40 m^2/g) was obtained by calcining $Nb_2O_5 \cdot nH_2O$ (CBMM International LTDA, AD-32) in air at 773 K for 1 h. Two Rh/Nb_2O_5 catalysts (0.5 and 5.0 wt%) were prepared by impregnating the Nb_2O_5 powder with an aqueous $RhCl_3$ solution. The 0.5 wt% catalyst (designated by A) was reduced in a flow of hydrogen at 473 K for 1 h, and the 5.0 wt% catalyst (designated by B) was calcined in air at 973 K for 30 h. The CO + H_2 reactions over these catalysts were carried out in a closed circulating system (670 cm^3; CO/H_2 = 1/2, 66.7 kPa) with a liquid N_2 trap. The activities were measured at the CO conversion between 1 and 5%, and the products were analyzed by GC-MS (ANNELVA, TE-600S) and a gas chromatograph. Before each catalytic reaction, the catalyst (0.5 - 1.0 g) was treated in O_2 at 673 K followed

TABLE 1. Changes in the amount of H_2 chemisorption (H/Rh) after the H_2 treatments at different temperatures.

Catalyst		Temperature of the hydrogen treatment		
	Rh(wt%)	473 K(Normal)	573 K	773 K(SMSI)
A	0.5	0.35	0.18	0.03
B	5.0	0.037	0.011	0.00

by the H_2 treatment at different temperatures (473, 573, or 773 K) and evacuation *in vacuo* at 723 K, and the amount of H_2 chemisorption was measured *in situ* at room temperature. The time of each treatment step was 1 h, and the space velocity of O_2 or H_2 was 3000 h^{-1}.

Table 1 shows the H/Rh (chemisorbed H atoms/total Rh atoms) ratios after the H_2 treatments at the different temperatures. The suppression of hydrogen chemisorption was observed by increasing the temperature of the H_2 treatment. It should be noted that the H/Rh ratios (0.35 and 0.037) were reproducible if the samples, which had been reduced in H_2 at 773 K, were retreated in O_2 at 673 K followed by the H_2 treatment at 473 K. These behaviors are in good accordance with those of the TiO_2-supported metal catalysts,1) and indicate that the SMSI state was induced by the H_2 treatment at 773 K in these Rh/Nb_2O_5 catalysts.

Figure 1 shows the effect of the pretreatment temperature on the specific activities of the CO + H_2 reaction on the two catalysts. Note that the turnover frequencies were based on the H/Rh values after the H_2 treatment at 473 K (i.e., the number of chemisorbed H atoms in the normal state). The catalytic activities in the SMSI state fell by a factor of 10^2. The catalysts after the H_2 treatment at 573 K showed the intermediate catalytic activities. These results are quite different from the case of the TiO_2-supported Pt and Pd systems, where the most active catalysts were, reportedly, the ones in the SMSI state.4) Sulfur poisoning of the metal is unlikely to explain this behavior, since the sulfur content of the Nb_2O_5 support was 12 ppm (only ca. 0.4 μmol/g·Nb_2O_5). It is suggested that the nature of SMSI in the Nb_2O_5-supported system may be different from that in the TiO_2-supported system.

It is interesting to note that SMSI caused a marked decrease in catalytic activity for other reactions such as the hydrogenolysis of n-butane and ethane in the case of the TiO_2-supported metal catalysts.2) This tendency is similar to the case of Rh/

TABLE 2. Activity and selectivity of Rh/Nb_2O_5 catalysts at 443 K (in the normal state) and at 503 K (in the SMSI state).

Catalyst		Product selectivity/% a)							T.F.b) x 10^4
		C_1	(C_2-C_4)	$(C_2-C_4)^=$	C_{5+}	MeOH	EtOH	CO_2	s^{-1}
A	Normal	26.7	18.8	33.4	20.9	trace	trace	0.2	3.78
	SMSI	44.0	14.2	34.0	6.7	0.3	trace	0.8	7.13
B	Normal	18.8	5.8	39.0	22.5	0.8	8.5	4.6	3.81
	SMSI	19.9	5.7	40.9	23.4	0.6	4.5	5.0	7.43

a) carbon base; namely, $100n\ C_n/\Sigma n\ C_n$, where C_n is the concentration (mol%) of the product molecule, and n is the number of carbon atoms in the product molecule.

b) based on the H/Rh values in the normal state (Table 1).

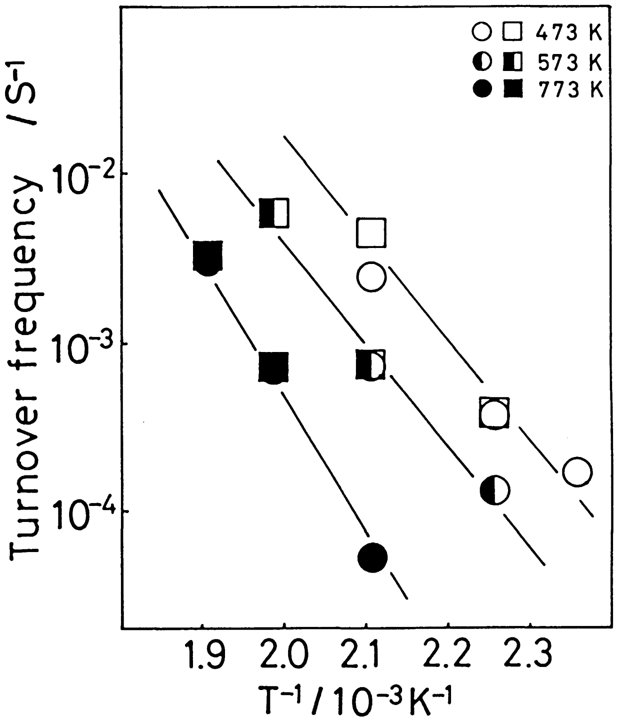

Fig.1. Arrhenius plots for the rates of the CO + H_2 reaction over Rh/Nb_2O_5 catalysts (A, circles; B, squares). The temperatures of the H_2 treatment are indicated in the figure.

Nb_2O_5 catalysts.[6)] Therefore, the behavior of the TiO_2-supported metal catalysts for the CO + H_2 reaction is unique and one of current topics in the field of metal-support interaction in supported metal catalysts.[7)] Further work will be needed to elucidate the reason why the difference in the behaviors exists between the Nb_2O_5 and TiO_2 supports in the case of CO hydrogenation.

Table 2 shows an example of the product distribution for the two catalysts. It seems that the product selectivity is not so different between the normal and SMSI states as the difference in the catalytic activity. Note that the activity in the SMSI state was so low at 443 K that it was difficult to compare the selectivity at the same temperature. On the other hand, it may be noted that a considerable amount of ethanol was produced on the catalyst B even in the SMSI state at the higher reaction temperature (503 K), while no oxygenated compounds was formed on the catalyst A. The olefin/paraffin ratio in the C_2 - C_4 components was also different between A and B. These selectivities seem to depend on the metal dispersion. However, Table 2 and Fig.1 suggest that the turnover frequency (T.F.) did not differ between the high and low dispersion of catalysts. More detailed studies of the CO + H_2 reaction over the Rh/Nb_2O_5 catalysts are now in progress in comparison with the case of Rh/TiO_2 catalysts.

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