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Ruthenium–Niobia Interaction in Nb_2O_5-Supported and Nb_2O_5-Modified Ru Catalysts

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The effect of H_2 reduction treatments on H_2 chemisorption, ethane hydrogenolysis, and CO hydrogenation over Nb_2O_5-supported and Nb_2O_5-modified Ru catalysts has been studied to elucidate the nature of the metal-oxide interaction, and the results are compared with those of a SiO_2-supported Ru catalyst. The Ru/Nb_2O_5 and Nb_2O_5–Ru/SiO_2 catalysts after high-temperature reduction at 500 °C showed a typical SMSI behavior, while a specific Ru–niobia interaction, which resulted in a higher ethane hydrogenolysis activity, was induced even after low-temperature reduction at 200 °C.

There has been much interest in the strong-metal support interactions (SMSI) as well as in the effect of oxide promoter in supported metal catalysts.[1,2] The so-called SMSI refers to the peculiar interactions occurring between metal particles and a reducible oxide, like TiO_2 and Nb_2O_5. In the SMSI state, specific catalytic and chemisorptive behaviors appear: Hydrogen chemisorption ability and alkane hydrogenolysis activity decrease drastically after high-temperature reduction (HTR) at 500 °C.[1—3] The case of TiO_2-supported metal catalysts has been widely studied since the work of Tauster and co-workers.[4] However, relatively little attention has been paid to Nb_2O_5-supported metal catalyst systems.

Ko et al.[5,6] studied Ni-niobia interaction in Nb_2O_5-supported and Nb_2O_5-modified Ni catalysts, which exhibit typical SMSI behavior, and the extent of the SMSI interaction has been studied from the activities of ethane hydrogenolysis (as a test reaction). We have studied extensively **Rh**–niobia interaction in Nb_2O_5-supported (**Rh**/Nb_2O_5) and Nb_2O_5-modified (Nb_2O_5–**Rh**/SiO_2) systems.[7—9] The **Rh**-niobia interaction in the Nb_2O_5–**Rh**/SiO_2 catalysts was as strong as that in the **Rh**/Nb_2O_5 catalysts; i.e., the ethane hydrogenolysis activity decreased with increasing catalyst reduction temperature (e.g., depression of about 4 to 7 orders of magnitude after HTR at 500 °C compared with low-temperature reduction (LTR) at 100 °C).[8—10] From these results and other evidences, so called "decoration model" has been proposed as a model of SMSI: The presence of a reduced oxide (NbO_x) on the metal surface may physically block active sites, affecting a large ensemble of atoms to constitute the active sites (geometric effect).[1—3]

On the other hand, no work has been published for the extent of the SMSI interaction in a Ru-niobia system except the one by our group.[11] We have recently studied NH_3 synthesis reaction over Nb_2O_5-supported and Nb_2O_5-modified Ru catalysts.[11] We will report here the nature of Ru-niobia interaction in the Ru catalysts from H_2 chemisorption and ethane hydrogenolysis studies. Moreover, the effect of the Ru-niobia interaction on CO hydrogenation is reported, and the results are compared with those of a non-SMSI Ru/SiO_2 catalyst.

Experimental

Ru/Nb_2O_5 and Ru/SiO_2 catalysts (5 wt% Ru) were prepared by incipient wetness impregnation of Nb_2O_5 (CBMM International LTDA)[7] and SiO_2 (JRC-SIO-3)[12] with an aqueous ruthenium(III) chloride solution, followed by H_2 reduction at 500 °C for 1 h. A Nb_2O_5-modified Ru/SiO_2 catalysts was prepared by incipient wetness impregnation of the Ru/SiO_2 catalyst with an aqueous solution of $(NH_4)_3[Nb(C_2O_4)_3O]$, followed by air calcination at 500 °C for 3 h to decompose the niobia precursor. The Nb_2O_5 loading was chosen so that the Nb/Ru atomic ratio was 3.0.

The H_2 chemisorption measurements were carried out in a conventional volumetric adsorption apparatus, and detailed procedures were described before.[13] The amount of total H_2 chemisorption uptake was expressed in terms of H/Ru (the ratio of the number of adsorbed H atoms to the number of total Ru atoms). The catalytic activity measurements for the ethane hydrogenolysis reaction were performed in a microcatalytic pulse reactor.[7—9] Before use the catalysts were treated in O_2 flow at 500 °C for 1 h in the catalytic reactor. For each measurement, pretreatment of the catalyst was made:[7—9] O_2 oxidation at 400 °C for 1 h, followed by H_2 reduction for 1 h at different temperatures (100—500 °C). CO hydrogenation reaction was carried out by using a high-pressure flow reactor system used for the NH_3 synthesis study.[11] The reaction was carried out at 20 $kg\,cm^{-2}$ using a 1 : 2 mixture of CO and H_2 (W/F=10 gh/CO-mol). The XRD measurements were performed by an X-ray diffractometer (Rigaku Co. , Ltd.) equipped with a graphite monochromator for Cu $K\alpha$ radiation (40 kV, 30 mA).[9,10] The mean Ru particle size was calculated from the XRD line broadening measurement using the Scherrer equation,[14] and the Ru dispersion was calculated from the mean particle size assuming the spherical metal particles.[15]

Results and Discussion

H_2 Chemisorption. Table 1 shows the Ru particle sizes from the XRD measurements and the H/Ru values from the H_2 chemisorption studies. For the Ru/SiO_2 catalyst, the H/Ru value (0.061) after the LTR treatment is roughly in reasonable agreement with the Ru dispersion determined by XRD. No big change of the H/Ru value was observed after the HTR treatment of the Ru/SiO_2 catalyst. On the other hand, the

Table 1. Ru Dispersion Measured by XRD and H_2 Chemisorption Value (H/Ru)

Catalyst	XRD		H/Ru[a)]	
	d(nm)[b)]	Dispersion	HTR[c)]	LTR[d)]
Ru/SiO_2	13.4	0.070	0.054	0.061
Ru/Nb_2O_5	9.2	0.098	0.0022	0.011
Nb_2O_5–Ru/SiO_2	13.4	0.070	0.0031	0.039

a) The number of chemisorbed H atoms/the number of total Ru atoms. b) Mean size of Ru particles determined from XRD. c) After high-temperature reduction (HTR) at 500 °C. d) After HTR, O_2 treatment at 400 °C followed by low-temperature reduction (LTR) at 200 °C.

H/Ru values for the niobia-supported (Ru/Nb_2O_5) and niobia-modified (Nb_2O_5–Ru/SiO_2) catalysts were decreased significantly after HTR. The changes in the H/Ru value were reversible: The H_2 chemisorption capacity was restored by O_2 treatment at 400 °C followed by LTR at 200 °C. This phenomenon is characteristic of SMSI behavior.[1—3)] It should be noted that the H/Ru value of the Nb_2O_5–Ru/SiO_2 catalyst was significantly less than that of the unmodified Ru/SiO_2 catalyst, which suggests that the Ru surface was partially covered with niobia (NbO_x) even after LTR at 200 °C. Such Ru–niobia interaction may also be present for the Ru/Nb_2O_5 catalyst after LTR at 200 °C, since the H/Ru value after LTR was significantly lower than the Ru dispersion evaluated by the XRD line broadening measurement (Table 1). The similar phenomenon (i.e., the decoration with NbO_x even after LTR) was also observed for the Nb_2O_5-modified **Rh**/SiO_2 catalysts.[9)] On the other hand, we have reported that **Rh**NbO_4 was formed during O_2 calcination of the Nb_2O_5–**Rh**/SiO_2 catalaysts at a high temperature (e.g., 700 °C).[10,16,17)] In the case of the present Ru catalysts, however, the XRD study showed no evidence for the formation of a Ru–Nb double oxide during the O_2 treatment.

Ethane Hydrogenolysis. Figure 1 shows the ethane hydrogenolysis activities of the Ru/SiO_2 and Nb_2O_5–Ru/SiO_2 catalysts as a function of catalyst reduction temperature. No change in the activity was observed for the unmodified Ru catalyst. On the contrary, the catalytic activity of the Nb_2O_5-modified Ru catalyst was decreased drastically with increasing the reduction temperature (Nos. 3 and 4, filled circles). The degree of the activity suppression after HTR at 500 °C was about 4 orders of magnitude, compared with that after LTR at 100 °C. The catalyst showed the typical SMSI behavior as shown in Fig. 1: The activity is increased by O_2 treatment at 400 °C followed by LTR at 100 °C (No. 5), and decreased again after HTR at 500 °C (No. 7). It should be noted that the activities after LTR at 100 °C and at 200 °C (Nos. 1 and 2, filled circles) were much higher than those of the Ru/SiO_2 catalyst (Nos. 1 and 2, open circles). Such higher activities were not observed in the case of the Nb_2O_5–**Rh**/SiO_2 catalysts: The catalytic activities were lower than or similar to those of the corresponding unmodified **Rh**/SiO_2 catalysts.[8,9,14)]

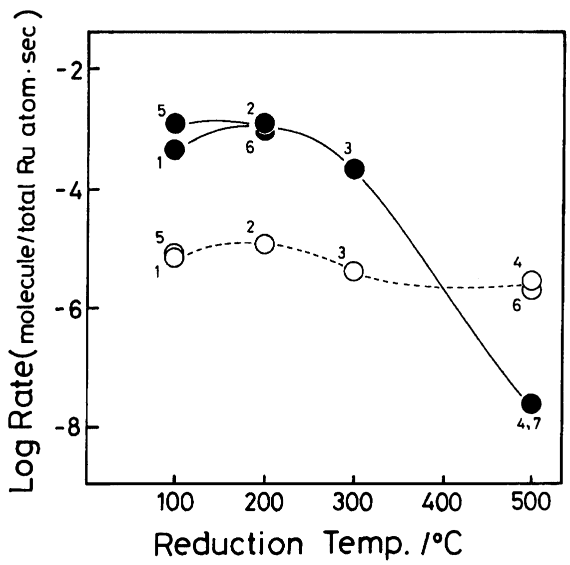

Fig. 1. Changes in the ethane hydrogenolysis activity (at 112 °C) after the sequential oxidation–reduction treatments: open circles, the Ru/SiO_2 catalyst; filled circles, the Nb_2O_5–Ru/SiO_2 catalyst. The numbers in the figure mean the order of the H_2 treatment preceded by the O_2 treatment at 400 °C.

Figure 2 shows the ethane hydrogenolysis activities of the Ru/Nb_2O_5 catalyst as a function of catalyst reduction temperature. The activity was relatively low after LTR (Nos. 1 and 2), probably due to the incomplete reduction of ruthenium oxide to ruthenium metal by the

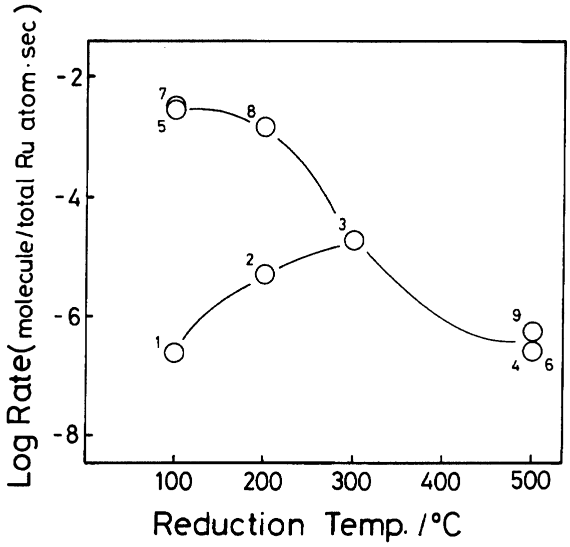

Fig. 2. Change in the ethane hydrogenolysis activity (at 112 °C) after the sequential oxidation–reduction treatments of the Ru/Nb_2O_5 catalyst. The numbers in the figure mean the order of the H_2 treatment preceded by the O_2 treatment at 400 °C.

Table 2. Activity and Selectivity of CO Hydrogenation over the Ru Catalysts (at 250 °C)

Catalyst	Pretreatment[a]	Activity[b]	TOF[c]	Selectivity (%)[d]					
				C_1	[C_2–C_4]	[C_2–C_4]$^=$	C_{5+}	CO_2	Oxy[e]
Ru/SiO_2	LTR	1.2	2.0	6.6	17.9	18.2	55.9	1.4	0
	HTR	1.2	2.4	4.0	20.7	17.5	55.6	2.2	0
Ru/Nb_2O_5	LTR	0.88	8.0	19.3	14.1	25.5	38.5	1.7	0.9
	HTR	0.15	7.5	Trace	23.5	41.4	16.7	9.1	9.3
Nb_2O_5–Ru/SiO_2	LTR	0.55	1.4	23.6	13.4	24.3	34.3	2.9	1.5
	HTR	0.060	1.9	Trace	26.4	29.2	30.1	9.3	5.0

a) LTR: H_2 treatment at 200 °C; HTR: H_2 treatment at 500 °C. b) $\times 10^{-2}$ molecules converted per total Ru atoms per sec. c) $\times 10^{-1}$ s^{-1} ; based on the H/Ru values. d) Carbon base. e) C_2–C_4 oxygenates.

LTR treatments. Once the catalyst was reduced by the HTR treatment at 500 °C, it showed the typical SMSI behavior (No. 4 to No. 9 in Fig. 2). The activity change between LTR and HTR was about 4 orders of magnitude, which suggests that the extent of the Ru-niobia interaction is similar to that of the Nb_2O_5–Ru/SiO_2 catalyst.

CO Hydrogenation. Table 2 shows the results of the CO+H_2 reaction over the Ru catalysts. For the Ru/SiO_2 catalyst, there was almost no change in the activity and selectivity between LTR and HTR. For the Ru/Nb_2O_5 and Nb_2O_5–Ru/SiO_2 catalysts, the activity was suppressed significantly after HTR. However, the TOF values appeared to be similar between LTR and HTR, if calculated by using the H/Ru values. The activity suppression after HTR was also observed in the **Rh**/Nb_2O_5 catalyst system,[3,18] and a detailed discussion on the effect of SMSI on the activity of CO hydrogenation over the **Rh** catalysts has been made in the Ref. 3. The product selectivity (see Table 2) was changed significantly after HTR: The CH_4 formation was suppressed severely, and the olefin/paraffin ratio ([C_2–C_4]$^=$/[C_2–C_4]) and the C_2–C_4 oxygenates increased.

In contrast to the case of the ethane hydrogenolysis reaction, the CO+H_2 activity of the Nb_2O_5–Ru/SiO_2 catalyst after LTR was lower than that of the Ru/SiO_2 catalyst. However, it is noteworthy that the rate of CH_4 formation was increased for the Nb_2O_5–Ru/SiO_2 and Ru/Nb_2O_5 catalysts after LTR, as shown in Table 2. A specific Ru–niobia interaction, which increases the ethane hydrogenolysis activity as well as the CH_4 formation rate in CO hydrogenation, may be induced by the niobia promoter even after LTR. From our recent study of the N_2+H_2 reaction over the Ru catalysts,[11] the NH_3 synthesis activity after LTR was higher than that of the Ru/SiO_2 catalyst, and we have proposed an electronic (or ligand) effect for the activation of N_2 molecules as well as the geometric effect due to the decoration of the Ru surface with NbO_x.

In conclusion, the nature of Ru–niobia interaction in the Ru/Nb_2O_5 and Nb_2O_5–Ru/SiO_2 catalysts after the HTR treatment appears to be similar to that of **Rh**–niobia interaction: The decoration of the metal surface with NbO_x (the geometric effect), which results in the decrease in the activities of ethane hydrogenolysis and CO hydrogenation. However, a specific Ru–Nb_2O_5 interaction is present even after LTR, which results in the higher activity of ethane hydrogenolysis. The product selectivity in CO hydrogenation was affected significantly by the Ru–Nb_2O_5 interaction; in particular the CH_4 formation rate was suppressed severely after HTR. Both geometric and electronic effects may be taken into account to elucidate in more detail the nature of the Ru–niobia interaction.

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