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STRONG METAL-SUPPORT INTERACTION (SMSI) BEHAVIOR OF Rh/Nb_2O_5 CATALYST STUDIED BY ETHANE HYDROGENOLYSIS AND HYDROGEN CHEMISORPTION

Kimio KUNIMORI, Katsunori ITO, Kiyoyuki IWAI, and Toshio UCHIJIMA
Institute of Materials Science, University of Tsukuba, Sakura-mura,
Ibaraki 305

The high-temperature (773 K) pretreatment of a Rh/Nb_2O_5 catalyst in He as well as in H_2 caused drastic decrease (by 10^3 in He, by 10^6 in H_2) in the activity of ethane hydrogenolysis. Considering also the behavior of hydrogen chemisorption, there appears to be a difference in the nature of SMSI between Rh/Nb_2O_5 and Rh/TiO_2 systems.

Considerable attention has been given recently to the strong metal-support interaction (SMSI) of Group VIII metals with titania (TiO_2) and other reducible oxides since the work of Tauster et al.[1,2] However, relatively little attention has been paid to the niobia (Nb_2O_5)-supported metal catalysts (e.g., Ni[3], Rh[4]). We have recently studied the SMSI effect on CO hydrogenation over Rh/Nb_2O_5 catalysts, and found the different behaviors from the case of Rh/TiO_2 catalysts.[4] In continuation of the work, ethane hydrogenolysis (a structure-sensitive reaction) has been studied as a probe reaction over the Rh/Nb_2O_5 catalysts. Haller and co-workers[5,6] have studied the same reaction over Rh/TiO_2 catalysts, and found a severe suppression of the activity after the high-temperature H_2 treatment (SMSI behavior). Therefore, it will be useful to compare our results on Rh/Nb_2O_5 with those on Rh/TiO_2.[5,6] This paper first reports the SMSI behavior (including hydrogen chemisorption) for the Rh/Nb_2O_5 system.

The Nb_2O_5 support (BET, 9 m^2/g) was obtained by calcining niobic acid (CBMM International LTDA) in air at 973 K for 1 h. A 0.5 wt% Rh/Nb_2O_5 catalyst was prepared by the incipient wetness impregnation of the Nb_2O_5 powder with an aqueous $RhCl_3$ solution followed by reduction in H_2 at 773 K for 1 h. The activity measurements for the ethane hydrogenolysis reaction were performed in a pulse reactor. The catalyst (1.0 g) was placed in a Pyrex glass tube connected to stainless-steel piping by Swagelock fittings. Purified He gas was used as the carrier gas (flow rate, 70 cm^3/min) and a pulse (1 cm^3/min) of a mixture gas (C_2H_6, 2.7%; H_2, 31.8%; He balance) was injected by a jacketed switching valve purged with He. The impurity level of the carrier gas was less than 0.05 ppm in O_2. Analysis was performed by an on-line gas chromatograph. The reaction rate was calculated from the conversion (below 5%) and a residence time (assumed to be the catalyst bed volume ratioed to the carrier flow rate),[5] and expressed in molecules converted per total Rh atoms per s. Hydrogen chemisorption measurements were carried out by conventional volumetric adsorption apparatus, and

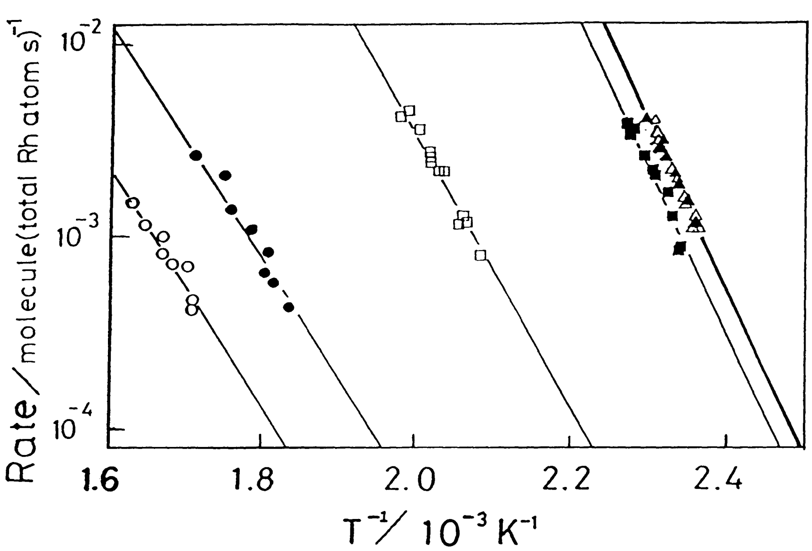

Fig.1. Arrhenius plot of the rate of ethane hydrogenolysis over the Rh/Nb_2O_5 catalyst (effect of the reduction temperature). The O_2 treatment at 673 K was performed before the H_2 treatment at the following temperatures. (The time of each treatment step was 1 h.)

▲ : 373 K △ : 423 K ■ : 473 K □ : 573 K ● : 673 K ○ : 773 K

detailed procedures were described elsewhere.$^{7)}$

Figure 1 shows the effect of reduction temperature on the catalytic activity of ethane hydrogenolysis. There was almost no change in the activity among the data at low-temperature reduction (373, 423, and 473 K). However, the H_2 treatment at high temperatures (573 - 773 K) resulted in the severe suppression of the activity (e.g., by ca. 6 orders of magnitude at 773 K) relative to the low-temperature reduction (373 - 473 K). It should be noted that the phenomena were quite reversible: i.e., the catalytic activity was restored, if the catalyst was retreated in O_2 at 673 K followed by the low-temperature reduction (the SMSI phenomenon). The activation energy appears to be almost constant (ca. 40 kcal/mol) among the data at different reduction temperatures. The effect of high-temperature treatment in the carrier gas (i.e., He) was also studied. As shown in Fig.2, the catalytic activity after the He treatment at 773 K decreased by about three orders of magnitude, compared with the low-temperature reduction at 473 K (open triangle in Fig.2). It should be noted again that the catalytic activity was restored, if the catalyst was retreated in O_2 at 673 K followed by the low-temperature reduction. Figure 3 shows the H_2 chemisorption behavior as a function of the reduction temperature. It has been considered that the reversibly adsorbed hydrogen (H_{rev}), measured by re-adsorption after evacuation in vacuo at room temperature for 10 min, is also associated with Rh metal.$^{7)}$ The amount of total chemisorption (H/Rh value), as well as the reversible one, decreased by increasing the reduction temperature.

The observed SMSI behavior of the Rh/Nb_2O_5 catalyst is reconciled qualitatively

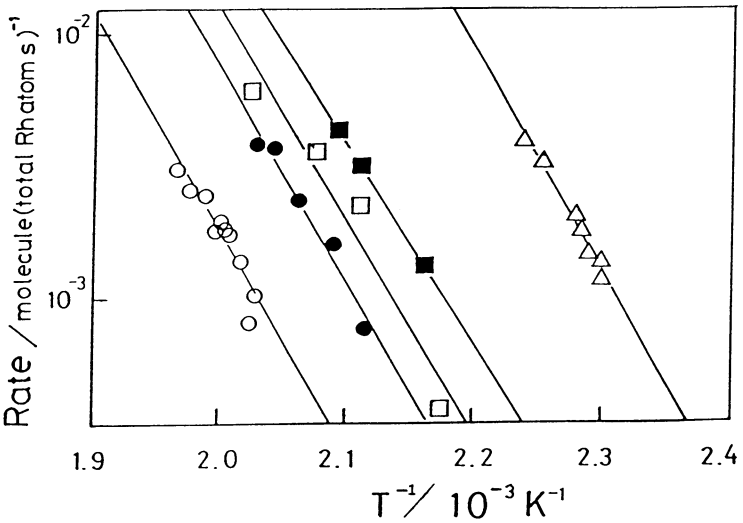

Fig.2. Arrhenius plot of the rate of ethane hydrogenolysis over the Rh/Nb_2O_5 catalyst (effect of the He treatment). The O_2 treatment at 673 K followed by H_2 reduction at 473 K was performed before the He treatment at the following temperatures. (The time of each treatment step was 1 h.)

○ : 773 K ● : 723 K □ : 673 K ■ : 573 K △ : H_2 473 K (reference)

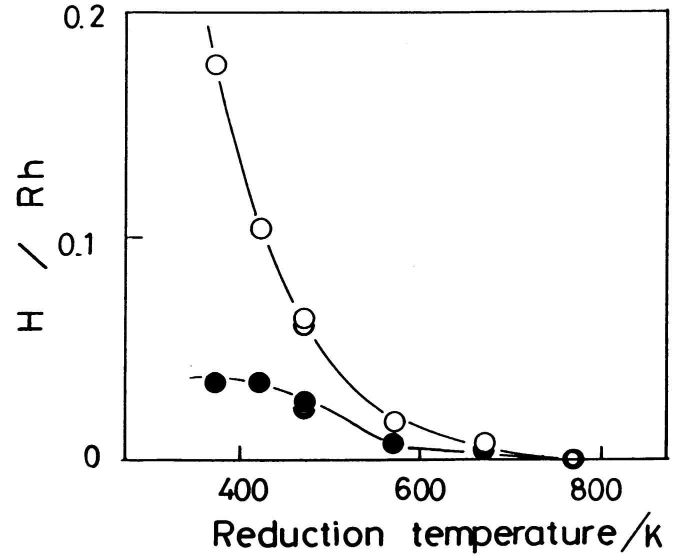

Fig.3. The effect of the reduction temperature on the amount of H_2 chemisorption at room temperature. The Rh/Nb_2O_5 catalyst was pretreated in O_2 at 673 K, followed by H_2 reduction at each temperature and evacuation in vacuo at 723 K. (The time of each treatment step was 1 h.)

○ : total H_2 chemisorption ● : reversible H_2 chemisorption (H_{rev})

with that of the Rh/TiO_2 catalysts.[6,8] However, the present study has revealed some different aspects in the Nb_2O_5-supported system:

(1) The high-temperature H_2 treatment caused much more severe suppression in the

activity of ethane hydrogenolysis than the case of the TiO_2-supported system (e.g., by ca. 10^3 for a low-dispersion Rh/TiO_2 catalyst).[6,8]

(2) The high-temperature He treatment also resulted (at least partly) in SMSI state.

(3) The H/Rh value decreased signigicantly when the reduction temperature was raised from 373 K to 473 K, although there was no change in the catalytic activity after the H_2 treatment at the low temperatures (373 - 473 K).

The observed effect of the high-temperature treatment in the inert gas (He) may be consistent with a model for SMSI, migration of reduced species (TiO_x) of the support onto the metal particle, recently proposed for the Rh/TiO_2 system.[8] In our Rh/Nb_2O_5 system, it is likely that NbO_x produced at the low-temperature H_2 reduction starts the accelerated migration at the higher temperature even in the inert gas. The depression of the hydrogenolysis activity following the high-temperature treatment may be caused by the migration of molecular NbO_x from the support over the Rh particle.

It has been considered that, in the TiO_2-supported system, the low-temperature reduction at 473 K leads to the normal chemisorption behavior.[1] The abnormal H_2 chemisorption behavior (the drop from 373 K to 473 K) in the Rh/Nb_2O_5 catalyst even after the low-temperature reduction may be, in part, due to the effect of the evacuation in vacuo at the high temperature (723 K) before the adsorption measurement, because the evacuation may be essentially the same as the treatment in the inert gas. A proper method should be exploited for the evaluation of the true percentage exposed in this system.

Summing up, there appears to be some difference in the nature of SMSI between Rh/Nb_2O_5 and Rh/TiO_2. Possible interpretation may be the difference in the chemical and/or geometrical nature of NbO_x and TiO_x. However, further extensive study of metal/Nb_2O_5 system will be needed for detailed understanding of SMSI phenomenon.

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