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STRONG RHODIUM-NIOBIA INTERACTION ON SILICA SURFACE FORMED BY HIGH-TEMPERATURE CALCINATION TREATMENT

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Air calcination of a Rh-Nb_2O_5/SiO_2 catalyst (Nb : Rh = 1 : 1) at high temperature (900 ° C) produced a single phase of $RhNbO_4$ detected by X-ray diffraction. This catalyst system, followed by high-temperature reduction at 500 ° C, was found to exhibit a strong metal-support interaction behavior from H_2 or CO chemisorption and ethane hydrogenolysis studies.

The pioneering work of Tauster et al. [1] has stimulated numerous studies of strong metal-support interaction (SMSI) effects on the chemisorption and catalytic properties of metal catalysts; not only for catalysts supported on SMSI oxide (TiO_2, Nb_2O_5, or V_2O_3) [2–4], but also for metal/non-SMSI oxides (SiO_2 etc.) promoted with SMSI oxides [4–7]. In the course of investigating Nb_2O_5-promoted Rh/SiO_2 catalysts, which exhibited SMSI behavior in ethane hydrogenolysis studies [7], we have found that air calcination of a Rh-Nb_2O_5/SiO_2 catalyst at high temperature (700–900 ° C) produced a new phase ($RhNbO_4$) detected by X-ray diffraction [8]. The aim of this work is to study chemical behaviors of such a new phase that is present in SMSI systems after the calcination at high temperature, since this chemistry will affect the degree of Rh-Nb_2O_5 interaction after H_2 reduction. We now report that a $RhNbO_4/SiO_2$ system, followed by a high-temperature reduction, exhibits a significant SMSI behavior in H_2 or CO chemisorption and ethane hydrogenolysis studies.

A 4.1 wt% Rh/SiO_2 catalyst was prepared by impregnating the SiO_2 support (JRC-SIO-3 [9]), which had been precalcined in air at 900 ° C to avoid a possible structural change during the following calcination process, to incipient wetness with an aqueous solution of $RhCl_3$. The impregnated material was dried at 120 ° C overnight, and impregnated with an aqueous solution of $(NH_4)_3[NbO(C_2O_4)_3]$ [7], followed by calcination in air at 900 ° C for 3 h in a muffle furnace. The loading of Nb_2O_5 was chosen so that the atomic ratio of Nb/Rh was unity.

The H_2 and CO chemisorption measurements were carried out by a conventional volumetric adsorption apparatus, and detailed procedures were described

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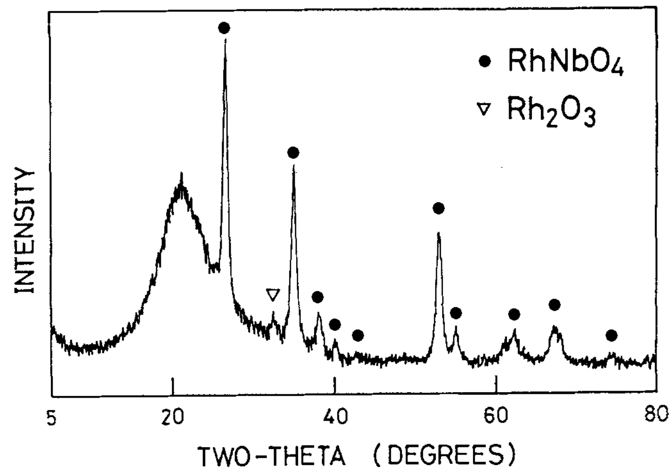

Fig. 1. X-ray diffraction pattern of the Rh-Nb_2O_5/SiO_2 catalyst after the air calcination at 900 ° C (scan speed: 0.5 °/min).

elsewhere [10]. The catalytic activity measurements for the ethane hydrogenolysis reaction were performed in a microcatalytic pulse reactor. Purified He gas was used as the carrier gas (flow rate, 70 cm^3/min) and a pulse (1 cm^3) 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 detailed procedures for the measurements were reported previously [3,8]. The catalyst was treated in O_2 at 500 ° C (or 400 ° C) followed by H_2 reduction at desired temperature for 1 h before each chemisorption or activity measurement. X-ray diffraction (XRD) measurement was performed by an X-ray diffractometer (Rigaku Co. Ltd) equipped with a graphite monochromator for Cu Kα radiation (40 kV, 30 mA).

As shown in fig. 1, the XRD pattern of the Rh-Nb_2O_5/SiO_2 catalyst calcined at 900 ° C contains the new peaks attributed to a $RhNbO_4$ compound (assuming the tetragonal structure of $FeNbO_4$ from the standard ASTM XRD data) [8]. It should be noted that calcination treatment of the same catalyst (Nb : Rh = 1 : 1) at 700 ° C resulted in the formation of three phases (Rh_2O_3, Nb_2O_5, and $RhNbO_4$). Although a small contribution from the Rh_2O_3 phase is observed in fig. 1, $RhNbO_4$ was formed almost exclusively on the SiO_2 surface by the calcination treatment at the higher temperature (900 ° C). The X-ray diffraction study showed that the $RhNbO_4$ compound did not exhibit any reduction after low-temperature reduction (LTR) at 200 ° C, but was reduced to Rh metal by high-temperature reduction (HTR) at 500 ° C [8].

The chemisorption capacity and the catalytic activity were measured after the $RhNbO_4$ compound was decomposed by the H_2 reduction at 500 ° C. Figure 2 shows the catalytic activity and the chemisorption values (H/Rh, CO/Rh) as a function of catalyst reduction temperature. The ethane hydrogenolysis activity was suppressed severely by HTR at 500 ° C (No. 1 in fig. 2a), but was restored by

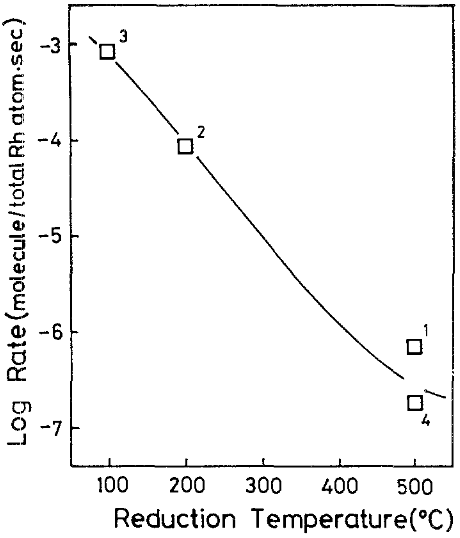

Fig. 2. (a). Effect of catalyst reduction temperature on the ethane hydrogenolysis activity (at 162 ° C). The O_2 treatment at 400 ° C was performed before the H_2 reduction at the given temperature.

O_2 treatment at 400 ° C followed by LTR at 100 ° C and 200 ° C (Nos. 2 and 3). The subsequent HTR treatment (No. 4 in fig. 2a) reduced activity by about 4 orders of magnitude relative to the LTR at 100 ° C. As shown in fig. 2b, the H_2

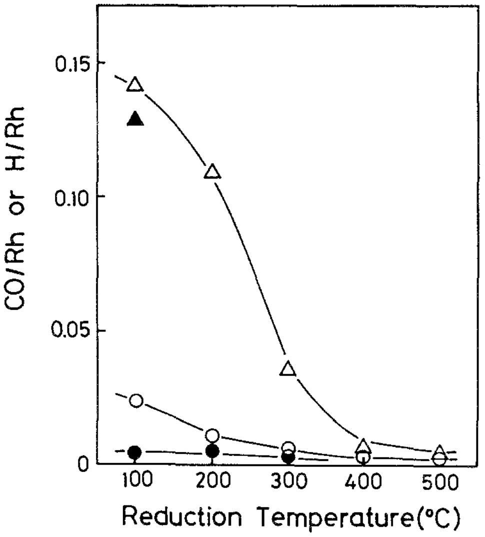

Fig. 2. (b). Effect of catalyst reduction temperature on the amount of H_2 or CO chemisorption (at 25 ° C). The O_2 treatment at 500 ° C was performed before the H_2 reduction at the given temperature. The measurement of H_2 or CO adsorption was carried out after the evacuation in vacuo at the catalyst reduction temperature (open symbols) or at 450 ° C (filled symbols); H/Rh: △, ▲; CO/Rh: ○, ●. It should be noted that the chemisorption and activity measurements were carried out after the $RhNbO_4$ compound was decomposed by the HTR at 500 ° C.

chemisorption capacity was decreased drastically with increasing catalyst reduction temperature. These phenomena are characteristic of SMSI behavior [3,7]. However, the CO chemisorption behavior was anomalous from the usual standpoint of SMSI[1]: CO/Rh was significantly lower than H/Rh even after LTR. In particular, CO/Rh was suppressed almost to zero by evacuation treatment at 450 ° C. However, no significant change was observed in H/Rh after the same evacuation treatment at 450 ° C (see fig. 2b).

The above results show that a new compound can be formed between metal and SMSI oxide promoter by calcination at high temperature. The new phase ($RhNbO_4$) in the present catalyst system exhibits significant SMSI behavior after the HTR at 500 ° C. The anomalous suppression of CO chemisorption would not be explained by a simple model such as geometric blockage of the Rh surface [2–7]. A strong Rh-Nb_2O_5 interaction, perhaps including electronic, may result from H_2 reduction of the $RhNbO_4$ phase. The characterization of this catalyst system will be the subject of further investigation to figure out chemical changes taking place on the SiO_2 surface during the thermal treatment in the gas (H_2, O_2) and in vacuo.

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