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Metal-Oxide Interaction in Alumina-Promoted Rh/SiO_2 Catalyst. Effect of H_2 Treatment on H_2 Chemisorption and Cyclohexane Hydrogenolysis

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An Al_2O_3-promoted Rh catalyst, containing Al_2O_3 deposited onto a Rh/SiO_2 catalyst, exhibited an SMSI behavior: a significant suppression of both the H_2 chemisorption capacity and the cyclohexane hydrogenolysis activity by high-temperature reduction and their recovery by O_2 treatment at 673 K followed by low-temperature reduction.

Much interest has been paid to the metal catalysts supported on TiO_2 and other reducible oxides since the observation of strong metal-support interaction (SMSI) behavior by the Exxon group.[1] We have recently shown that an Nb_2O_5-promoted Rh catalyst, containing Nb_2O_5 deposited onto a Rh/SiO_2 catalyst, exhibited an SMSI behavior, the interaction being as strong as that exerted by a bulk Nb_2O_5 support (SMSI oxide).[2] This finding may be related to the recently proposed model for SMSI: the presence of an oxide species (TiO_x etc.) on the metal surface is responsible for the suppression of the H_2 chemisorption capacity after high-temperature reduction (the "decoration" model).[3-5] On the other hand, a metal/Al_2O_3 (non-SMSI oxide, according to Tauster et al.[1]) system has been also reported to exhibit an SMSI behavior, although the mechanism could be different from that of the TiO_2-supported system.[6,7] The present study of Al_2O_3-promoted catalysts was initiated to address the question: how general are the additive effects of metal oxide (Al_2O_3 in this study) other than SMSI oxides such as Nb_2O_5. We now report preliminary results on the hydrogen chemisorption, the temperature-programmed desorption (TPD) of H_2, and the dehydrogenation and hydrogenolysis of cyclohexane over Al_2O_3-promoted Rh/SiO_2 catalysts.

Two Al_2O_3-promoted Rh catalysts (0.5 wt% as Rh, 6.0 wt% as Al_2O_3) were prepared in this study:

(1) The 0.5 wt% Rh/SiO_2 catalyst (Japan Reference Catalyst, No.16; JRC-S3-0.5Rh)[8] was impregnated with an aqueous solution of $Al(NO_3)_3$, dried in air at 393 K overnight, and then calcined in air at 773 K for 1 h to decompose the alumina precursor. This catalyst was designated here as $Al_2O_3//Rh/SiO_2$.

(2) The SiO_2 support [JRC-SIO-3 (S3)][8] was first impregnated with the same Al_2O_3 solution used for (1), and dried in air at 393 K overnight, followed by the calcination in air at 773 K for 1 h. The resulting promoted support was further impregnated with an aqueous solution of $RhCl_3$, dried in air at 393 K, and calcined again in air at 773 K for 1 h. This catalyst was designated here as $Rh//Al_2O_3/SiO_2$.

Before each activity or chemisorption measurement, the catalysts were treated in situ in O_2 at 673 K for 1 h, followed by reduction in H_2 for 1 h at different temperatures(373 - 773 K).

Hydrogen chemisorption measurements were carried out at room temperature by conventional volumetric adsorption apparatus, and detailed procedures were described elsewhere.[6] The TPD measurements were performed in a flow system with a quadrupole mass spectrometer as a detector.[9] The catalyst was treated in O_2 at 673 K followed by the H_2 reduction at a given temperature (373 - 773 K) and the He treatment at 773 K. After H_2 was adsorbed at room temperature on the pretreated catalyst, the temperature was raised at 20 K/min in a He flow of 30 cm^3/min.

The cyclohexane dehydrogenation and hydrogenolysis activity measurements were performed in a pulse reactor similar to that described in Ref.10. The carrier gas was He. The reactant gas was a mixture of cyclohexane, H_2, and He obtained by jointing a stream of H_2 and He with another He stream passed through a saturator of cyclohexane thermostatted at 283 K. The H_2/cyclohexane ratio was 40. A pulse (1 cm^3) of the mixture gas 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 results of the H_2 chemisorption over the promoted Rh catalysts are given in Table 1. For comparison, the measurements were also carried out on the unpromoted 0.5 wt% Rh/SiO_2 catalyst (JRC-S3-0.5Rh), which had been calcined in air at 773 K for 1 h. As shown in Table 1, the Al_2O_3//Rh/SiO_2 catalyst exhibited a significant loss of H_2 chemisorption capacity after HTR. It should be noted that the amount of H_2 chemisorption (H/Rh value) was restored to the original one (0.23) after the catalyst was retreated in O_2 at 673 K followed by LTR (SMSI behavior). On the

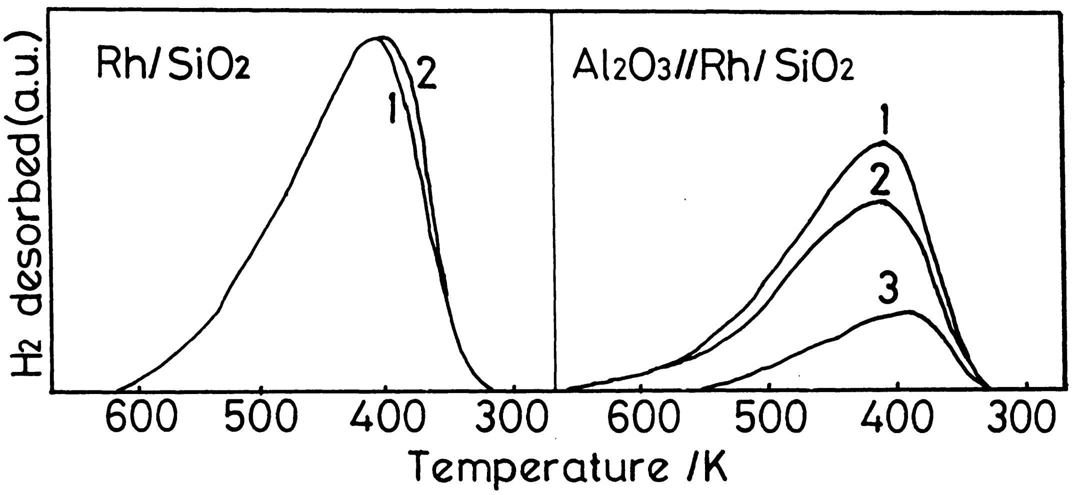

Fig.1. The effect of the reduction temperature on the H_2 TPD spectra from the promoted and unpromoted Rh/SiO_2 catalysts. The reduction temperature was as follows: 1. 473 K, 2. 773 K for the Rh/SiO_2 catalyst; 1. 373 K, 2. 573 K, 773 K for the Al_2O_3//Rh/SiO_2 catalyst.

Table 1. The hydrogen chemisorption and the cyclohexane reaction on the promoted and unpromoted Rh/SiO_2 catalysts

Catalyst	Treatment[a]	H/Rh[b]	Rate[c] at 500 K cyclohexane dehydrogenation[d]	Rate[c] at 500 K cyclohexane hydrogenolysis[e]
Rh/SiO_2	LTR	0.34(0.16)	0.018	0.80×10^{-3}
	HTR	0.28(0.15)	0.045	1.26×10^{-3}
$Al_2O_3//Rh/SiO_2$	LTR	0.23(0.07)	0.108	8.74×10^{-3}
	HTR	0.06(0.02)	0.108	0.48×10^{-3}
$Rh//Al_2O_3/SiO_2$	LTR	0.63(0.34)	-----	---------
	HTR	0.59(0.27)	-----	---------
Rh/Al_2O_3	LTR	0.98(0.49)	0.104	1.25×10^{-2}
	HTR	0.94(0.47)	0.131	1.94×10^{-2}

a) LTR and HTR imply low-temperature reduction at 473 K and high-temperature reduction at 773 K, respectively, preceded by O_2 treatment at 673 K.
b) Atomic ratio of chemisorbed H to total Rh. The amount of reversibly adsorbed hydrogen, which is also associated with Rh metal, is shown in parentheses.[10)]
c) Molecules converted per total Rh atoms per s.
d) Rate of benzene formation. e) The main product was CH_4.

other hand, no severe suppression of the H/Rh value was observed on the $Rh//Al_2O_3/SiO_2$ and Rh/SiO_2 catalysts after HTR. These results are in good agreement with those from the H_2 TPD spectra, as shown in Fig.1. The amount of H_2 desorbed from the $Al_2O_3//Rh/SiO_2$ catalyst was decreased significantly with increasing the reduction temperature, while no big change in the TPD profiles was observed between LTR and HTR for the unpromoted Rh/SiO_2 catalyst. It should be also noted that no change in the TPD spectra from the $Rh//Al_2O_3/SiO_2$ catalyst was observed between LTR and HTR.

The rate of the cyclohexane reaction (both dehydrogenation and hydrogenolysis) is also compared for the promoted and unpromoted catalysts in Table 1. The hydrogenolysis activity of the $Al_2O_3//Rh/SiO_2$ catalyst decreased drastically (by a factor of 18) after HTR, compared with that after LTR. However, it may be noted that another intrinsic effect of HTR may be present in the case of the Rh/SiO_2 catalyst, judging from a small increase in the dehydrogenation activity after HTR.[11)] It may be also noted that the catalytic activity of the cyclohexane reaction (both dehydrogenation and hydrogenolysis) after LTR was considerably higher on the $Al_2O_3//Rh/SiO_2$ catalyst than on the Rh/SiO_2 catalyst. Presumably, Al_2O_3 may act as a promoter for this reaction: for instance, it was reported that the activity of cyclohexane dehydrogenation was strongly enhanced by the additive (Au) on Pt surface.[12)]

The drastic suppression in the activity of the structure-sensitive reaction (i.e., hydrogenolysis of cyclohexane), as well as the significant loss of the H_2 chemisorption capacity, after HTR suggests that a strong metal-oxide interaction was induced in the Al_2O_3//Rh/SiO_2 catalyst after HTR. It may be plausible that part of Al_2O_3 was present on the Rh surface, because the H/Rh value after LTR was lower on the Al_2O_3//Rh/SiO_2 catalyst than on the Rh/SiO_2 catalyst. The alumina species on the Rh surface may play an important role in the properties of chemisorption and catalysis. In contrast, the Rh//Al_2O_3/SiO_2 catalyst does not exhibit any SMSI behavior. The H/Rh value after LTR of the Rh//Al_2O_3/SiO_2 catalyst was higher than that of the Rh/SiO_2 catalyst. It may be considered that most of Rh was highly dispersed on Al_2O_3 supported on SiO_2, presumably due to the preparation method used for the Rh//Al_2O_3/SiO_2 catalyst. For a comparison, the data for 0.5 wt% Rh/Al_2O_3 catalyst (JRC-A4-0.5Rh,[8)] No.15) are also given in Table 1. The high H/Rh value after LTR indicates that the Rh particles are highly dispersed on Al_2O_3, and no change in the chemisorption capacity was observed after HTR. The catalytic activity of the cyclohexane reaction (both dehydrogenation and hydrogenolysis) did not change significantly between LTR and HTR.

Although the extent of the Rh-alumina interaction in the Al_2O_3//Rh/SiO_2 catalyst seems to be not so strong as that in the Nb_2O_5-promoted Rh/SiO_2 catalyst,[2)] the effect of oxide species on metal surfaces may be generalized to include non-SMSI oxides such as Al_2O_3. More detailed work including the catalyst characterization is now in progress in this laboratory.

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