

The SMSI Effect in the System Rh/TiO₂ at High Metal Loading

Noble metal catalysts on certain supports such as TiO₂, V₂O₅, Nb₂O₅, exhibit a significant depression of hydrogen and CO chemisorption after reduction at temperatures higher than 700 K, without remarkable sintering of the metal particles (1). This so-called SMSI effect (strong metal-support interaction) has a strong influence on the catalytic properties. Vannice reported on a higher activity of the catalysts in the SMSI state for CO hydrogenation and on an improved selectivity to higher hydrocarbons (2-4). On the other hand, for the reactions such as hydrogenation and hydrogenolysis of hydrocarbons a significant decrease of activity has been found in the SMSI state (5-8). In our investigation we studied the properties of 5 wt% Rh/TiO₂ catalysts in connection with SMSI, and found a depression due to the SMSI effect not only in the chemisorption of H₂, but also the activity of the hydrogenation of CO (9).

In the present study, the influence of metal loading in the Rh/TiO₂ system on the SMSI behavior was investigated. Our main interest dealt with the consumption of hydrogen during the SMSI formation by high-temperature reduction and with the dependence of the depression of chemisorption on the metal loading and particle size. Therefore we prepared catalysts with 25 and 60 wt% Rh on TiO₂ (anatase) and examined the H₂ chemisorption as well as the catalytic activity of CO-H₂ reaction on these catalysts after definite pretreatments. In this note, we report on the formation of the SMSI state and the chemisorption of hydrogen. The results of the catalytic experiments will be reported elsewhere (10).

EXPERIMENTAL

The catalysts were prepared by impregnating the support TiO₂ (Aerosil P-25, 50 m²/g) with an aqueous solution of RhCl₃ · 3H₂O and subsequent drying on air at 383 K. The pretreatment of the catalysts, the adsorption and reaction measurements were performed in a closed gas circulation system with a liquid-nitrogen cold trap. The pretreatments included reduction with hydrogen at low temperature (573 K) and calcination with oxygen at 723 K. To generate the SMSI state the catalysts were reduced with hydrogen at 723 K overnight after the low-temperature reduction. The amounts of consumed hydrogen or oxygen during the pretreatment were measured volumetrically. Adsorption measurements were carried out at room temperature with 150-200 Torr of H₂ and waited until no more uptake was observed (about 1 h).

RESULTS AND DISCUSSION

Table I shows the results of the hydrogen adsorption on the catalysts after reduction at low temperature (LTR) and in the SMSI state. For each sample several cycles of reduction at low and high temperatures and calcination were performed. It is evident from this table that the dispersion decreased after the first cycle but remained unchanged then at the stable value. Similar results were obtained by Sexton *et al.* (11) by XPS experiments on Rh/TiO₂ catalysts. The LTR data show that the dispersion of Rh in the 25% sample is higher if the catalyst is first calcined in oxygen and then reduced, probably because of the better fixing

TABLE 1

Chemisorption and Consumption of H₂ on Rh/TiO₂ Catalysts (cm³ (STP)/g-Rh)

Catalysts	Treatments temp. (K)	LTR	SMSI	Ratio of H ₂ ads. on SMSI/LTR	H ₂ cons. (red. 732 K)	H ₂ cons.
		H ₂ ads. (H/Rh)	H ₂ ads. (H/Rh)			H ₂ ads (LTR)
25 wt% (first calcination)	O ₂ (723), H ₂ (573)	16.6(0.15)	1.5(0.014)	0.09	31.1	1.9
	O ₂ (723), H ₂ (573)	12.9(0.12)	1.1(0.010)	0.08	24.0	1.9
	O ₂ (723), H ₂ (573)	13.5(0.12)				
25 wt% (first reduced)	H ₂ (573)	12.7(0.12)	0.8(0.008)	0.07		
	O ₂ (723), H ₂ (573)	8.6(0.08)	1.1(0.010)	0.13	17.6	2.0
	O ₂ (723), H ₂ (573)	8.4(0.08)	1.4(0.013)	0.17	16.9	2.0
60 wt%	H ₂ (573)	3.6(0.033)	0.7(0.007)	0.21	8.7	2.4
	O ₂ (723), H ₂ (573)	3.1(0.028)	0.8(0.008)	0.29	7.9	2.5

of the initial dispersity by the calcination. The data for the catalysts in the SMSI state show that the amount of the chemisorbed hydrogen is reduced significantly in all cases.

It is remarkable that even in the case of 60 wt% Rh/TiO₂ we could observe a SMSI behavior after the reduction at 723 K. The extent of depression of hydrogen adsorption actually decreased with increasing particle size (the ratio SMSI/LTR increases), but even with 60 wt% Rh/TiO₂ catalyst this depression of hydrogen adsorption is significant. In this context it is interesting to mention the results obtained by Sexton *et al.* (11), who have shown by TPR that even in a mixture of Pt powder with TiO₂, the TiO₂ is reduced at temperatures between 673 and 773 K, whereas pure TiO₂ is reduced at above 823 K. In all cases, the normal state could be obtained again by the treatment with O₂ at 723 K and subsequent reduction at 573 K (Table 1). In the case of 60 wt% Rh/TiO₂ this reoxidation was very slow. It requires 10 days to reach 80% reoxidation whereas only a few hours were sufficient in other cases. Here the situation is similar to the observation of Fogar *et al.* (6) for the Ir/TiO₂ system, in that the catalysts with a lower dispersion (<0.1) need to be under more severe conditions (higher temperatures) for reoxidation.

As already mentioned we estimated the

amount of hydrogen consumed during the reduction at higher temperature (723 K) required to produce the SMSI state. This consumption was measured after reduction at 573 K, H₂ chemisorption, and subsequent evacuation at 573 K. The corresponding figures are shown in Table 1. As a product of the reduction at higher temperatures, water was detected by gas chromatography in an amount which approximately corresponds to the consumed hydrogen. The ratio between the amount of hydrogen consumed and that chemisorbed after LTR is constant for each sample. The plots of this ratio result in a very good correlation (Fig. 1)

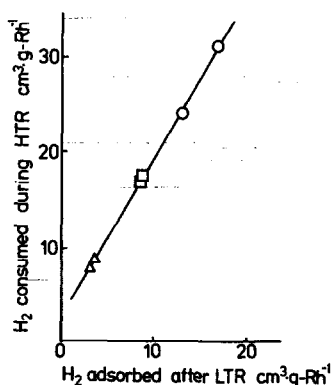


FIG. 1. The relationship between the amount of hydrogen consumed during high-temperature reduction (HTR) and the amount of hydrogen chemisorbed after low-temperature reduction (LTR). (○) 25 wt%, first calcined; (□) 25 wt%, first reduced; (Δ) 60 wt%.

with a slope of 1.7 (± 0.1) and intersection of the abscissa at 2.6 (± 1.4) cm³ (STP) H₂/g-Rh. According to these data a small amount of hydrogen, which corresponded to approximately 2% of the Rh content, is consumed independently of the Rh surface atoms whereas the main part of hydrogen is related to the chemisorbed hydrogen by a factor of 1.7. The actual meaning of these figures is not quite clear at present and needs further investigation, but there seems to be proof that there is a connection between the amount of metal atoms exposed and the amount of hydrogen consumed during formation of the SMSI state. A plausible explanation of these results is that TiO₂ around Rh metal particles is reduced by hydrogen to form water, whose amount may be proportional to the surface area of Rh metal.

Our results apparently support the recent view that SMSI is caused by migration of reduced TiO_x ($1 < x < 2$) on the metal surfaces (13–17), because of the good correlation between the amount of the surface metal atoms and the amount of hydrogen consumption during the high-temperature reduction of 1 wt% Pt/TiO₂. They found a linear correlation between the amount of consumed hydrogen and the decrease of H₂ chemisorption in the SMSI state. From their work it is possible to estimate the ratio of consumed hydrogen to chemisorbed hydrogen after reduction at 473 K to be from 2 to 4. This is in qualitatively good agreement with our results and also supports the idea of a connection between the metal surface and the consumed hydrogen during high-temperature reduction.

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