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SUPPRESSION OF CO HYDROGENATION ACTIVITY OF Pt/TiO_2 CATALYST BY THE SMSI TREATMENT AND ITS RECOVERY DURING THE REACTION

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The catalytic activity of CO + H_2 reaction over a Pt/TiO_2 catalyst decreased significantly after high-temperature reduction at 773 K (the SMSI treatment), but almost recovered during the reaction due to the reverse effect of O atoms (or water molecules) formed.

High activities of the titania-supported metals (Ni, Pd, Pt etc.), compared with the ones supported on the other conventional oxides (SiO_2 and Al_2O_3 etc.), have been reported in the case of CO hydrogenation,1) and these enhancements were initially suggested to be associated with the decrease in chemisorption capability after high-temperature reduction (HTR) at 773 K (the SMSI effect) by Vannice et al.2) Recently, they have recognized that the reaction rates of Pt/TiO_2 catalysts after HTR were similar to those after low-temperature reduction (LTR) at 473 K (the normal state).3) We have recently demonstrated in the niobia-supported system that SMSI caused a severe depression of the catalytic activity, but was reversed by water produced and/or oxygen atoms from the reactant CO during the course of the reaction, and suggested that the same reverse effect should also occur in the titania-supported system by the production of the oxygen atoms sufficient to destroy SMSI during the reaction.4) However, the activities of the titania-supported metal catalysts appeared to be similar between LTR and HTR probably due to the easier recovery from the SMSI state to the normal one than the case of the niobia-supported metal catalysts, thereby failing to discuss clearly the "true" activity in the SMSI state.4) The information about the amount of oxygen necessary to destroy SMSI is now available from our gas-consumption measurements of Pt/TiO_2 catalysts: the number of the oxygen atoms for the recovery was approximately the same magnitude as that of Pt atoms in the catalyst.5) Therefore, it may be possible to demonstrate the reverse effect during the CO + H_2 reaction by operating at a condition of relatively low conversion. This paper reports that the initial activity of a Pt/TiO_2 catalyst after HTR was significantly suppressed and that the reverse effect occurred during the reaction.

A Pt/TiO_2 catalyst (1 wt% Pt) was prepared by impregnating the TiO_2 powder (Degussa, P-25) with an aqueous H_2PtCl_6 solution followed by the oxidation at 723 K and the H_2 reduction at 473 K. The CO + H_2 reactions were carried out at temperatures between 473 K and 523 K in a closed circulating system (670 cm^3, CO/H_2 = 1/2, 66.7 kPa) with a liquid nitrogen trap, and the reaction products were analyzed by GC-MS and two gas chromatographs (FID, TCD).4) As shown in Table 1, three types of pretreatments of the catalyst (0.5 g) were done, and the amount of hydrogen chemisorption was measured in situ at room temperature by the volumetric adsorption technique5) before each run of the reaction. The time of each treatment step was 1 h, and the space velocity of O_2 or H_2 was 3000 h^{-1}. The turnover frequency (T.F.) is defined as the number of CO molecules reacted per sec/the number of H atoms chemisorbed in the normal state (i.e., 0.41 in Table 1).

The T.F. value at 503 K and the activation energy in the normal state (No.1 in Table 1) were roughly consistent with those (at 548 K) by Vannice et al. 3) The T.F. value after the SMSI treatment (No.2 in Table 1) was initially low (2.7×10^{-4} s^{-1} in 5 h), but increased to 9.7×10^{-4} s^{-1} in ca. 20 h. Figure 1 shows the time dependence of the T.F. values at three temperatures. Furthermore, as shown in No.3 in Table 1, the contact with oxygen at room temperature resulted in a partial recovery of the H_2 chemisorption capacity, which is in agreement with the previous results.6,7) The subsequent run of the reaction showed that the activity was partly recovered even in the initial stage (Fig.1). These results suggest that SMSI is almost destroyed by the O atoms (or water molecules) produced during the reaction. It would take only a few hours to produce the amount of O atoms sufficient for the recovery in the runs at the high temperatures (503 K and 523 K), judging from our O/Pt measurements.5) However, the increase in the activity seems to level off at these temperatures. The higher temperatures (more than 523 K) may be needed to attain the complete recovery. We also suspect that a deactivation process (e.g., due to carbon deposition) may be present because of the runs for a long time. On the other hand, no big change in the product selectivity (carbon base) was observed with time: methane, 60%; C_2-C_7, ca. 5%; CO_2, 20%; dimethyl ether, ca. 15%.

Although the Pt/TiO_2 catalyst system has been studied extensively by many workers, the mechanism of SMSI seems to be still controversial.8-10) It has been reported that SMSI caused significant decreases in the catalytic activities of hydrogenolysis, hydrogenation and dehydrogenation of hydrocarbons.7) For the CO + H_2 reaction, Vannice et al. have proposed a new model, which is a combination of the "migration" mechanism for SMSI9) with the IMSI (interfacial metal-support interaction) mechanism for the active sites,11) based on high activity of Ti-doped Pt powder.12) This new model leads one to expect an enhancement of catalytic activity by SMSI. However, the present results do not reconcile with this model. No enhancement of the activity was observed in the states of both partial and almost complete

Table 1. The amounts of hydrogen chemisorption (H/Pt) and the catalytic activities at 503 K after the pretreatments

No.	Pretreatment[a]	H/Pt[b]	T.F. x 10^4 /s^{-1}
1	O_2 673 K, H_2 473 K	0.41	16.7[c]
2	H_2 773 K	0.01	2.7-9.7[d]
3	H_2 773 K, O_2 at r.t.[e]	0.16	7.8[d]

a) After the pretreatment, the evacuation in vacuo was performed at 723 K. b) chemisorbed H atoms/total Pt atoms in the catalyst. c) The activation energy was 22.4 kcal/mol. d) See Fig.1. e) followed by H_2 reduction at 473 K.

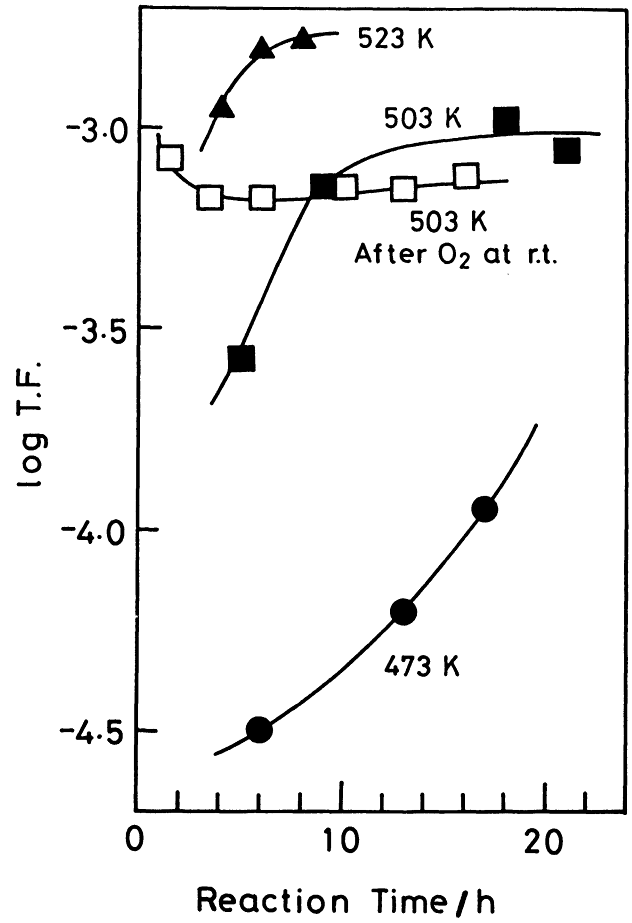

Fig.1. Changes in the T.F. values with time during the CO + H_2 reaction on the Pt/TiO_2 catalyst after HTR at 773 K.

suppression of hydrogen chemisorption capacity. The initial activity after HTR may be (at least) one order of magnitude lower than after LTR, although we cannot still deduce precisely the "true" activity in the SMSI state. More sophisticated experiments will be needed to elucidate the detailed mechanism of SMSI and its effect (including the reverse effect) on the CO hydrogenation.

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