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Effect of Titania over Silica as Support for Platinum Catalyst on Butane Hydrogenolysis

The group VIII metals/TiO_2 systems have received attention in strong metal-support interaction (SMSI) (*1–3*) because of its promising potential in controlling the catalytic performance (activity and selectivity) of the supported metal catalysts. Concerning the support, it has been reported that the SMSI behavior strongly depends on the nature and/or environment of the TiO_2 (*4, 5*). The nature of the dispersed TiO_2 on other metal oxides should be different from that of bulk TiO_2 (*6, 7*). Thus, the metal-support interaction between dispersed TiO_2 and the Pt particle can be expected to be different from that occurring on bulk TiO_2. In this note, we report the evidences for the metal-support interaction between dispersed TiO_2 phase on SiO_2 and supported Pt particles by the combined TPR–TPD technique (*8*) and butane hydrogenolysis. The two types of the metal-support interactions (''light'' SMSI and ''deep'' SMSI) playing different roles in H_2 adsorptivity and hydrogenolysis activity of platinum particles are proposed.

The samples of dispersed TiO_2 on SiO_2 (TiO_2/SiO_2) with different TiO_2 amounts (2.9 and 11.4 mmol g^{-1}) were prepared by the method reported elsewhere (*7*). The Pt/TiO_2/SiO_2 catalysts were prepared by the impregnation of the TiO_2/SiO_2 with aqueous solution of chloroplatinic acid, followed by drying at 383 K and calcining at 773 K for 3 h. The amount of Pt was adjusted to be 2 wt% for all Pt/TiO_2/SiO_2 catalysts. The Pt(2 wt%)/TiO_2 bulk catalyst was prepared by the impregnation of TiO_2 with aqueous solution of chloroplatinic acid (*8*). The TPR apparatus used in this study was described in detail elsewhere (*8*). The two H_2 TPD experiments (heating rate 15 K/min, carrier Ar) were carried out successively after the TPR measurement (heating rate 10 K/min, carrier 3% H_2 in Ar). In the first TPD, the sample was cooled to room temperature in the presence of the reductive gas, then the carrier gas was switched into a pure Ar to start the TPD measurement. The final temperature in the first TPD run was 873 K. The sample was cooled to room temperature in pure Ar, the reductive gas was admitted at room temperature for 1 min, and then the second TPD was started. Prior to the TPR measurement, the sample was calcined at 773 K in air for 2 h and heated in a flowing Ar at 573 K for 2 h.

Butane hydrogenolysis to methane, ethane, and propane was carried out in a closed recirculation reactor at 573 K with a mixture of 20 Torr butane and 100 Torr H_2 (1 Torr = 133.3 Nm^{-2}) on the catalyst pretreated in an H_2 flow (30 cm^3 min^{-1}) at 623 or 773 K for 2 h. The conversion and selectivity were calculated by the method described by Bond *et al.* (*9*).

The typical TPR, the first and second TPD profiles (for Pt/TiO_2(11.4)/SiO_2 sample treated by H_2 at 623 K) are shown in Fig. 1. No appreciable H_2 consumption appeared above 623 K for the samples. For the first TPD, the adsorbed hydrogens onto the sample during TPR measurement and cooling in the presence of reductive gas are detected. Since all H_2 species adsorbed on the surface are considered to be removed from the surface at the end of the first TPD, the second TPD profiles represent the evolved H_2 species resulted from H_2 adsorption at room temperature (*8*). The peak temperature for

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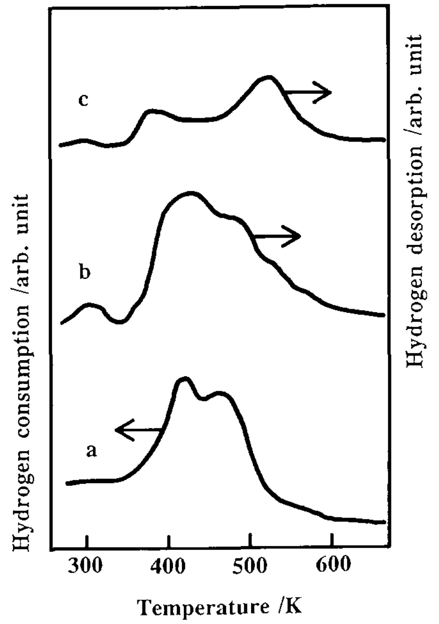

FIG. 1. TPR and TPD profiles of the Pt/TiO_2 (11.4)/SiO_2 sample. (a) TPR profile, (b) first TPD profile, (c) second TPD profile. The TPD profiles were obtained after TPR measurement up to 623 K. The TPD profiles were measured by increasing the sensitivity of the detector.

high-temperature desorption peak in the second TPD for the Pt/TiO_2(11.4)/SiO_2 is higher than those for the Pt/TiO_2(2.9)/SiO_2 and Pt/SiO_2 samples. This indicates the generation of stronger H_2 adsorption sites by increasing the TiO_2 content.

The amounts of H_2 consumption determined from TPR profiles up to 623 K were larger for the Pt/TiO_2/SiO_2's than for Pt/SiO_2 and were much higher than that required to reduce all PtO particles to metallic Pt, i.e., H_2/Pt = 1 (Table 1, H_2/Pt values). If we assume that the initial oxidation state of platinum in the Pt/TiO_2/SiO_2 samples is the same as that in Pt/SiO_2, H_2 should be consumed not only in reduction of PtO to metallic Pt but also in reduction of Ti^{4+} ions to Ti^{3+} on the TiO_2/SiO_2 samples via hydrogen spillover mechanism (*10–12*).

The amount of desorbed H_2 from the Pt/TiO_2/SiO_2 samples depends upon the final temperature in the preceding TPR run (H_2 treatment temperature) and the TiO_2 contents. The total amounts of desorbed H_2 in the first TPD are included in Table 1. The amount of desorbed H_2 increased greatly as the TiO_2 content increased from 2.9 to 11.4 mmol g^{-1}. The amount of H_2 chemisorbed on the Pt/TiO_2(11.4)/SiO_2 was larger for the samples treated at 773 K than those treated at 623 K. The amounts of desorbed H_2 in the second TPD are also given in Table 1.

The desorbed amounts were almost the same for the Pt/SiO_2, Pt/TiO_2(2.9)/SiO_2, and Pt/TiO_2(11.4)/SiO_2. For Pt/TiO_2(2.9)/SiO_2, the desorption peak was not appreciable in the first or second TPD measurements; H_2 adsorption scarecely occurred on the Pt/TiO_2(2.9)/SiO_2 treated with H_2 at 773 K. From the above results, it is suggested that with Pt/TiO_2(2.9)/SiO_2, the SMSI state facilitates too deeply to be released during the first TPD (treatment with Ar at 873 K). This clearly demonstates that the degree of the SMSI is controlled by changing the amount of interacting component. This might be caused both by the higher reducibility for the TiO_2 phase in TiO_2(2.9)/SiO_2 than for the other TiO_2/SiO_2 samples and by different TiO_2 structures with different TiO_2 contents, as evidenced by EXAFS/XANES spectroscopy (*7*).

The TOFs for butane hydrogenolysis and product selectivities at the initial stage of the reaction over the catalysts pretreted at 623 and 773 K are summarized in Table 1. The butane hydrogenolysis proceeded faster for the Pt/TiO_2/SiO_2 catalysts than for the Pt/SiO_2 and Pt/TiO_2 catalysts. This is attributed to the promotional effect of addition of TiO_2 on SiO_2. This type of enhancement of hydrogenolsysis activity has been reported on Rh/TiO_2 (bulk) after low-temperature H_2 treatment with high Rh dispersion (*2*). For all catalysts, the activities were higher for the catalysts pretreated at 623 K than for the catalysts pretreated at 773 K. The decrease in the activity on raising the pretreatment temperature was much larger for the catalysts containing 2.9 mmol g^{-1} TiO_2 than for the catalyst containing 11.4

TABLE 1

Product Selectivities, H/Pt Values, and Turnover Frequencies (TOF) of the $Pt/TiO_2/SiO_2$ Catalysts Pretreated with H_2 at 623 and 773 K

Catalyst	TiO_2 content (mmol g^{-1})	Pre. temp. (K)	H_2/Pt[a]	H/Pt[b]	H/Pt[c]	TOF (min^{-1})	Selectivity to		
							C_1	C_2	C_3[d]
Pt/SiO_2	0	623	0.50	0.10	0.21	0.72	39.0	39.5	21.5
$Pt/TiO_2/SiO_2$	2.9	623	0.99	0.09	0.22	6.64	45.3	18.7	36.0
	2.9	773	—	0.06	<0.06	<0.60	44.5	20.6	34.9
	11.4	623	1.67	0.24	0.22	23.5	47.8	18.4	33.8
	11.4	773	—	0.42	0.40	4.44	51.3	4.4	44.3
Pt/TiO_2	—	623	0.47	0.37	0.12	0.36	41.0	16.0	43.0
	—	773	—	0.49	nm[e]	—	38.9	17.5	43.6

[a] Value of consumed H_2 per platinum was determined by TPR profiles up to 623 K.
[b] Determined from the corresponding first TPD profiles.
[c] Determined from the corresponding second TPD profiles.
[d] C_1, methane; C_2, ethane; C_3, propane.
[e] Not measurable.

mmol g^{-1} TiO_2. A distinct difference in the selectivity was also observed between Pt/SiO_2 and the other catalysts. The selectivity for C_2 was high for Pt/SiO_2 as compared to $Pt/TiO_2/SiO_2$ catalyst. The selectivities of the $Pt/TiO_2/SiO_2$ catalysts were similar to those of Pt/TiO_2 bulk in the sense that the selectivities for C_2 were low and those for C_1 and C_3 were high.

The states of platinum on the TiO_2/SiO_2 supports are different than those on the SiO_2 in reducibility, H_2 adsorptivity, and catalytic property. The platinum particles should interact with titanium oxide phases dispersed over SiO_2 surface after H_2 treatment to alter the energetics for reactant adsorption (*13*). In SMSI state, platinum particles strongly interact with titania suboxide (TiO_x) in the vicinity of the platinum particle (*14–16*). In a deep SMSI state occurring for the $Pt/TiO_2(2.9)/SiO_2$, platinum may fully interact with TiO_x species. As a result, platinum particles cannot adsorb H_2 strongly and lose the butane hydrogenolysis activity. For $Pt/TiO_2(11.4)/SiO_2$, the SMSI state of platinum is light, and the uninteracted Pt surface is left to some extent. By such a light interaction of platinum particles with dispersed TiO_2 phase, the strong H_2 adsorption sites are generated, and thus the promotional effect of TiO_2 is realized. The origin of the SMSI behaviors in the $Pt/TiO_2/SiO_2$ catalysts and the roles of the dispersed TiO_2 phases are still matters for further investigation.

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