Effects of Particle Size on the Desorption Behaviour of Hydrogen from Silica-supported Platinum Catalysts

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Temperature-programmed desorption experiments on hydrogen over Pt/SiO_2 catalysts show that the activation energy for the desorption of hydrogen, which desorbed between 60 and 300 °C, increases with an increase in the average platinum particle size.

The size of metal particles in supported platinum catalysts, as well as other supported metal catalysts, is thought to affect the catalytic activity, selectivity, and life of the catalysts.[1-3] From a fundamental standpoint, it is important to study the adsorptive and desorptive behaviour of hydrogen over these platinum catalysts. T.P.D. (temperature-programmed desorption) experiments on hydrogen with platinum catalysts have already been performed;[4,5] however, the effect of particle size on the T.P.D. behaviour has not been reported. We have now investigated the desorption behaviour of hydrogen from Pt/SiO_2 catalysts as a function of metal particle size by use of a T.P.D. technique.

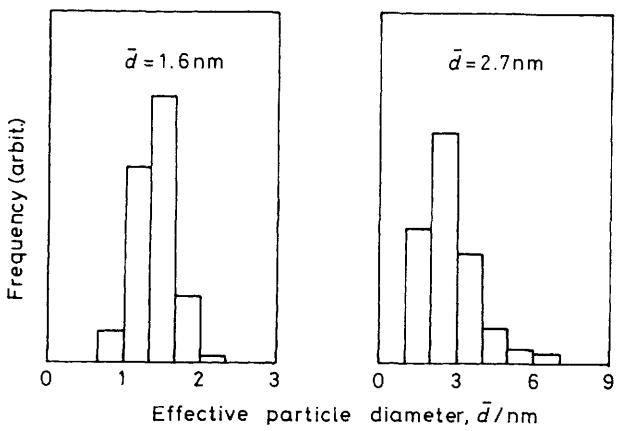

Figure 1. Typical particle size distributions for two Pt/SiO_2 catalysts. Catalyst: 1.26 wt% Pt/SiO_2; $\bar{d}$: mean particle diameter.

Platinum was impregnated on SiO_2 powder (Japan Reference Catalyst, JRC-SIO-1, 166 m^2 g; pellets were crushed in an alumina mortar) by an ion-exchange method using $[Pt(NH_3)_4]Cl_2$. The content of chloride ion in the catalysts was not checked; however, only a small amount of chloride ion was detected in the filtrate of an aqueous suspension of the platinum ammonium/silica. The mean diameter of the platinum particles, $\bar{d}$, was controlled by varying the ignition and reduction conditions in the preparation of the catalysts, as shown in Table 1. The average diameter of the platinum particles was determined for each sample subsequent to the T.P.D. experiments by removing the catalyst sample from the vacuum system and examining it by transmission electron microscopy (T.E.M.). Figure 1 shows typical particle size distributions for two Pt/SiO_2 catalysts. The T.P.D. behaviour was followed by measuring the variation in pressure due to desorption of hydrogen from the sample with an ionization

Table 1. Preparation of the Pt/SiO_2 catalysts.

	Calcination			Reduction			
Pt loading (wt%)	Atmosphere	Temp./°C	Time/h	Atmosphere	Temp./°C	Time/h	Mean diameter/nm
1.26	1 atm air flow	250	3	1 atm H_2 flow[a]	450	4	1.6
"	"	"	"	"	"	14	"
"	$P(O_2)$ = 30 Torr	450	6.5	$P(H_2)$ = 30 Torr	"	12	2.2
"	1 atm air flow	"	"	"	"	"	2.7
"[b]	"	"	8	"	150	9	3.6
0.36	"	550	"	"	"	6	4.3

[a] 100 ml/min. [b] Wet platinum ammonium/silica was calcined.

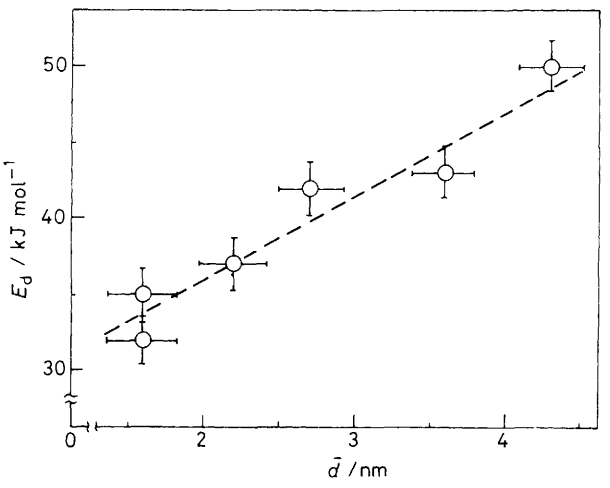

Figure 2. Apparent activation energies for the desorption of hydrogen, which desorbs in the range 60—300 °C, from Pt/SiO_2 catalysts. Catalysts: 0.36 wt% Pt/SiO_2 and 1.26 wt% Pt/SiO_2; hydrogen adsorption: 10 Torr of H_2 at 60 °C for 15 min after evacuation of the sample at 450 °C; heating rate: 20—100 °C/min.

gauge. The desorbed gas was also analysed by mass spectrometry.

Although about three hydrogen peaks have been found in T.P.D. curves over a wide temperature range for the H_2–Pt system,[4] we noted only the hydrogen peak which appeared at 60—300 °C. The adsorbed hydrogen seems to be dissociative, because the peak temperature, T_M in the T.P.D. curve shifted to lower temperature when the hydrogen pressure in the hydrogen adsorption procedure increased. The activation energy for the desorption of hydrogen was calculated,[6] assuming that the desorption was a second-order process.

Figure 2 shows the phenomenological activation energy for the desorption of hydrogen, as a function of mean particle diameter in the range 1.6—4.3 nm. As the average particle diameter increased in this range, the activation energy increased from about 34 kJ mol^{-1} at $\bar{d}$ = 1.6 nm to 50 kJ mol^{-1} at $\bar{d}$ = 4.3 nm. This suggests that hydrogen is adsorbed more strongly as the platinum particle size increases in this range. As with the band structure of small palladium particles, the top of the valence band of platinum particles shifts to higher binding energy from the Fermi level with decreasing particle size.[7,8] Since the valence band shift will lower the adsorption energy of hydrogen on platinum particles,[9] the activation energy for the desorption of hydrogen decreases with decrease in the particle size.

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