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Surface Modification of Supported Platinum Catalysts by Heat Treatment

This communication reports the rather unusual surface modification of metal catalyst by heat treatment. Historically, catalytic activities of metals have been interpreted in terms of bulk properties such as electron band theory, correct geometry, and lattice spacing of surface atoms (*1–3*). It is generally accepted that surface atoms with different nearest neighbor coordination numbers should in some way reflect their activities and corner atoms with the lowest coordination number are the most active sites (*4*). It is quite logical to assume that the thermodynamic statilities of the surface atoms are: corner atom (3m) (*5*), edge atom (2M), and face atom (1M).

Recently, attention has been focused on pretreatment of Pt catalysts to vary the active site distribution. Several papers have reported the modification of the catalytic activity by high-temperature heat treatment (*6–9*). However, little attention has been paid to the cooling treatment. If the metal surface is treated with high enough temperature to dislocate the surface atoms to thermodynamically unstable states and the states then frozen with rapid cooling, we might be able to generate a high population of more active sites, which might be equivalent to corner atoms. On the other hand, if the surface is treated at the high temperature and cooled slowly, then a high population of the less active sites, which might be equivalent to face atoms, could result. Indeed, the above assumption is strongly supported by the following experimental results.

To investigate the assumption described above, chemisorption and TPD measurements with hydrogen were carried out using 1 wt% Pt/γ-Al_2O_3 and 1 wt% Pt/SiO_2 catalysts. The catalysts for these experiments were prepared by impregnation of chloroplatinic acid on γ-Al_2O_3 and SiO_2 and reduction for 12 h in hydrogen stream at 400°C following normal procedure (P-1). A given amount of the catalyst, 1 g for chemisorption test and 2 g for TPD, was packed in a quartz tube and then treated at 700°C for 1 h followed by slow cooling to room temperature over 1 h (P-2). After the chemisorption and TPD tests with the P-2 catalyst, the catalyst samples in the tubes were again heated to 700°C with evacuation to 6×10^{-6} Torr for 1 h and then quenched rapidly in liquid nitrogen (P-3). The P-3 catalyst samples after the corresponding tests were consequently heated to 450°C with evacuation to 6×10^{-6} Torr for 1 h and then cooled slowly to room temperature over 1 h (P-4).

The adsorption measurements were made by a conventional BET apparatus equipped with a capacitance manometer. The hydrogen uptakes were determined at 25 ± 3°C on reduced and evacuated samples as described elsewhere (*6*). Before each run, the catalysts prepared as described above were treated in hydrogen for 1 h at room temperature under atmospheric pressure, and excess hydrogen was removed by flowing nitrogen carrier gas for 1 h at room temperature. During this time, stable baselines were obtained on the recorder chart for all the catalyst samples. The results of H_2 adsorption from the P-1 to the P-2 could be caused by sintering of the dispersed metal on the support at high temperature. It is noticeable that the sintering is more predominant in presence of oxygen than hydrogen (*11*).

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TABLE 1

Hydrogen Uptakes with Different Pretreatments

Catalyst	Pretreatment	H_2 uptakes (ml/g)	
		H_2 atmosphere	O_2 atmosphere
Pt/γ-Al_2O_3	P-1	0.55	0.57
	P-2	0.24	0.13
	P-3	0.33	0.15
	P-4	0.23	0.07
Pt/SiO_2	P-1	0.39	0.40
	P-2	0.18	0.11
	P-3	0.24	0.14
	P-4	0.19	0.07

It is rather interesting to find increased hydrogen adsorption of P-3 compared to P-2 even though the P-3 catalyst was prepared by further consecutive heat treatment of the P-2 catalyst. The hydrogen adsorption tests for the P-4 catalyst was conducted to prove that the increased hydrogen adsorption of P-3 did not result from splitting of catalyst particles due to rapid cooling in liquid nitrogen. The hydrogen adsorption of P-4 was dropped back to that of P-2. It was expected that sintering would not take place at the lower temperature used to prepare P-4. The experimental results described above support the premise that the heat treatment and rapid cooling can generate a high population of more active sites which could be equivalent to 3M site of Siegel *et al.* (*5*) or corner atom with the lowest coordination number.

To verify the results of hydrogen adsorption determinations, the distribution curves of hydrogen adsorption sites of Pt/γ-Al_2O_3 catalyst were determined by TPD experiments. TPD was done in a flow system similar to that described by Menon and Froment (*12*). Hydrogen was adsorbed on the respective catalysts prepared as above and the adsorbed hydrogen was later desorbed into the nitrogen carrier gas by programmed heating of the catalyst samples. The concentration of the desorbed gas was measured by a thermal conductivity detector and recorded. The results of the TPD tests are shown in Fig. 1 and they are quite reproducible. It is noticeable that the peak for P-1 around 300°C disappeared after heat treatment (P-2). However, the TPD curve of P-3, which was prepared by heat treatment of 700°C followed by rapid cooling in liquid nitrogen, shows a dramatic increase of peak intensity around 500°C. The TPD experiments with Pt/SiO_2 gave similar curves to Pt/γ-Al_2O_3 except for the P-1 curve. At this time, it is obvious that the total hydrogen uptake is increased, as shown in Table 1 with P-3 compared to P-2.

However, it can be presumed that there are six different hydrogen atoms chemisorbed on the corner, edge, and face atoms of the metal surface as shown in Fig. 2. The bond strength of each M—H bond should be different from each other. The bond strength of H1—M should be the weakest one while H3—M be the strongest one of the six possible H—M bonding. Therefore, the TPD peak for H1 would show up at a lower temperature while that of H3 would appear at higher temperature than any other adsorbed hydrogen on the metal surface. In other words, the TPD peak of H3

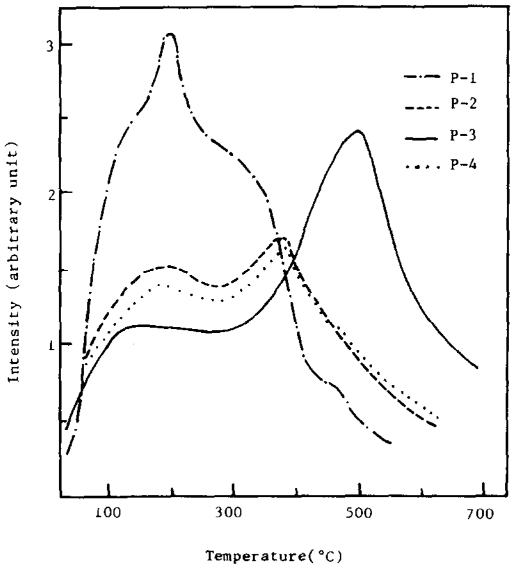

FIG. 1. The TPD chromatograms of H_2 with different pretreatments.

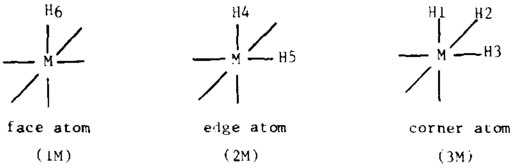

FIG. 2. Schematic models of H_2 adsorption type.

would be larger in the TPD curve when the population of H3—M is higher. Under this assumption, the peak of the TPD curve around 500°C could be assigned to H3 of corner atom sites on the surface. The TPD peak of H3 round 500°C is increased dramatically after the heat treatment at 700°C followed by rapid cooling in liquid nitrogen. Davis and Somorjai (*14*) observed three distinct kinds of hydrogen adsorbed on Pt crystal surfaces employing the flash desorption technique. They discussed their results in comparison with Collins and Spicer's experiments (*15*) and suggested that the hydrogen desorbed at the lowest temperature might be from terraces, the hydrogen desorbed at the intermediate temperature from steps, and the hydrogen desorbed at the highest temperature from kinks. Their observations agree with our results and support the above assumption strongly.

All the experimental results discussed above indicate that the proposed heat treatment with rapid cooling can generate a higher population of active 3M sites for catalysis. This could be an important discovery for catalyst preparation. Preliminary data obtained using the Single Turnover Procedure (*16*) on catalysts treated in this way has shown that the P-3 types of catalyst has enhanced activity over the P-2. Further work in this area is in progress.

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