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STRONG METAL-SUPPORT INTERACTION IN ALUMINA SUPPORTED PLATINUM CATALYSTS

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After heat treatments of Pt-Al_2O_3 catalysts in H_2 and O_2 at high temperatures, drastic changes both in H_2 and O_2 chemisorption occurred in spite of no change of Pt particle size. The extent of the changes was found to be quite different among the alumina supports used. The phenomenon relates to a strong metal-support interaction, and some aspects of different behaviors on these alumina supports were discussed.

Hydrogen chemisorption and hydrogen-oxygen titration methods are widely used to determine the percentage exposed (metal dispersion) of supported metal catalysts.[1,2] Recently, Dautzenberg and Wolters[3] reported that pretreatments of alumina supported Pt catalysts in H_2 at high temperatures (above 500°C up to 675°C) cause the apparent decrease in H/Pt (chemisorbed H atoms/total Pt atoms), while the metal crystallite sizes remain constant, and oxidation at 500°C restores the capacity to chemisorb hydrogen. According to their proposition, most of published studies concerning "sintering" and "redispersion" would be reconsidered. This study deals with the effects of heat treatments in H_2 and O_2 of various Pt-Al_2O_3 catalysts. We have observed more drastic decreases both in H/Pt and O/Pt (chemisorbed O atoms/total Pt atoms) after treatments of Pt catalysts in H_2 even at lower than 500°C, and found that the extent of changes depends on the alumina supports. In the case of TiO_2 supports, Tauster et al.[4] have observed the drastic decrease in H/Pt, and such phenomena have been attributed to strong metal-support interactions.

The H_2 and O_2 chemisorption studies were performed at room temperature with a conventional static vacuum apparatus. Pressure measurements were made with a Baratron capacitance pressure gauge. Pt-Al_2O_3 catalysts (0.5 wt%) were prepared by impregnation technique using H_2PtCl_6 aqueous solutions, followed by H_2 reduction at 500°C. Alumina supports were chosen mainly from the Japan Reference Catalysts (JRC)[5] as shown in Fig.1. Pretreatments were performed before the H_2 chemisorption; (a) the H_2 treatment at e.g. 500°C and 50 torr, followed by evacuation at 450°C for 60 min, (b) the O_2 treatment at 450°C and 50 torr, followed by reduction in H_2 at 300°C for 60 min and evacuation at 450°C for 60 min. The O_2 chemisorption was measured after the H_2 chemisorption followed by evacuation at 450°C for 60 min.

Table 1 shows typical results of changes in H_2 and O_2 chemisorption values after the pretreatments in the case of the catalyst supported on the alumina JRC-ALO-2. H/Pt decreases after the H_2 treatment even at 430°C, and increases after the O_2 treatment. Especially, reduction of the same catalyst at 500°C for more than

10 hours decreases the H_2 chemisorption to completely zero, and thereafter the oxidation at 450°C increases it again.[6] On the other hand, O/Pt remains almost constant to a certain limit, but decreases sharply to near zero after the extensive reduction at 500°C. A high power X-ray diffraction analysis (40 kV, 100 mA) and transmission electron microscopic measurements (100 kV) revealed that platinum in all catalyst materials remained highly dispersed even when H/Pt and O/Pt values decreased to near zero.

Table 1. Changes in H_2 and O_2 chemisorption values after the heat treatments in the case of the Pt catalyst supported on the alumina JRC-ALO-2.

Treatment	O_2 450°C 1 hr	H_2 430°C 27 hr	H_2 430°C 15 hr	O_2 450°C 1 hr	H_2 500°C 3 hr	H_2 500°C 3 hr	H_2 500°C 5 hr	O_2 450°C 1 hr
H/Pt	1.35	0.88	0.52	1.26	0.32	0.15	0	1.34
O/Pt	0.69	0.65	0.67	0.67	0.42	0.25	0.06	0.70

Table 2. H_2 and O_2 chemisorption values after the heat treatments in the case of the Pt catalyst supported on the alumina JRC-ALO-4.

Treatment	O_2 450°C 1 hr	H_2 450°C 13 hr	H_2 500°C 14 hr	O_2 450°C 1 hr	H_2 600°C 10 hr	H_2 650°C 14 hr	O_2 450°C 1 hr
H/Pt	1.28	1.16	1.06	1.28	1.10	0.97	1.02
O/Pt	0.62	0.64	0.62	0.62	0.70	0.72	0.51

In the case of JRC-ALO-4, however, the extent of changes in the H/Pt values as well as O/Pt was very small even after the reduction at 600°C for 10 hours as shown in Table 2. Sintering may have occurred rather slightly after the reduction at 650°C, because the oxidation did not restore the H/Pt value to the initial one.

The data on the H/Pt decline rates of different alumina supported Pt catalysts during the H_2 treatment at 500°C were collected in Fig.1. The Al_2O_3(A) was prepared in the same way as that of Dautzenberg and Wolters.[3] The decline rate was very small as shown in Fig.1, and in good agreement with their results. The more drastic effect was observed in the cases of Neobead C, JRC-ALO-5, and JRC-ALO-2 as compared with Al_2O_3(A) and JRC-ALO-4. Especially, the effect on the Neobead C supported catalyst is outstanding. JRC-ALO-1 exhibited the intermediate rate.

All the supports were so-called γ-alumina, and almost pure except Neobead C and JRC-ALO-5 which contained iron (ca. 0.5 wt%) as an impurity. However, no evidence for the effect of iron on this phenomenon was found. For instance, we prepared the impure Pt catalysts supported on JRC-ALO-4, by intentional addition of iron from 0.3 wt% to 1.0 wt%, but no change of the decline rate was found.

X-ray diffraction patterns of all the alumina supports used were measured with same conditions, as shown in Fig.2. Although all the sample have a structure of so-called γ-alumina, the intensity and width of each peak were different among the aluminas. The less extent of crystallization of alumina, the larger the decline rate is. Crystallinity of γ-alumina is considered to be one of main factors for this phe-

nomenon.

The consumption of hydrogen was observed during the treatment in H_2 at 500°C. The quantity of hydrogen consumed reached far beyond that for the reduction of platinum oxide. Hydrogen was consumed much faster in the cases of Neobead C, JRC-

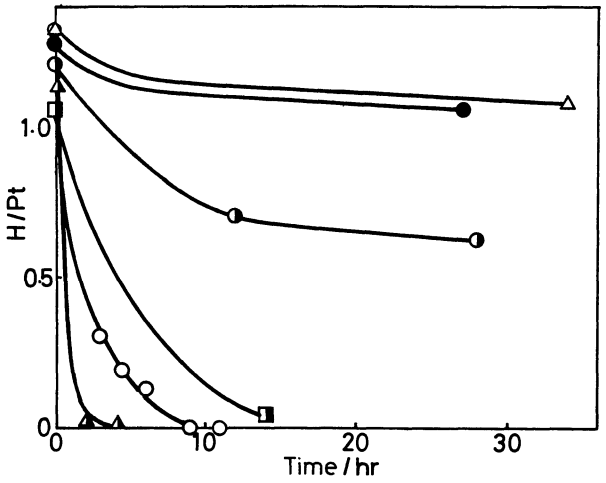

Fig.1. Decrease of H/Pt during the heat treatments of different alumina supported Pt catalysts in H_2 at 500°C.
Alumina support
◑ JRC-ALO-1 △ Al_2O_3(A)*1
○ JRC-ALO-2 ● JRC-ALO-4
◨ JRC-ALO-5 ▲ Neobead C*2
*1 Preparation in the same way as that of Dautzenberg and Wolters[3)]
*2 Mizusawa Ind. Chem. Ltd.

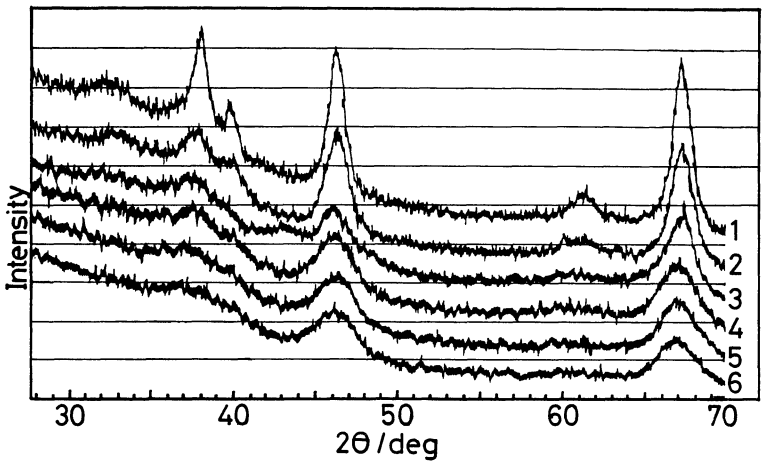

Fig.2. X-ray diffraction of the alumina supports (Cu K_α, 30 kV, 15 mA).
1. Al_2O_3(A)
2. JRC-ALO-4
3. JRC-ALO-1
4. JRC-ALO-5
5. Neobead C
6. JRC-ALO-2

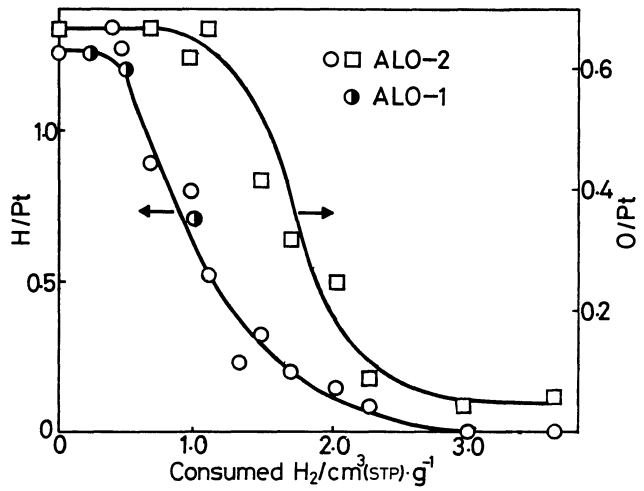

Fig.3. H/Pt and O/Pt vs. the volume of hydrogen consumed during the treatment in H_2 at 500°C.

ALO-5, and JRC-ALO-2 than JRC-ALO-1, JRC-ALO-4, and Al_2O_3(A). Fig.3 shows the relation between H/Pt (or O/Pt) and the quantity of hydrogen consumed. When the H/Pt value as well as O/Pt reached to near zero, the number of consumed hydrogen atoms was about 10 times as many as that of total Pt atoms. It can be considered that part of surface alumina in the neibourhood of the small Pt particles was reduced during the treatment in H_2 at 500°C,[7] and such a compounds as $Pt \cdot Al_2O_{3-x}$ can not chemisorb not only hydrogen but also oxygen. Den Otter and Dautzenberg assumed alloy type bonding between Pt and Al of the partially reduced Al_2O_3.[8] In the present stage, we have no detailed information about the chemical nature of such a compounds. Nevertheless, we can refer to these drastic effects as a strong metal-support interaction (SMSI) which is quite similar to that observed by Tauster et al.[4] It is worth noting that even O_2 chemisorption shows a drastic change due to the SMSI as can be seen in Fig.3.

The drastic effects may be important in the sense of not only the problem of determining the metal dispersion of Pt catalysts but also the possible changes of intrinsic nature of platinum, catalytic activity and selectivity.[9] A more detailed chemical nature of such a compounds caused by the SMSI should be studied more intensively.

References and Notes

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4) S. J. Tauster, S. C. Fung, and R. L. Garten, J. Am. Chem. Soc., 100, 170(1978).
5) Japan Catalysis Society has provided a series of γ-alumina supports for common use in order to minimize disagreements of the results by different researchers. See SHOKUBAI(CATALYST), 21, 62(1979); 22, 110, 115(1980).
6) The O_2 treatment at 450°C for 60 min is enough to restore the H/Pt and O/Pt values to the initial ones even after the severe hydrogen treatment. This oxygen treatment is very important to obtain the reasonable value of percentage exposed of Pt.
7) An attempt of measuring and distinguishing the H_2O produced by reduction from that produced by another processes such as slow dehydroxylation at 500°C is now proceeding in this laboratory.
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