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# Preparation of Platinum Cluster Catalyst Supported on Porous Chelate Resin-Metal Complexes for Hydrogenation of Olefin and Diene

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Platinum cluster catalysts supported on chelate resin-metal complexes were prepared by reduction of platinum ions immobilized on the supports which were characteristic of high porosity. The initial rate of hydrogen uptake in the hydrogenation of olefin or diene over the catalysts increases with the surface area of the resin supports.

Homogeneous dispersions of the platinum clusters$^{1-3)}$ have been prepared by reduction of hexachloroplatinic acid under the mild conditions in the presence of water-soluble polymers or surfactants,$^{4-8)}$ and have been found to work as highly active and selective catalysts for hydrogenation of olefins and photochemical hydrogen evolution from water. However, it is hard to separate the clusters from the reaction mixtures for the repeated usages. To overcome this problem the platinum clusters were supported on the polystyrene-based chelate resins (CR) having iminodiacetic acid moieties, but their activity was much lower than that of the homogeneous system.$^{9)}$ Recently it has been found that the surface area of the chelate resin can be increased in three orders of magnitude by complexing with multi-valent cations like Al(III) and by drying after having been washed with ethanol.$^{10)}$ Here we use the chelate resin-metal complexes dried from ethanol as the supports for the platinum clusters which are produced by reduction of $PtCl_6{}^{2-}$ after immobilization of the ions on the resin. With this method we have succeeded in immobilization of the platinum clusters on the porous chelate resin, and have found the good relationship between their catalytic activities and the surface areas of the resin supports.

The dry type catalysts were prepared as follows: To a solution of $AlCl_3 \cdot 6H_2O$ (9.31 g, 38.6 mmol) in distilled water (50 cm$^3$) were added the water-swollen beads (10 g) of the chelate resin which is composed of the copolymer of styrene and divinylbenzene with iminodiacetic acid groups

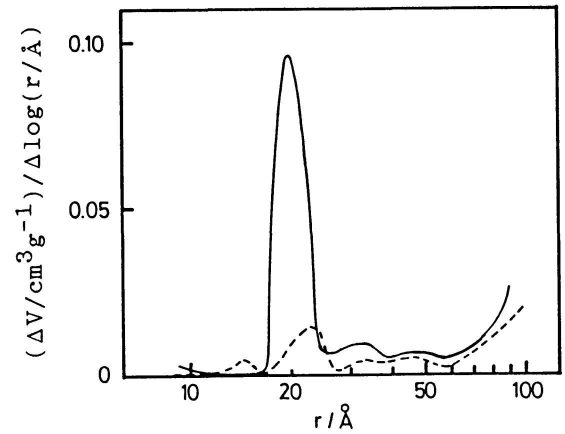

Fig. 1. Pore size distribution of CR-Al (——) and CR-Al-Pt (---). ΔV is the sum of the volume for the pores having radii between r and r+Δr.

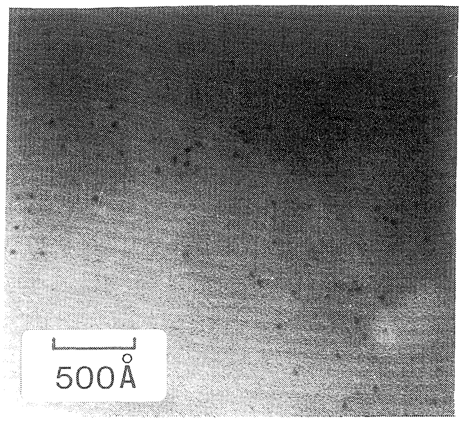

Fig. 2. Transmission electron micrograph of the platinum clusters in the sliced CR-Al-PT beads. The magnification is 400,000.

(Mitsubishi Chemical Industry Co. Ltd., CR-10, containing 25.7 mmol of iminodiacetic acid moieties. Mean diameter is ca. 0.5 mm. Grain size range is 1190-297 μm.). The mixture was shaken by a mechanical shaker for a day to immobilize Al(Ⅲ) ions on the resin beads to produce the chelate resin-aluminum complexes (abbreviated as CR-Al). An aqueous solution of hexachloroplatinic acid ($1.93 \times 10^{-3}$ mol $dm^{-3} \times 10.7$ $cm^3$ = 20.6 μmol) was added to CR-Al (0.8 g as a dry chelate resin) to immobilize $PtCl_6^{2-}$ on the complex supports, and then the platinum ions on CR-Al were reduced by an aqueous solution of $LiBH_4$ resulting in the platinum clusters supported on CR-Al (abbreviated as CR-Al-Pt). The platinum cluster catalysts supported on the chelate resin-sodium(Ⅰ) complexes and -magnesium(Ⅱ) complexes (abbreviated as CR-Na-Pt and CR-Mg-Pt, respectively) were prepared by exchanging Al(Ⅲ) ions of CR-Al-Pt with Na(Ⅰ) and Mg(Ⅱ) ions by adding NaOH and $MgCl_2$ to the CR-Al-Pt catalysts, respectively. Each complex catalyst was washed with 50 $cm^3$ of ethanol for 4 times.

The specific surface areas of the dry chelate resin-metal ion complexes and the resin complex-supported platinum catalysts were measured by a BET method. The surface areas of CR-Al and CR-Na were 83.9 and 2.51 $m^2$ $g^{-1}$, respectively. The surface area of CR-Al-Pt was 16.2 $m^2$ $g^{-1}$, which is smaller than that of CR-Al, but still much larger than that of CR-Na. Figure 1 illustrates the pore size distributions of the dry CR-Al and CR-Al-Pt. The difference between the both pore size distributions of CR-Al and CR-Al-Pt clearly indicates that the platinum clusters occupy the pores of about 20 Å in radius of the chelate resin. The mean diameter of the clusters themselves was calculated to be 26 Å from the transmission electron micrograph shown in Fig.2.

The resin complex-supported platinum cluster catalysts with high

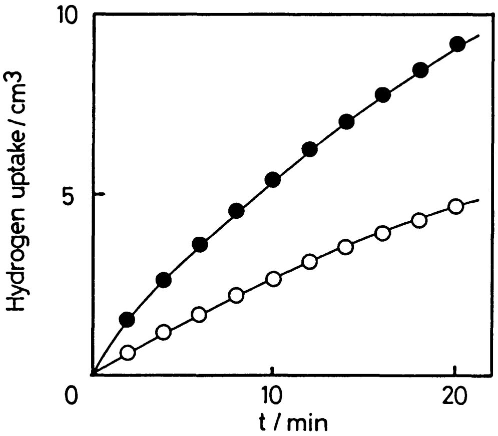

Fig. 3. The hydrogenation of 1,3-cyclooctadiene by the platinum clusters supported on the chelate resin-Al(Ⅲ) complex dried from ethanol (●) and from water (○).

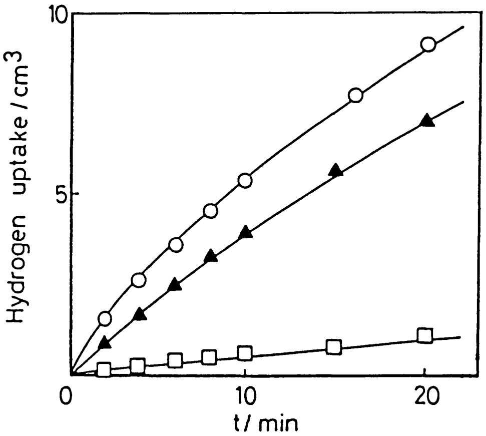

Fig. 4. The hydrogenation of 1,3-cyclooctadiene by the platinum clusters supported on the chelate resin-metal complex.
(○): Al(Ⅲ), (▲): Mg(Ⅱ), (□): Na(Ⅰ).

surface area were applied to the hydrogenation of olefins. The dispersions of the dry catalysts (0.8 g, containing 20.6 $\mu$mol of platinum) in ethanol (19 $cm^3$) were kept in a 50 $cm^3$ flask under 1 atm of hydrogen at 30 ℃ until no hydrogen gas was uptaken. Then, 0.5 mmol of the substrate in 1 $cm^3$ of ethanol was added to the dispersions. Hydrogen uptake was traced by a gas burette during the reaction.

Figure 3 illustrates the hydrogenation curves of 1,3-cyclooctadiene (COD) over the CR-Al-Pt catalysts. The initial rate of hydrogen uptake over the catalyst dried directly from water is not so fast as that from ethanol. This order of the rates seems to be consistent with that of the surface areas of the catalysts, because the surface area of the catalyst dried from water (4.1 $m^2$ $g^{-1}$) is much lower than that from ethanol (16.2 $m^2$ $g^{-1}$).

The hydrogenation rate also depends on the kind of metal ions involved in the supports as shown in Fig.4. The initial rate of hydrogen uptake increases in the order : Na(Ⅰ)< Mg(Ⅱ)< Al(Ⅲ). This order corresponds to the increasing order of the surface area as shown in Table 1. It has been clarified that the high catalytic activity of the platinum clusters on the resin-metal ion complex supports is attributed to the increase in the surface area of the catalyst.

The hydrogenation of various olefins, such as cyclohexene (CHE), cycloheptene (CHpE) and cyclooctene (COE), was also carried out by using CR-M-Pt(M=Na, Mg, Al) dried from ethanol. The initial rates and the surface areas are shown in Table 1. The initial rate increases in the order of Na(Ⅰ) < Mg(Ⅱ) < Al(Ⅲ), which is the same as that for COD.

The addition of these metal ions decreased the catalytic activity in

Table 1. Initial rate of hydrogen uptake over the platinum cluster catalysts supported on the chelate resin-metal ion complexes[a)]

| Catalyst | Surface area $m^2\ g^{-1}$ | Initial rate / $cm^3\ min^{-1}$ | | | |
|---|---|---|---|---|---|
| | | COD | CHE | CHpE | COE |
| CR-Na-Pt | 1.5 | 0.057 | 0.021 | 0.090 | 0.022 |
| CR-Mg-Pt | 13.7 | 0.404 | 0.089 | 0.244 | 0.058 |
| CR-Al-Pt | 16.2 | 0.543 | 0.615 | 0.982 | 0.260 |

a) See text for abbreviation.

the case of the colloidal dispersions of platinum clusters protected by poly(N-vinyl-2-pyrrolidone) (a homogeneous system). On the contrary, in the chelate resin-supported system the addition of metal ions did increase the catalytic activity by means of increasing the surface area.

In summary we have successfully prepared the new platinum cluster catalysts supported on the chelate resin complexes involving Na(Ⅰ), Mg(Ⅱ) and Al(Ⅲ), respectively. The catalytic activity of the supported clusters increased with the increasing valency of the metal ions used for the support in the order of Na(Ⅰ) < Mg(Ⅱ) < Al(Ⅲ), which is consistent with the increase in the surface area of the resin.

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