Control of Selectivity Based on the Diffusion Rates of the Reactants in the Oxidation of Mixed Hydrocarbons with Molecular Oxygen over Silica-coated Pt Catalysts

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Pt metal catalyst covered with silica layers oxidized methane preferentially in the competitive oxidation of methane and isobutane with gaseous oxygen. Selectivity in the competitive oxidation of mixed hydrocarbons over the catalyst was controlled by the diffusion rates of the reactants in the silica layers which wrapped Pt metal particles.

Control of the selectivity in catalytic reactions is one of challenging subjects. For example, the shape selectivity in catalytic reactions was described for the first time by Mobil research workers.[1] At present, some categories of shape selectivity have been described in the literatures, i.e., reactant shape selectivity, product shape selectivity, transition-state shape selectivity, and so on.[2,3] Zeolites such as ZSM-5 show the promising catalytic performance for the shape selectivity of reactants or products in the alkylation of aromatics and in the catalytic cracking of hydrocarbons.[4] The shape selectivity by zeolite catalysts results from the size of micropores in them.

We have studied the preparation of catalysts by using microemulsion and their catalytic performances.[5,6] By the preparation method, various metals or metal oxides such as Fe_3O_4, Ni, Co, Pt, Rh, and so on can be covered uniformly with silica layers. Because the catalytically active metal components in the catalysts are present in the center of spherical silica particles with a porous structure, the catalysts would show the reactant selectivity for catalytic reactions.

In the present study, silica-coated Pt metal particles were utilized as catalysts for the competitive oxidation of methane and other higher hydrocarbons (ethane, propane, and isobutane) with gaseous oxygen. We would report the specific catalytic performance of silica-coated Pt metals for the reactant selectivity.

Pt catalysts coated with silica (denoted as coat-Pt hereafter) were prepared by using water-in-oil microemulsion. Microemulsion system was prepared by adding aqueous H_2PtCl_6 into surfactant solution in cyclohexane. Polyoxyethylene($n = 15$)cetyl ether was utilized as a surfactant. Nanoparticles of a compound containing Pt cations were synthesized by addition of aqueous NH_3 in the microemulsion system. Hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) were performed at 323 K by addition of TEOS and aqueous NH_3 into the microemulsion system. Precipitates thus obtained were washed with isopropanol several times after filtration, and calcined at 623 K for 2 h under air stream. The calcined samples were washed with aqua regia at room temperature in order to remove Pt species which were not covered with silica layers. Pt loading of coat-Pt after the treatment with aqua regia was estimated to be 5.7 wt % with XRF. Silica-supported Pt catalysts (denoted as imp-Pt hereafter) were prepared with a conventional impregna-
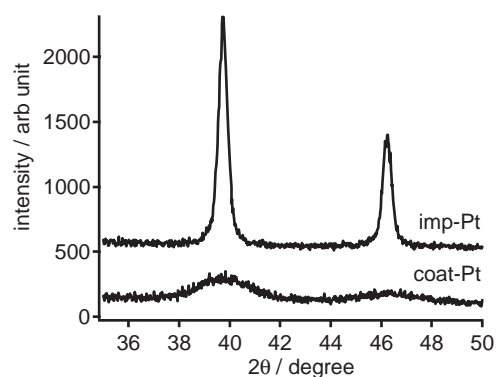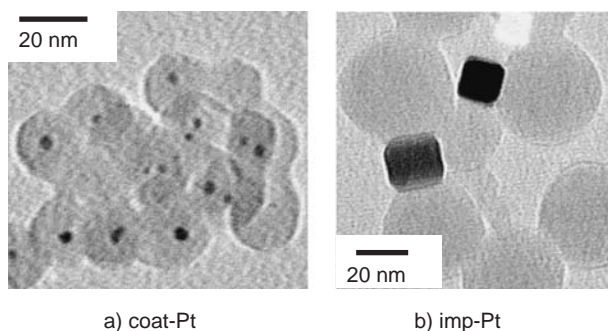

Figure 1. XRD patterns of coat-Pt and imp-Pt catalysts.

tion method. Loading of Pt in imp-Pt catalysts was estimated to 6.8 wt %. The silica supports for imp-Pt were prepared with a similar method to the preparation of coat-Pt.

Competitive oxidation of methane and other higher hydrocarbons (ethane, propane, and isobutane) with gaseous oxygen was performed at atmospheric pressure with a conventional gas-flow system with a fixed catalyst bed. The catalyst samples diluted with quartz sands were packed in a tubular reactor made from quartz (length = 300 mm and inner diameter = 8 mm). Prior to the reaction test, the catalysts were reduced with hydrogen at 573 K for 1 h. After the pretreatment of the catalysts, mixed gases of hydrocarbons and oxygen were introduced into the reactor at 573 K. During the reaction test, a part of effluent gases from a catalyst bed was sampled out and analyzed by on line G.C.

Figure 1 shows XRD patterns of coat-Pt and imp-Pt catalysts. Both the catalysts were reduced with hydrogen at 573 K prior to the measurement of XRD patterns. Two diffraction lines were observed at 39.5 and 46.5 degrees in the XRD patterns of both the catalysts. These diffraction lines can be assignable to crystallized Pt metal. The diffraction lines for coat-Pt were significantly broader than those for imp-Pt. These results indicated that the crystallized size of Pt metal in coat-Pt was smaller than that in imp-Pt.

Figure 2 shows TEM images of coat-Pt and imp-Pt treated with hydrogen at 573 K. For both the TEM images, many circular substances with diameters of 15–30 nm and darker spots could be found. Taking the results of XRD patterns in Figure 1 into consideration, the darker spots and the circular substances in the TEM images could be assigned to Pt metal particles and spherical silica particles, respectively. As for the coat-Pt catalyst, a Pt metal particle with diameters smaller than 5 nm was observed in the center of a spherical silica particle, whereas the metal particles with diameters larger than 10 nm were located

Figure 2. TEM images of coat-Pt and imp-Pt catalysts.

on the spherical silica surface for the imp-Pt catalyst. These results strongly suggest that Pt metal particles can be covered with silica layers uniformly by the preparation method using the microemulsion system.

　　Figure 3 shows the results of the competitive oxidation of methane and other higher hydrocarbons with gaseous oxygen over coat-Pt and imp-Pt catalysts at 573 K. In the reaction test, methane and another hydrocarbon (ethane, propane, or isobutane) were introduced with gaseous oxygen into the reactor. The conversions of methane and another hydrocarbon were shown in Figure 3. Complete oxidation of hydrocarbons proceeded selectively and gaseous oxygen was consumed completely in all the reaction tests shown in Figure 3. In the reaction test of methane and ethane over imp-Pt catalyst, the conversion of ethane was significantly higher than that of methane. As for the reaction tests of methane and propane, and of methane and isobutane over imp-Pt catalyst, the conversion of propane or isobutane was appreciably higher than that of methane. These results are reasonable because methane is the most inactive for the oxidation with gaseous oxygen among all the hydrocarbons.

　　The conversions of methane and ethane in the reaction test over coat-Pt catalyst were almost the same levels as those over imp-Pt catalyst. On the other hand, the relative conversion of methane to propane or isobutane was higher in the reaction over coat-Pt catalyst, compared to that over imp-Pt catalyst. In the competitive oxidation of methane and propane, the relative conversion of methane to propane was 0.8 for coat-Pt catalysts, whereas the relative conversion was 0.3 for imp-Pt catalysts. In addition, relative conversion of methane to isobutane was 2.6 for coat-Pt catalyst, whereas the relative conversion for imp-Pt was 0.2. It should be noted that the relative conversion of methane to another hydrocarbon in each reaction over coat-Pt catalyst was gradually larger as the molecular weight of another hydrocarbon increased. This order in the reactivity of hydrocarbons for the oxidation over coat-Pt catalyst was just opposite to that over imp-Pt catalyst.

　　As described in Figure 3, the conversions of methane and ethane over coat-Pt catalyst were similar to those over imp-Pt catalyst, while the relative conversion of methane to isobutane for coat-Pt was significantly higher than that for imp-Pt catalyst. These results can be explained by the difference in the diffusion rates of the reactant molecules. In the competitive oxidation over coat-Pt catalyst, the reactants (hydrocarbons and oxygen) were contacted with catalytically active Pt metal particles after they
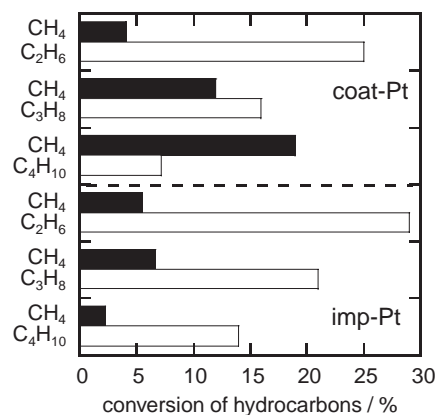
Figure 3. Conversion of hydrocarbons in the competitive oxidation of mixed hydrocarbons with gaseous oxygen over coat-Pt and imp-Pt catalysts at 573 K. Catalyst = 0.030 g, flow rate = 40 mL min^{-1}, P(CH$_4$) = 25 kPa, P(C$_2$H$_6$) or P(C$_3$H$_8$) or P(i-C$_4$H$_{10}$) = 25 kPa, P(O$_2$) = 25 kPa, and P(Ar) = 25 kPa.

diffused in silica layer with pore structures. The pore structure of coat-Pt catalyst was estimated by the adsorption and desorption of Ar at the boiling point of liquid Ar. The results showed the distribution of pore diameters with the maximum at ca. 1 nm for the coat-Pt catalyst. The diffusion rates of the reactants in silica layers of coat-Pt should be faster in the order of methane > ethane > oxygen > propane > isobutane, assuming that their diffusion rates are controlled by Knudsen diffusion. In the competitive oxidation of methane and ethane with gaseous oxygen over coat-Pt catalyst, the diffusion rates of the reactants are faster in the order of methane > ethane > oxygen. It is likely that relative conversion of methane to ethane over coat-Pt catalyst did not depend on the diffusion rates of methane and ethane, because the diffusion of oxygen was a rate-determining step in the oxidation. In contrast, in the competitive oxidation of methane and isobutane with gaseous oxygen over coat-Pt catalyst, the diffusion rates of the reactants in silica layers are faster in the order of methane > oxygen > isobutane. Thus, methane should react with oxygen preferentially on Pt metal particles due to the low diffusion rate of isobutane. This is one of the reasons why relative conversion of methane to isobutane over coat-Pt catalyst was significantly higher than that over imp-Pt catalyst. From the results described earlier, we conclude that silica-coated metal or metal oxide catalysts show the reactant selectivity based on the difference in the diffusion rates of the reactant molecules in many catalytic reactions.

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