Preparation of silica-coated Pt metal nanoparticles using microemulsion and their catalytic performance

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Abstract

Pt–SiO₂ catalysts were prepared by using water-in-oil type microemulsion. The catalysts were prepared by hydrolysis of tetraethylorthosilicate in the microemulsion containing Pt species, followed by calcination in air and reduction with H₂. This preparation method for Pt–SiO₂ provided Pt metal nanoparticles with a diameter of ca. 6 nm covered uniformly with silica layers, while a conventional impregnation method formed Pt metal particles supported on the silica surface. The Pt catalysts coated with silica (coat-Pt) showed different catalytic performance for the competitive oxidation of mixed hydrocarbons from Pt catalysts supported on silica (imp-Pt), i.e. in the competitive oxidation of methane and iso-butane, coat-Pt catalysts preferentially oxidized methane, while iso-butane was oxidized selectively over imp-Pt catalysts. The results of the adsorption of Ar on coat-Pt showed that silica in coat-Pt had porous structures of pore diameters < 1 nm. Because the porous structure of silica, which wrapped Pt metal particles, controlled the diffusion rate of reactant molecules, coat-Pt showed a specific catalytic performance for competitive oxidation.

Keywords: Pt metal nanoparticle covered with silica; Microemulsion; Competitive oxidation of hydrocarbons

1. Introduction

Development of a catalytic system that can produce required products with high selectivity and yield is a very important subject in catalyst chemistry. Selectivity in catalytic reactions could be controlled by utilizing the porous structure of the catalysts. 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 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. The utilization of porous structure of the catalysts is one of the promising ways to improve the selectivity in the catalytic reactions.

We have studied the preparation of silica-supported metal catalysts by using microemulsion [5,6]. In the preparation methods, nanoparticles containing metal cations were formed in the microemulsion and then hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) were performed in the microemulsion. By this preparation method, nanoparticles of various metals or metal oxides such as Fe₃O₄, Ni, Co, Pt, Rh and so on can be covered uniformly with silica layers. We demonstrated that the silica-coated metal or metal oxide catalysts showed high resistibility to the sintering of metals or metal oxides [2,3]. Zeolites such as ZSM-5 show 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. The utilization of porous structure of the catalysts is one of the promising ways to improve the selectivity in the catalytic reactions.

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porous structure, the catalysts would show reactant selectivity for catalytic reactions.

In the present study, silica-coated Pt metal particles were prepared using microemulsion and characterized by XRD, Pt L_{III}-edge EXAFS, TEM and adsorption of Ar. In addition, these catalysts were utilized for the competitive oxidation of methane and other higher hydrocarbons (ethane, propane and iso-butane) with gaseous oxygen. We would report the specific catalytic performance of silica-coated Pt metals for reactant selectivity.

2. Experimental

Silica-coated Pt catalysts with different Pt loadings (denoted as coat-Pt, hereafter) were prepared by using microemulsion. Water-in-oil type microemulsion was prepared from aqueous H_{2}PtCl_{6}, polyoxyethylene(n = 15) cetyl ether (denoted as C-15, hereafter) and cyclohexane. The molar ratio of C-15 to Pt atoms was kept constant to 118 for the preparation of all the silica-coated Pt catalysts. Then, aqueous ammonia (23 molm^{-1}) was added into the microemulsion to form nanoparticles of some Pt compound. The amount of aqueous NH_{3} added into the microemulsion was adjusted to NH_{3}/Pt = 3 as a mole ratio. In order to cover the nanoparticles containing Pt species with silica, TEOS was added into the microemulsion. The molar ratios of Pt to silicon atoms were changed from 9 to 91 for the preparation of silica-coated Pt catalysts. Hydrolysis and polycondensation of TEOS were performed by addition of aqueous NH_{3} into the microemulsion. The amount of aqueous NH_{3} added into the microemulsion was adjusted to C-15/H_{2}O = 23 as a mole ratio. The precipitates thus obtained were washed with 2-propanol three times, and dried for ca. 12 h at 353 K. The dried samples were calcined in air for 2 h at 623 K. The samples were washed with aqua regia at room temperature for 1 h in order to remove Pt species which were not covered with silica. The treatment of coat-Pt with aqua regia was repeated three times.

Silica-supported Pt catalysts (denoted as imp-Pt, hereafter) were prepared by a conventional impregnation method. The silica support was prepared by a similar method to the preparation of silica-coated Pt described above. The silica was impregnated into aqueous H_{2}PtCl_{6} at 363 K and was dried up. The samples were calcined in air for 2 h at 623 K.

The loadings of Pt for all the catalysts were estimated by XRF spectroscopy (Horiba Co. MESA-500W). XRD patterns of the catalysts were measured with a Rigaku RINT-2500KS using Cu Kα radiation at room temperature. The crystallite sizes of Pt metal in the catalysts were estimated by using Scherrer equations from a full-width at half-maximum of a diffraction line due to Pt metal (2θ = 39.5°).

TEM images of the catalysts were measured with a JEM-200CX (200 kV).

The distribution of pore sizes of silica in coat-Pt catalysts was estimated by adsorption of Ar at 87 K. Prior to the experiment of Ar adsorption, the catalysts were evacuated at 533 K for 3 d.

Pt L_{III}-edge EXAFS spectra were measured on the beam line BL-10B at Photon Factory in the Institute of Materials Structure Science for High Energy Research Organization at Tsukuba in Japan (Proposal no. 2005G194). Pt L_{III}-edge EXAFS spectra were measured in transmission mode with a Si (3 1 1) monochromator at room temperature. Prior to the measurements, the catalysts were reduced with hydrogen at 573 K and were packed in a bag made from polyethylene under Ar at room temperature. The analysis of EXAFS data was performed by using an EXAFS analysis program, REX (Rigaku Co.). For EXAFS analysis, the oscillation was extracted from the EXAFS data by a spline smoothing method. The oscillation was normalized by the edge height around 70–100 eV above the threshold. The Fourier transformation of k^{3}-weighted EXAFS oscillation was performed over the range of k = 4–15.5 Å\(^{-1}\). Inversely Fourier-transformed data for each Fourier peak were analyzed by a curve-fitting method, using phase-shift and amplitude function extracted from the EXAFS spectrum for Pt foil.

The oxidation of hydrocarbons over the catalysts was performed with a conventional gas-flow system at an atmospheric pressure. The powder catalysts (0.03–0.06 g) diluted with quartz sand (2.0 g) were packed into the quartz reactor (inner diameter = 1 cm and length = 40 cm). The catalysts were reduced with hydrogen at 583 K. After hydrogen remaining in the reactor was purged out with Ar, hydrocarbon mixtures (methane, ethane, propane and iso-butane) and oxygen were introduced into the reactor. The temperatures of the catalyst beds during the oxidation of hydrocarbons were monitored with a thermocouple which was installed in the middle of the catalyst bed. A part of effluent gases from the catalyst bed was sampled out and analyzed by online gas chromatographs.

3. Results and discussion

3.1. Characterization of catalysts

Coat-Pt catalysts with different Pt loadings were prepared by changing the mole ratio of TEOS to H_{2}PtCl_{6} in the microemulsion. The loadings of Pt in the catalysts were estimated by XRF spectra to be 0.7, 2.2, 5.3 and 5.7 wt%. Hereafter, coat-Pt with Pt loading = 0.7, 2.2, 5.3 and 5.7 wt% will be denoted as coat-Pt(0.7), coat-Pt(2.2), coat-Pt(5.3) and coat-Pt(5.7), respectively. silica-supported Pt catalysts (imp-Pt) with different Pt loadings were also prepared with a conventional impregnation method. Pt loadings in imp-Pt catalysts were changed from 0.3 to 6.8 wt%. The Pt loading for imp-Pt is shown in parenthesis after imp-Pt, for example imp-Pt(0.3) for imp-Pt with Pt loading = 0.3 wt%.
Fig. 1 shows XRD patterns of coat-Pt and imp-Pt with different Pt loadings. These XRD patterns of the catalysts were measured after the reduction with hydrogen at 573 K. In all the XRD patterns, sharp diffraction lines were observed at $2\theta = 39.5^\circ$ and $46.5^\circ$ in addition to a broad peak at $2\theta = \text{ca. } 22^\circ$. The former and the latter lines are assignable to crystallized Pt metal and amorphous silica. Thus, Pt species in coat-Pt and imp-Pt were present as crystallized Pt metal. From a full-width at half-maximum of diffraction peak due to Pt metal at $2\theta = 39.5^\circ$, crystallite sizes of Pt metal in coat-Pt and imp-Pt with different Pt loadings were estimated. The results are shown in Fig. 2. As for coat-Pt catalysts, an average crystallite size of Pt metal did not change significantly in spite of the change in Pt loading from 0.7 to 5.7 wt%. The average crystallite size of Pt in coat-Pt was maintained to ca. 6 nm. In contrast, an average crystallite size of Pt metal in imp-Pt increased from 16 to 34 nm with Pt loadings. In addition, an average crystallite size of Pt metal in coat-Pt was always smaller than that in imp-Pt over all the range of Pt loadings tested in the present study. These results suggested that the preparation method for coat-Pt using microemulsion could make an average crystallite size of Pt metal constant (ca. 6 nm) even when the Pt loadings were significantly changed.

Fig. 3 shows Pt L_{III}-edge $k^3$-weighted EXAFS spectra of coat-Pt catalysts with different Pt loadings, imp-Pt(6.8) and Pt foil. The features of EXAFS oscillations for coat-Pt with different Pt loadings and imp-Pt(6.8) were well consistent with that for Pt foil, indicating that Pt species in coat-Pt and imp-Pt were present as Pt metal mainly. Although Pt loadings for coat-Pt were changed from 0.7 to 5.7 wt%, the intensities of the EXAFS oscillations for the catalysts did not change appreciably. The intensity of EXAFS oscillation for coat-Pt was significantly smaller than those for imp-Pt(6.8) and Pt foil. Generally, the intensity of EXAFS oscillation for any metals depends on their crystallite size, i.e., the intensity becomes stronger with a larger crystallite size of the metals [7,8]. Thus, the average crystallite sizes of coat-Pt with different Pt loadings were similar to each other and the sizes were smaller than those of imp-Pt. These conclusions well coincide with those drawn by XRD patterns described earlier.

Fig. 4 shows Fourier transforms of Pt L_{III}-edge $k^3$-weighted EXAFS spectra (RSFs, radial structure...
The curves were fitted in the range of 4–15 Å⁻¹ and the k³-weighted EXAFS spectra described earlier, the former and the latter particles could be assignable to silica and Pt metal, respectively. As for the imp-Pt catalyst, Pt metal particles seem to be supported on the surface of silica particles. On the other hand, a Pt metal particle in all the coat-Pt catalysts was always observed at the center of silica particles. It should be noted that diameters of Pt metal particles in coat-Pt with different Pt loadings were very similar to each other, whereas the thickness of silica layers which wrapped the metal particles depended on the Pt loadings. From these results, it was concluded that Pt metal particles with a diameter ~5 nm could be covered uniformly with silica layers with different thicknesses by the preparation methods using microemulsion when the Pt loadings in coat-Pt were changed.

The adsorption of Ar at 87 K for coat-Pt catalysts was carried out in order to examine pore structures of silica layers which wrapped Pt metal particles. Fig. 6 shows the pore size distributions of coat-Pt catalysts. It was observed that all the coat-Pt catalysts had micropores with diameters smaller than 2 nm. Silica layers which wrapped Pt metal particles were composed of aggregates of primary particles of silica. The space among small silica particles would correspond to the micropores in silica layers. The pore size distributions were dependent on the Pt loadings of coat-Pt catalysts, i.e., pore structures grew gradually with higher Pt loadings. Especially, the fraction of micropores with diameters smaller than 1.0 nm increased significantly for coat-Pt catalysts with Pt loadings higher than 2.0 wt%.

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catalysts using microemulsion, the primary particles of silica or silica precursor were formed by hydrolysis of TEOS and they were deposited on the particles containing Pt species to form silica layers around the particles. The primary particles of silica or silica precursors would be deposited gradually on the micropores formed by their aggregates which had been deposited on the particles containing Pt species. This successive deposition of the silica precursors at the preparation stage of coat-Pt catalysts would bring about the consumption of micropore of silica layers. This would be one of the reasons why the fraction of micropore with smaller diameters decreased gradually with lower Pt loadings, i.e. thicker silica layers.

3.2. Catalytic oxidation of hydrocarbons

As described earlier, Pt metal particles in coat-Pt were covered uniformly with silica layers, while the metal particles in imp-Pt were supported on the silica surface. When coat-Pt is used as a catalyst for any reaction, the reactant molecules are diffused into silica layers which wrap Pt metal particles, followed by contact with the metal.
particles which work as catalytically active sites. As shown in Fig. 6, the silica layers in coat-Pt had porous structures with diameters smaller than 2 nm. The coverage of Pt metal catalysts with silica resulted in a change of their catalytic performance for the competitive oxidation of hydrocarbons. As shown in Fig. 7, the results on the competitive oxidation of methane and ethane over coat-Pt catalyst were very similar to those over imp-Pt catalyst. On the other hand, the conversion of methane in the competitive oxidation of propane and methane over coat-Pt catalyst was relatively higher than that for the reaction over imp-Pt catalyst. In addition, the conversion of methane was higher than that of iso-butane in the competitive oxidation of methane and iso-butane over coat-Pt catalyst, although iso-butane was oxidized preferentially over imp-Pt catalyst. The relative conversions of methane to other higher hydrocarbons for the coat-Pt catalyst become higher as the molecular weight of hydrocarbons mixed with methane become larger. This order in the reactivity of hydrocarbons for the competitive oxidation over coat-Pt was just opposite to that over imp-Pt catalyst. The preferential oxidation of methane over coat-Pt may be caused by differences in the diffusion rates of reactant molecules through silica layer covering Pt particles. In the competitive oxidation of hydrocarbons over coat-Pt catalyst, the reactant molecules are diffused in silica layers and they are contacted with Pt metal particles. The diffusion mechanism of the reactant molecules in the silica would be Knudsen diffusion because silica layers had micropores with a diameter smaller than 2 nm. A diffusion rate of a reactant molecule is faster as its molecular weight becomes smaller. Therefore, the diffusion rates of the reactant molecules in silica layer should be faster in the order of methane > ethane > oxygen > propane > iso-butane. As described earlier, little difference in the relative conversion of methane to ethane was observed in their competitive oxidation over imp-Pt and coat-Pt. This would be due to the slowest diffusion of oxygen among all the reactants. Methane and ethane are not oxidized until oxygen molecules reach the surface of Pt metal. On the other hand, in the competitive oxidation of methane and propane, and methane and iso-butane, the diffusion rates are faster in the order of methane > oxygen > propane > iso-butane. Thus, methane should be oxidized preferentially with oxygen over coat-Pt catalyst.

Fig. 8 shows the results on the competitive oxidation of methane and iso-butane over coat-Pt catalysts with different Pt loadings. The amount of coat-Pt catalysts was adjusted to keep the amount of Pt atoms in the reactor constant for all the reaction tests. The results in Fig. 8 showed the tendency that the conversion of methane increased and that of iso-butane decreased gradually with higher Pt loadings in coat-Pt catalysts. As described earlier, the thickness and porous structures of silica layers in coat-Pt depended on the loading of Pt. The number of pores with a diameter smaller than 1 nm increased significantly lower than those of the other hydrocarbons. Generally, methane is the most inactive for oxidation among all the hydrocarbons. Therefore, the present results on the competitive oxidation of hydrocarbons over imp-Pt catalyst were reasonable. The coverage of Pt metal particles with silica resulted in a change of their catalytic performance for the competitive oxidation of hydrocarbons.
with higher Pt loadings as shown in Fig. 6. The increase in the number of the pores with diameters smaller than 1 nm would cause preferential oxidation of methane in the competitive oxidation of methane and iso-butane over coat-Pt. In addition, the difference in the relative conversion of methane to iso-butane should depend on the distance of diffusion for their molecules, i.e. the thickness of silica layers in the present study. It is well accepted that the ability of separation of molecules with different sizes by porous materials becomes lower with shorter distance of diffusion for their molecules. As shown in Fig. 8, the relative conversion of methane to iso-butane for coat-Pt(5.7) was lower than that for coat-Pt(5.3), although the number of micropores with diameters <1 nm for coat-Pt(5.7) was higher than that for coat-Pt(5.3). This would be due to the difference in the diffusion distance between coat-Pt(5.3) and coat-Pt(5.7). The thickness of silica layer of coat-Pt(5.7) was thinner than that of coat-Pt(5.3), as shown in TEM images.

4. Conclusion

From the results described above, we summarize the present study as follows:

1. Pt metal particles covered with silica layers could be formed by the preparation method using microemulsion. Pt metal particles with a diameter = ~6 nm could be covered with silica layers of different thicknesses when Pt loadings were changed.

2. Coat-Pt catalysts oxidized methane preferentially in the competitive oxidation of methane and iso-butane. The porous structure of silica, which wrapped Pt metal particles, controlled selectivity in the catalytic reaction.

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