Effects of Organosilica-derived Microporous Coverage of Carbon-supported Pt Catalysts on Dehydrogenation of Cyclohexane

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Pt catalysts covered with an organosilica layer containing phenyl and/or methyl groups showed higher conversion in the dehydrogenation of cyclohexane, compared with Pt catalysts covered with a silica layer containing no functional groups. Micropores formed in the organosilica layer owing to the decomposition of functional groups by heat treatment resulted in this increase in catalytic activity which is dependent on the functional groups contained in the organosilica layer.

Organic–inorganic nanocomposites prepared by a sol–gel process have attracted a great deal of attention with respect to their applications such as catalysts, sensors, and membranes, because of their superior chemical and physical properties. In particular, organically functionalized materials based on the condensation of organosilanes have interesting effects on the porosity, adsorption and diffusion of reactants, and ultimately on the control of the surface reactivity.[1,2]

We have studied supported metal catalysts covered with a silica layer. These catalysts show a high resistance to sintering at high temperatures[3] and peculiar catalytic performances such as competitive oxidation of hydrocarbons because the active sites in the catalyst are covered with a silica layer with a porous structure.[4] However, since the pore size of the silica layer is very small (<1 nm), reactants are confined to small molecules, such as gas molecules, lower alcohols, or hydrocarbons. If the pore size of the silica layer covering the metal particles was to be increased, the range of applications for catalytic reactions using silica-coated metal particles would be expanded and the development of novel catalytic functions for the silica-coated catalysts could be expected.

In the present study, carbon-supported Pt catalysts covered with silica layers using organosilanes as the silica source were prepared and used for the dehydrogenation of cyclohexane. The catalysts covered with organosilica layers containing phenyl or methyl groups showed higher conversion than that covered with a silica layer without any functional group.

Carbon black (CB) (Vulcan XC-72 supplied by Cabot Co.) was utilized as a support for Pt particles. The coverage of CB-supported Pt metal particles with a silica layer was performed using hydrolysis of some organosilanes. CB was immersed in an aqueous solution containing H_2PtCl_6, and aqueous NH_3 was added into the solution to form Pt complex species on the CB. After filtration of this solution, the sample was dispersed in a solution containing aqueous NH_3, and the successive hydrolysis of 3-aminopropyltriethoxysilane and tetraethoxysilane (TEOS) or other organosilanes, such as, phenyltriethoxysilane (PhTES), methyltriethoxysilane (MTES) was performed at 333 K for 1.5 h to form the organosilica layer containing functional groups on the CB. Finally, the sample was dried at 333 K, followed by heat treatment in an atmosphere of H_2 at different temperatures. Hereafter, the obtained sample is denoted as SiO_2 (organosilane)/Pt/CB. For comparison, CB-supported Pt metal particles (Pt/CB) were prepared by a conventional impregnation. The amounts of Pt, SiO_2, and CB in the samples were examined by XRF and TG analysis. Transmission electron microscopy (TEM) images of the samples were measured using Hitachi H-800 equipment.

Dehydrogenation of cyclohexane in a batch reactor (round bottom flask, 50 mL) was performed under reflux by heating at 523 K and cooling at 278 K at atmospheric pressure. One milliliter of reactant and 0.3 g of catalyst were used in the catalytic reactions. The hydrogen that was evolved from the reactant was collected in a gas buret and tracked volumetrically for 150 min.

The amount of Pt in all samples was about 1.5–2 wt %, and that of SiO_2 in SiO_2(TEOS)/Pt/CB, SiO_2(PhTES)/Pt/CB, and SiO_2(MTES)/Pt/CB was 55.1, 31.4, and 35.0 wt %, respectively. Figure 1 shows TEM images of SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB after heat treatment at 623 K for 3 h. In both TEM images, CB and highly dispersed Pt metal particles with diameters of 1 to 3 nm are observed. Both catalysts were immersed in aqua regia in order to remove Pt metal particles that were not covered by the silica layer. It was confirmed that most of the Pt metal particles remained on the catalysts, by evaluating the Pt contents by XRF. This result implied that Pt metal particles on CB were covered with an organosilica layer in both catalysts.

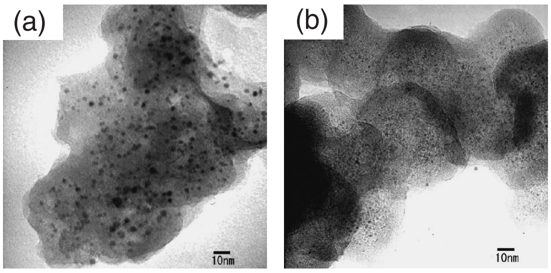

Figure 1. TEM images of (a) SiO_2(PhTES)/Pt/CB and (b) SiO_2(MTES)/Pt/CB.

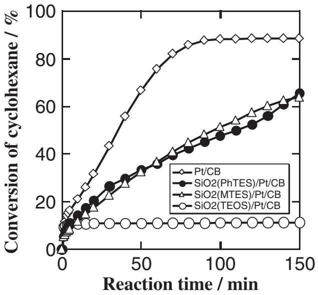

Figure 2. Time courses of conversion of cyclohexane with various SiO_2/Pt/CB catalysts after heat treatment at 623 K for 3 h.

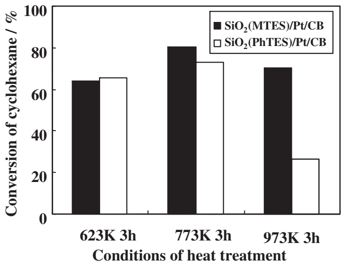

Figure 3. Conversion of cyclohexane after 150 min with SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB.

Catalytic reaction rates as shown by hydrogen evolution were studied. Figure 2 shows the time courses of conversion for the catalytic dehydrogenation of cyclohexane with various SiO_2/Pt/CB catalysts after heat treatment at 623 K for 3 h. The conversion using Pt/CB was about 90% after 150 min in this batch reactor. The conversion using SiO_2(TEOS)/Pt/CB was very low, ca. 10%. In contrast, conversions with SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB were both about 65%, significantly higher than that with SiO_2(TEOS)/Pt/CB. Figure 3 shows the conversions of cyclohexane after 150 min with SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB after heat treatments at different temperatures. The conversions obtained when using SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB increased to 70 and 80%, respectively, at 773 K. TG analysis showed that a slight weight loss began at 473 K in both catalysts, and a large weight loss was observed at about 573 K when using SiO_2(PhTES)/Pt/CB and at 773 K with SiO_2(MTES)/Pt/CB (not shown). Cyclohexane made contact with catalytically active Pt metal particles on the CB after they diffused into the silica layer. Thus this result indicates that the pore size in the silica layer is not large enough for the diffusion of cyclohexane in SiO_2(TEOS)/Pt/CB. On the other hand, micropores would form in the organosilica layer owing to the partial decomposition of phenyl or methyl groups by heat treatment[5] in SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB, resulting in an increase in the diffusion capability of cyclohexane into the organosilica layer.

In the case of heat treatment at 973 K, the conversion of SiO_2(MTES)/Pt/CB remained at 70%, while the conversion of SiO_2(PhTES)/Pt/CB decreased to 30%. Both Pt catalysts were investigated by TEM after heat treatment at 973 K, and agglomeration of Pt particles caused by sintering was not observed. These results imply that the surface structure of the organosilica layer causes the differences in conversion.

Measurement of the pore size of only the organosilica layer by N_2 adsorption was difficult because all catalysts include a CB support. Figure 4 shows FT-IR spectra of SiO_2(PhTES)/Pt/CB and SiO_2(MTES)/Pt/CB after heat treatment at different temperatures. Si–C bond absorption derived from phenyl groups was observed at 700 and 740 cm^{-1}, and Si–C bond absorption derived from methyl groups was observed at 1273 cm^{-1} in the dry samples; these peaks are in agreement with those from previous data.[5,6] The adsorption peaks of the phenyl group of SiO_2(PhTES)/Pt/CB were still observed at 623 K. These peaks decreased at 773 K and finally disappeared at 973 K. In contrast, the adsorption peak of the methyl group of SiO_2(MTES)/Pt/CB did not decrease much until 773 K, and a very small adsorption peak was still definitely seen at 973 K. This result also indicates that these functional groups decomposed by heat treatment, and interestingly, that the methyl groups were more resistant to decomposition than the phenyl groups. In the case of SiO_2(PhTES)/Pt/CB, the density growth of silica proceeded because of the decomposition of phenyl groups, then micropores would close at 973 K, resulting in a decrease in conversion. On the other hand, in the case of SiO_2(MTES)/Pt/CB, the density growth of silica did not proceed as much because existing methyl groups acted as templates and the micropores would remain. This would be a reason why the decrease in conversion would be suppressed. Thus the catalysts covered with silica layers containing phenyl or methyl groups are applicable to catalytic reactions that involve larger molecules than those that catalysts covered with a silica layer without a functional group are suitable for.

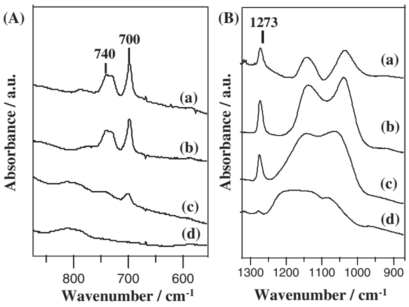

Figure 4. FT-IR spectra of (A) SiO_2(PhTES)/Pt/CB, (B) SiO_2(MTES)/Pt/CB after heat treatment at different temperatures. (a) Dry sample, (b) 623 K, (c) 773 K, (d) 973 K.

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