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Preparation and Activity of Layer Silicate-Supported Metal Catalyst

Kunio OHTSUKA* and Johji KOGA
Ceramics Research Institute, Mitsubishi Materials Corporation,
2270 Yokoze, Chichibu-gun, Saitama 368

A nickel(II) hydroxide-layer silicate intercalate was formed by mixing an expandable-layer silicate with a nickel(II) nitrate solution followed by urea hydrolysis at an elevated temperature. The hydrogen reduction of the intercalate generated nickel particles dispersed on the layer silicate crystal surface. The supported-nickel catalyst showed high activity for the hydrogenation of toluene to methylcyclohexane.

Previously we reported preparative procedures for the production of the metal-(layer silicate) nanocomposite particulates in which the layer silicate is uniformly covered with a metal layer.1,2) The preparation method involves the reduction of the layer silicate complexes which have surface precipitates obtained by using both the ion-exchange properties on the external surface of the silicates and precipitation from a homogeneous solution. In this method, the metal loading being controlled over a wide range, metal-(layer silicate) nanocomposites with the metal/silicate weight ratio of 47 : 1 were obtained. The present work has been undertaken primarily for the purpose of preparing well-dispersed, fine metal particles supported on layered silicate by this method. Further, the activity of the metal (Ni) as a catalyst has been examined for the hydrogenation of toluene as a model reaction. Ni-SiO_2, Ni-Al_2O_3, Cu-SiO_2, and Cu-Al_2O_3 catalysts were prepared so far by the homogeneous precipitation method.3-6) Expandable-layer silicates are characterized by having a lamellar structure and large cation-exchange capacities (100-300 mequiv/100 g of silicate) appearing on both inner and outer surfaces of the silicate.

A 10 wt% sol of sodium fluoride tetrasilicic mica, $NaMg_{2.5}Si_4O_{10}F_2$, from Topy Industries, Ltd., was purified and dried at 100°C according to our previous report.1) The theoretical cation-exchange capacity of the silicate is 254 mequiv/100 g of clay, and sodium ions are ion exchangeable.7) The silicate itself has no acid sites,8) but they are formed after ion exchange with cations having large polarizing power.9) A nickel/layer silicate catalyst was prepared, in a manner similar to that described in our previous report,1) as follows: 720 mL of water was added to 9.59 g of the clay powders and refluxed with stirring. Next the sol was poured gradually into 1000 mL of a 0.0516 M nickel(II) nitrate solution ($Ni(NO_3)_2 \cdot 6H_2O$, reagent grade) at room temperature while rapidly being stirred. The resulting suspension had a nickel(II) concentration of 0.0300 M and a Ni/(layer silicate) weight ratio of 0.325. The suspension was treated with an ultrasonic bath and refluxed with stirring until the silicates were dispersed. After cooling and addition of 6.20 g urea at room temperature, the suspension was aged at 95°C for 24 h to permit hydrolysis. The reaction vessel was then cooled with chilled water to terminate the reaction. The reaction product was collected by centrifugation, washed 5 times with water, dried at 100°C for 24 h, and lightly ground in a mortar. All water used was distilled and deionized. The resulting solid so prepared was calcined at 500°C for 2 h in air and reduced at 700°C for 2 h in flowing hydrogen (the rate of temperature rise in the reduction was 10°C/min). X-ray powder diffraction patterns were obtained using CuKα radiation. Crystallite sizes of the reduced nickel particles were measured from the X-ray line broadening using Scherrer's equation.[10)] The surface areas were measured by the BET method using nitrogen. The hydrogenation of toluene over the Ni/(layer silicate) catalyst was carried out using a fixed-bed flow reactor connected with gas chromatographs at atmospheric pressure. 100 mg samples were charged into a tubular quartz reactor (0.7 cm i.d. × 47 cm long), pretreated at 400°C for 2 h in H_2 (60 mL min^{-1}) and then cooled to the desired reaction temperature. Hydrogen gas was mixed with internal standard argon gas, bubbled through liquid toluene maintained at 30°C and then over the catalyst. Argon was 20 vol% and the hydrogen to toluene molar ratio was kept at 460 : 1. The W/F value for each reaction was 1.56 g mol^{-1} h, calculated by the weight of catalyst divided by the total flow rate of toluene and hydrogen; it became 718 g mol^{-1} h, when the calculation was made using only the flow rate of toluene. The hydrogen and argon were 99.99999% and 99.9995% pure, respectively. Toluene (reagent grade) was dried over 5A molecular sieves prior to use.

Table 1 presents the elemental analysis of the reaction product (clay complex) prepared by the urea hydrolysis in the presence of nickel(II) nitrate and the layer silicate. The product had a Ni/clay weight ratio of 0.30 and a surface area of 6 m^2/g. X-ray powder diffractometry gave evidence for the formation of nickel(II) hydroxide-layer silicate intercalation compounds[7)] in which nickel(II) hydroxide sheets are sandwiched between the silicate layers (Fig. 1). The reaction product had a d_{001} basal-spacing of 14.8 Å; the original layer silicate has a 9.6 Å basal-spacing. The (001) peak intensity was very weak compared with the (002) peak intensity. Moreover, no crystalline species could be detected on the XRD spectra of the resulting product as-prepared and as-calcined.[11)] This could be ascribed to the fact that no external surface precipitates occurred. We reported in our previous paper that layer silicate complexes with surface-grown nickel precipitates were

Table 1. Elemental Analyses of the Reaction Product (Layer Silicate[a)] Complex)

Component/wt%			Mole ratio			Ion-exchange	Ni/silicate
SiO_2	Na_2O	Ni	SiO_2	Na	Ni	ratio[b)]/%	(wt ratio)[c)]
40.87	1.05	20.3	4.00	0.20	2.03	80	0.30

a) Sodium fluoride tetrasilicic mica, $NaMg_{2.5}Si_4O_{10}F_2$, was employed.
b) Ion-exchange ratio was estimated by means of {1-Na (mole ratio)} × 100.
c) The amount of layer silicate was calculated from the silica content of the analysis.

formed by urea hydrolysis in the presence of nickel(II) nitrate and the layer silicate.$^{1)}$ However, in this study a nickel(II) hydroxide-layer silicate intercalate was produced. This can be rationalized by the difference in the amount of nickel ion neutralized between the two experiments: that is, a small amount of precipitated nickel ion favors the formation of the intercalate, whereas a large amount of precipitated nickel ion gives the layer silicate complex with surface precipitated material. Generally, the metal hydroxide-layer silicate intercalation compounds are obtained by titrating the metal salt solutions containing expandable-layer silicate with a base; the chemical formula of the intercalation compounds with 100% ion-exchange ratio is expressed by $[Me^{II}{}_x(OH)_{2x-1}(H_2O)]^{+1}(Mg_{2.5}Si_4O_{10}F_2)^{-1}$ ($1/2 \leqq X \leqq 3$).$^{9)}$ Hence the amount of the metal incorporated into the layer silicate is restricted to a small amount. In the case of nickel, the maximum nickel/clay weight ratio is 0.47 (the ratio varies with the degree of ion-exchange: when it is 80%, the maximum nickel/clay ratio is 0.47× 0.8 or 0.376). Since urea hydrolysis gradually raises the pH of the solution by the release of NH_3, the intercalate is formed when a small amount of Ni is neutralized (Ni/clay $\leqq$0.47) by the urea hydrolysis as well as by the titration with a base. On the other hand, when a large amount of Ni is neutralized (Ni/clay>0.47), the metal hydroxide-layer silicate intercalation compound is formed first and then metal ions in excess of the amount which can be intercalated are deposited on the outer surfaces of the silicate as the urea hydrolysis progresses, causing a layer silicate complex with surface precipitates. Hence in this work (nickel/silicate=0.30) the intercalate was formed; whereas in our previous report (nickel/silicate=0.76 to 8.01) layer silicate complexes with surface precipitates were observed. It should be noted, however, that the metal ions which can not form metal hydroxide-layer silicate intercalates will be precipitated solely on the external surface of the layer silicate by urea hydrolysis, even if a small amount of metal ions is neutralized.

Upon reduction of the intercalate, the basal-spacing decreased from 14.8 Å to 9.6 Å and this was accompanied by the appearance of nickel metal (Fig. 1). The H_2 reduction of the metal hydroxide-layer silicate intercalates leads to the migration of the reduced metal atoms out of the interlayer of the silicate to form highly divided metals on the outer surface of the silicate.$^{7)}$ The nickel content of the resulting products was 24.1 wt% and their specific surface area was 16 m^2/g. The crystallite sizes perpendicular to the (111) and (200) planes of the Ni were 80 Å and 69 Å, respectively.

Figure 2 illustrates the catalytic activity of the Ni/layer silicate catalyst toward the hydrogenation of toluene after a duration of 2.5 h. The toluene conversion to methylcyclohexane was almost quantitative at 175 °C. The amount of unreacted toluene in the product gas increased with increasing temperature above 175 °C, this drop in activity resulting mainly from catalyst deactivation due to coke deposition. Matsuo and Klabunde$^{12)}$ studied the hydrogenation of toluene using Ni/MgO catalysts, and also Coughlan and Keane$^{13)}$ studied with nickel-loaded Y zeolites. The changes in the activity with reaction temperature exhibited the same trend as we observed, although the temperature for the maximum toluene hydrogenation over their catalysts is higher than ours. Methane is likely formed by the subsequent partial hydrogenolysis of methylcyclohexane. Methods have been known for preparing supported-metal catalysts from clay minerals.[14] Such processes use the reduction of natural and synthetic clay minerals such as anionic clays and nickel-containing layered silicates which have nickel ions isomorphously incorporated. Our method provides new routes to supported-metal catalysts: fine metals are formed on the layer silicate by the reduction of the intercalation compounds, and bimetallic and multimetallic catalysts are derived from the biintercalation and multiintercalation compounds.

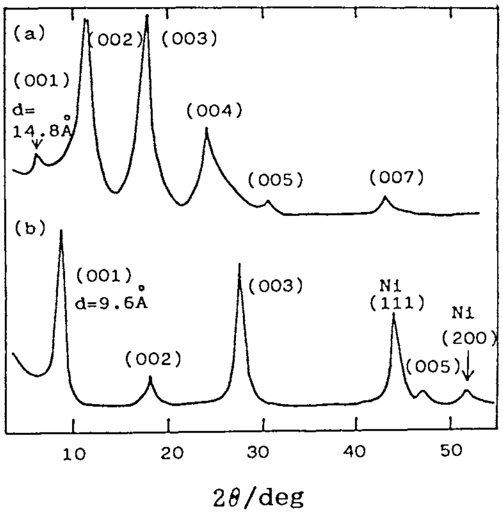

Fig. 1. Powder XRD patterns of (a) the reaction product and (b) the resulting product obtained by the H_2 reduction of (a).

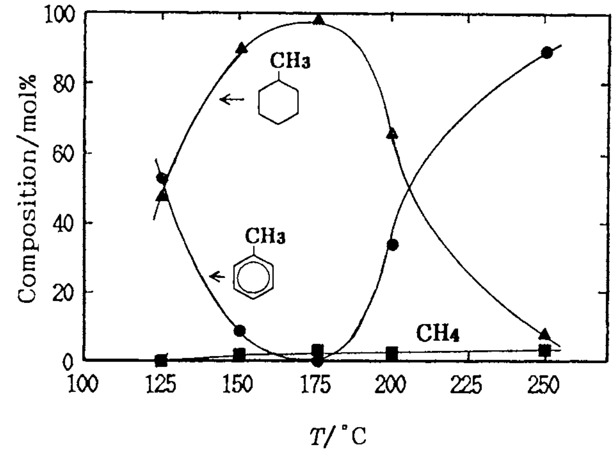

Fig. 2. Product distribution with reaction temperature over a Ni/layer silicate catalyst toward the hydrogenation of toluene. ● : toluene, ▲ : methylcyclohexane, ■ : methane.

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