Formation of Single Crystal of Hofmann Clathrate, $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$, at Higher Temperature by Means of Spray Pyrolysis of Sucrose and Nickel Nitrate

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Single crystal of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ was formed by the pyrolysis of mist of aqueous sucrose and nickel nitrate solution at higher temperatures as 873–1073 K in an inert gas without using harmful organic and inorganic compounds such as NH_3 and HCN.

The inclusion compounds in general, particularly clathrates, have been a subject of many theoretical and experimental studies as a result of their fundamental significance in understanding the nature of interactions between the molecular and ionic species, and also their practical importance.[1,2] Detailed spectroscopic studies of Hoffman clathrates with $Ni(NH_3)_2Ni(CN)_4 \cdot mG$ (G = benzene, benzene derivatives, H_2O, and so on) and the characterization of various metals and guest molecules have been carried out so far.[3–7]

Generally, clathrates were prepared in an aqueous phase, for example the compounds $M(daon)Ni(CN)_4 \cdot G$ (M = Co, Ni, or Cd; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) were prepared by adding 1,8-diaminooctane to a solution of $K_2Ni(CN)_4$, MCl_2, water, and ethanol saturated with the guest molecules.[4]

Most of metal complexes are prepared at relatively low temperatures near ambient temperature, because they are usually prepared in aqueous or organic medium. However, authors found the slightly selective formation of single crystal of Hofmann complex, $Ni(CN)_2(NH_3) \cdot 0.25H_2O$, during the pyrolysis of a mist of solution containing sucrose and nickel nitrate in an inert gas as Ar without using harmful and ligand compounds such as NH_3 and HCN at 873–1073 K, which are much higher temperatures than those in ordinal metal complex synthesis.

Sucrose (Wako pure chem. Co., reagent grade) as a carbon source and nickel nitrate (Wako Pure Chem. Co., Pure grade) were used. An aqueous solution containing sucrose and $Ni(NO_3)_2 \cdot 6H_2O$ was fed into a reactor made of stainless steel with 10 cm in diameter by a spray. Feed rates of the liquid and Ar as a carrier gas are shown in Figures. A schematic diagram of the reaction system is shown in Figure 1. The reactor is heated by a 40-cm electric heater. The gas stream after the reaction was introduced into a water trap and the products were collected into water. The recovered water containing products was separated by a magnet to two portions. Both portions were filtrated off, washed with pure water, and dried at 343 K overnight. The samples obtained were analyzed by XRD, TG-DTA, MAS-NMR, SEM, and TEM-ED.

First of all, we tried to check the products from component materials using this method and apparatus. The experiments using a sucrose solution without Ni salts and a sucrose free Ni salt solution were carried out. When a sucrose solution without Ni salt was sprayed into the reactor at 873, 973, 1073, and 1173 K, no carbon materials were obtained. This may be due to small space velocity and low reaction temperature for carbon formation. On the contrary, in the experiment using $Ni(NO_3)_2$ without sucrose, greyish black materials were recovered in a water trap. The SEM images revealed that the products were distorted spheres with 2–16 µm in diameter. Most of spheres appear to have an egg shell shape and have a hole in the wall. From TEM images of the sample showed that the particle appears to have an egg shell structure and that the wall seems to be composed of small particles with 0.15–0.37-nm diameter. It was shown by XRD that this products was composed of only NiO.

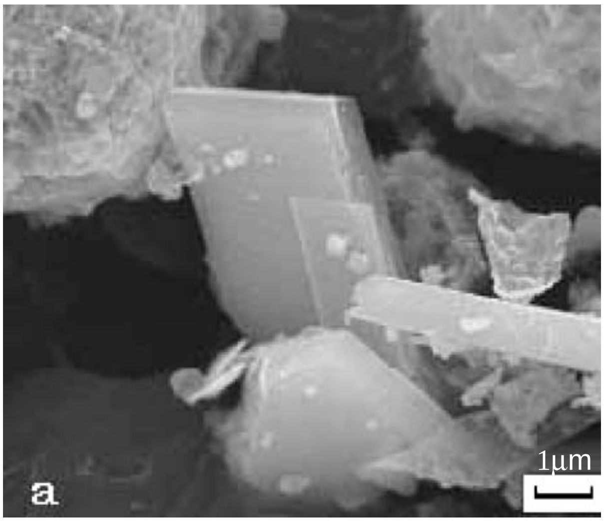

Figure 1. SEM image of the $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ formed at 873 K before separation by a magnet.

Experiments were carried out using a solution of 0.05 M $Ni(NO_3)_2$ and 0.05 M sucrose at various reaction temperatures. As expected, the products were obtained at 873–1173 K. At 873 K, distorted spheres with 2–20 µm in diameter and thin sheets larger than those of spheres in size were obtained. Spheres were similar to those from sucrose-free $Ni(NO_3)_2$ in shape and, each sphere had a hole in the wall. Presence of the hole suggested that inside materials come out through the hole at high temperatures and generate a sphere with an egg shell structure. From TEM image, Ni metal particles with 3–17 nm in diameter were dispersed in the products. The product at 973 K was composed of distorted spheres similar to those synthesized at 873 K in shape but the size was larger. Relatively small aggregate of platelets of about 2.2 µm and rectangular solids were formed (Figure 1). At 1073 K, size of spheres increased and the formation of aggregates of platelets and sheets were increased. Ni par-

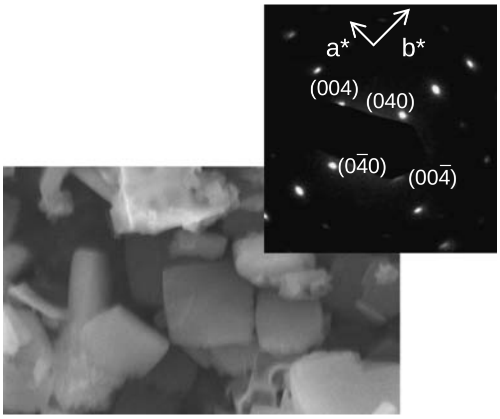

Figure 2. TEM image of nonmagnetic portion and electron diffraction of thin plate of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$.

ticles with 1.7–6.7 nm were dispersed in the obtained Ni–carbon composite, but no Ni particle was observed in the plates. Nickel particles with about 2.5 nm in diameter were well dispersed in the spheres suggesting that the spheres are Ni–carbon composites. Amount of rectangular solids and the size became smaller.

XRD spectra of the formed powder at different temperatures revealed that the product is composed of Ni metal and NiO were obtained in the sample prepared at 873 K. In the reaction at 973 K, intensity of peaks due to NiO decreased and intensity of peaks due to Ni increased. Small peaks due to $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ (ASTM # 15-0049) appeared at about 20 degree. At 1073 K, peaks of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ increased and peak of NiO was disappeared. In the products at 1173 K, all the diffraction peaks became less intense. Comparing XRD spectra to the SEM observation of the products, one can notice that the plates and rectangular body will be $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ which is one of clathrate compounds so called "Hofmann type."[7]

It is clarified that product is composed of NiO, Ni, C, and $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$. Seeing Ni compounds, Ni metal is paramagnetic; however, NiO and $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ contain nonmagnetic Ni species. So that separation by magnetic field was studied. Expectedly, the product at 873–1073 K can be separated to two portions by a magnet. SEM image of the nonmagnetic compounds is shown in Figure 2. As can be seen from the figure, the number of rectangular bodies has increased and no spheres were observed in the nonmagnetic portion. XRD spectra of the paramagnetic and nonmagnetic portions are shown in Figure 3. XRD pattern of nonmagnetic portion gave diffraction peaks due to $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ and a very small peaks due to Ni. On the other hand, the paramagnetic portion showed strong peaks due to Ni metal. These results clearly show that nonmagnetic portion is mainly composed of Hofmann clathrate and that the paramagnetic portion is mainly composed of Ni metal.

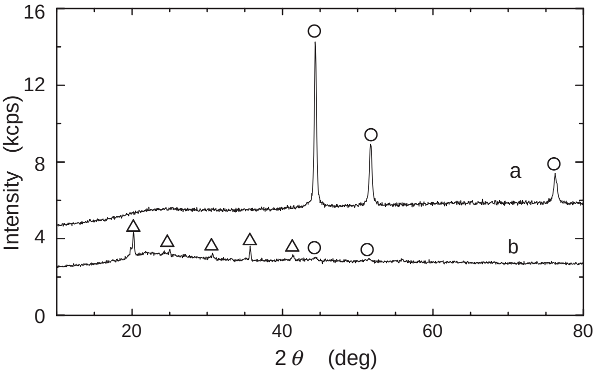

Figure 3. XRD patterns of (a) paramagnetic portion and (b) nonmagnetic portion of the products formed at 1073 K. △: $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$, ○: Ni.

TG–DTA analysis of both portions was carried out. The weight of paramagnetic compound was decreased slightly up to 650 K and then increased to 114.6% of the initial value. The sample after TG analysis was thought to be composed of only NiO because most part of the initial sample was composed of carbon and Ni metal. Therefore, the sphere-shaped products in the paramagnetic portion contained 90 wt % of Ni and 10% of carbon. It can be seen that the spheres are Ni-rich.

On the other hand, the weight of the nonmagnetic compound decreased about 20% up to 573 K and then decreased sharply at 601 K, and the final weight was roughly 52.8 wt % of the initial value. If the final compound is NiO, Ni content of the nonmagnetic portion was calculated to 41.5 wt %. Ni content of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ is 44.4 wt %. The result of TG–DTA analysis of the nonmagnetic portion is very close to theoretical Ni content. This also suggests that this portion is mainly composed of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$.

It is concluded from these experimental results that plate and rectangular body are single crystal of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$.

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