The Effect of Starting Source on the Concentration Distribution of Nickel Supported on Alumina

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Synopsis. The concentration profile and particle size of nickel supported on alumina spheres were easily controlled by varying the starting source materials of the impregnation solution. Further, the reduction behavior of nickel oxide supported on alumina was influenced by the starting nickel source material.

The catalyst activity and selectivity of supported metal catalyst are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method and the support composition. In particular, to improve the catalyst activity and durability it is necessary to control the distribution of metal particles in the catalyst. The control of a radial distribution of metal particles in the catalyst was easily achieved by changing factors as the impregnation period,[1)] the pH of impregnation solution[2)] and used additives.[3,4)] However, only a few investigations have been reported about the effect of the source material on the physical properties and reactivity of the catalysts.[5,6)]

In this paper, we wish to report on the effect of the starting source material on the metal particle distribution and physical properties of nickel supported on alumina sphere catalysts.

Experimental

The Ni/Al_2O_3 catalysts were prepared by impregnation of γ-alumina (JRC-ALO-3 supplied by Catalysis Society of Japan) with aqueous solution of the nickel salts (nickel acetate, nickel formate, nickel chloride and nickel nitrate) or aqueous ammonia (28%) of a nickel carbonate and the solution was evaporated at 100 °C. The impregnated samples were calcined in air at 450 °C for 2 h and, subsequently, reduced in a stream of hydrogen at 450 °C for 2 h. Typical properties of the support are given in Table 1. Nickel concentration profiles along the diameter of the catalyst cross section were measured by EPMA (JEOL JCXA-733). The catalyst was embedded in a thermoplastic resin. After solidification, raping film sheets were used to grind off the catalyst particles so as to expose the cross section. The sample was coated with a layer of carbon by vacuum deposition. The particle size of nickel was measured by TEM (Hitachi H-9000H). Finely ground catalyst particles were suspended in ethanol and then scooped up with a micromesh. These particles were dried under vacuum and used as a specimen. The reduction behavior of the catalyst was measured by TPR. Typically, 50-mg samples were used. Prior to reduction, each sample was dried for one hour in a stream of helium at 300 °C. On cooling the sample to room temperature, helium was replaced by hydrogen, then, the reactor temperature was raised (1 °C min^{-1}) and the hydrogen consumption was measured. The total nickel content in each catalyst was determined by chelate titration. A sample solution was prepared by dissolving the nickel of the catalyst in hydrochloric acid and filtering.

Table 1. Physical Properties of JRC-ALO-3[7,8)]

Composition	γ-alumina
BET surface area/m^2g^{-1}	121
Modal pore diameter /nm	10.0
Specific pore volume/m^3g^{-1}	5.28×10^{-7}
Average diameter/mm	3.0—3.2

Results and Discussion

First, the nickel concentration profile and total nickel contents in the alumina sphere of the prepared Ni/Al_2O_3 using various nickel solution were measured as shown in the Fig. 1. The nickel concentration profile in the support can be classified into two types. In the first type, the nickel atoms were uniformly distributed over the whole of alumina sphere (A and B). In the second type, the nickel atoms were concentrated in the vicinity of the outer surface of alumina sphere (C, D, and E). Further, the band widths of the nickel atom in the second-type concentration profile were changed by the starting source materials. In the case of nickel carbonate, the nickel atoms were sharply distributed on the outer surface of the alumina sphere. The thickness of the nickel band was estimated to be about 100 μm. On the other hand, the position of the nickel band seems to spread toward the center of the alumina sphere when nickel acetate and nickel formate were used. The Ni/Al ratio of impregnant was 50/950 but the total nickel contents of these catalysts were different from those of the starting source materials. The total nickel contents obtained by chelate titration were in good agreement with the analytical data from EPMA response for nickel. The differences of the nickel concentration profile and total nickel contents in the alumina sphere were attributed to the adsorption rate of nickel complex ion into the alumina.[9)]

The particle sizes of the nickel metal in the catalysts were observed by TEM as shown in Fig. 2. In the case of the catalysts prepared from nickel nitrate, nickel acetate and nickel chloride, the nickel metal particles were highly dispersed in an even size around 5 nm on the alumina spheres. On the other hand, the nickel metal particles of the catalysts prepared from nickel carbonate and nickel formate were observed in the form of larger crystallites. The nickel concentration profile produced from nickel acetate in alumina sphere was similar to that from nickel formate as shown in Fig. 1, but they differed from one another in the nickel particle size.

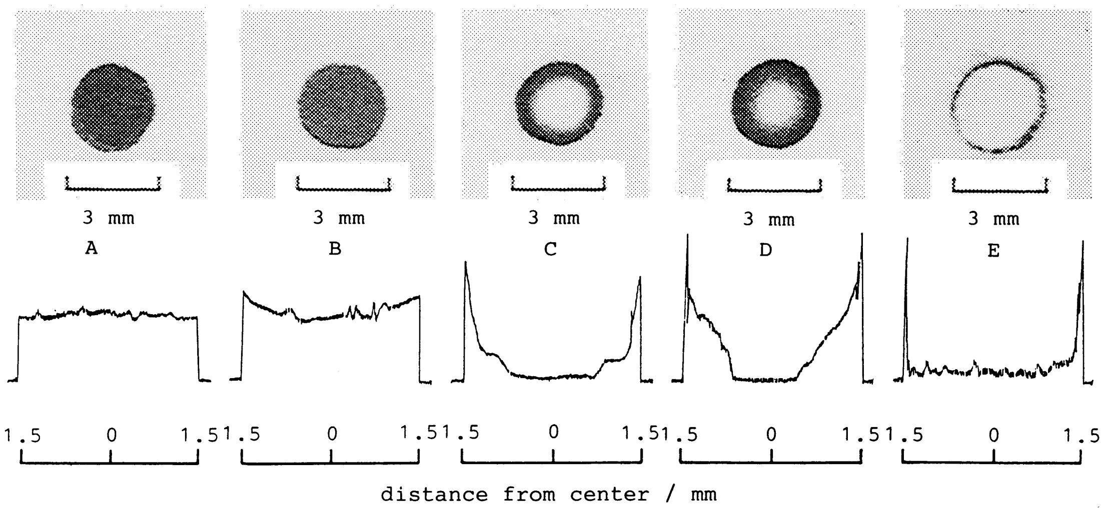

Fig. 1. Distribution of Ni atom in the catalysts measured by EPMA.
A: nickel nitrate (Ni/Al=37/923), B: nickel chloride (Ni/Al=36/924), C: nickel formate (Ni/Al=32/928), D: nickel acetate (Ni/Al=28/972), E: nickel carbonate (Ni/Al=19/981).

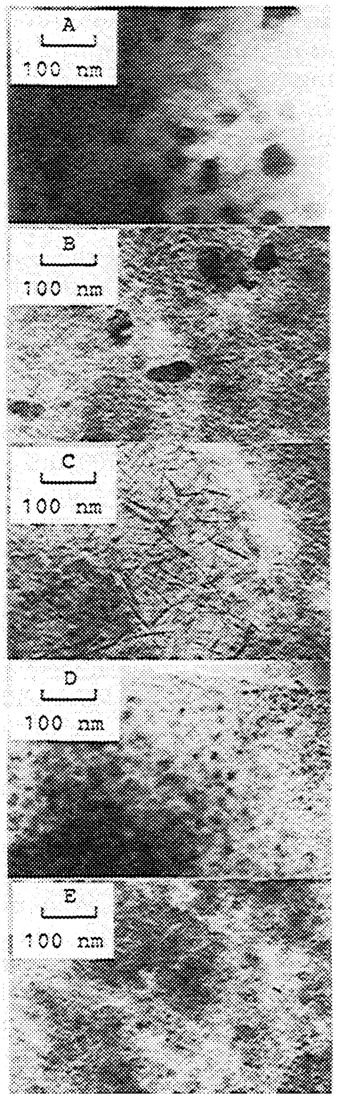

Fig. 2. TEM photograph of Ni in the catalyst reduced at 500 °C for 3 h.
A: nickel formate, B: nickel carbonate, C: nickel chloride, D: nickel acetate, E: nickel nitrate.

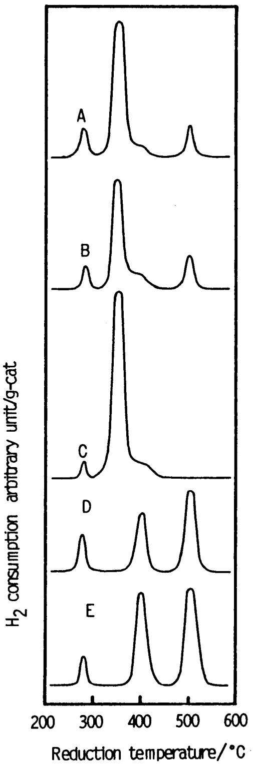

Fig. 3. TPR spectrum of supported nickel catalysts.
A: nickel nitrate, B: nickel acetate, C: nickel chloride, D: nickel formate, E: nickel carbonate.

The chemical interaction between nickel oxide and alumina was measured by TPR. Figure 3 shows the TPR spectrum change in relation to starting nickel source materials. The reduction peak of nickel oxide appeared at 280 °C. The main reduction peaks of the catalysts prepared from nickel nitrate, nickel chloride and nickel acetate were observed at 350 °C and a small peak appeared at 500 °C, while the main reduction peaks of the catalysts prepared from nickel carbonate and nickel formate appeared at 400 and 500 °C. It was found that the reduction of the catalysts prepared from nickel carbonate and nickel formate became very difficult compared with those prepared from nickel nitrate, nickel chloride and nickel acetate. The results from the morphology investigation on the nickel/γ-alumina catalysts(10) indicated that the difficulty in the reduction of the nickel oxide were responsible for the formation of nickel aluminate precursor and large nickel crystallites were produced by its reduction. According to the experimental results in Figs. 2 and 3, the nickel aluminate precursor was plausibly formed when nickel carbonate and nickel formate were used as starting source materials.

It is concluded that the starting nickel source has the remarkably effects on the nickel concentration profile and nickel particle size in the alumina spheres which are used as a support, when preparing the catalyst by the impregnation method.

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