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CONTROL OF Ni DISTRIBUTION IN Al_2O_3 SUPPORT USING ALKOXIDE TECHNIQUE

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The distribution of nickel atoms in alumina spheres was well controlled by varying impregnation period when the alumina spheres are immersed in a solution composed of nickel-ethlene glycolate and ethyl silicate.

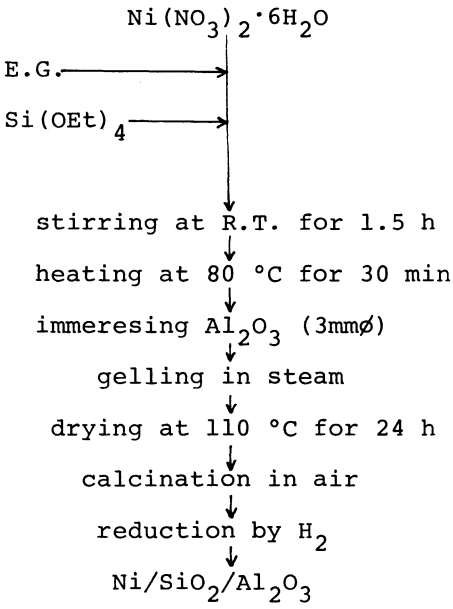
The control of metal particle size in a supported catalyst is of current interest.[1] The present authors have reported in earlier papers[2] that nickel metal particles in Ni/SiO_2 catalyst were well controlled in an even size level when the catalyst was prepared by simultaneous hydrolysis of Ni-ethlene glycolate and ethyl silicate, followed by drying, calcination and reduction in a hydrogen stream. This preparation method of catalyst has been called alkoxide technique. Although the alkoxide technique can easily be applied to the preparation of the other metal catalysts supported on silica,[3] a few disadvantages have been pointed out. One of them is that considerable amounts of the metal atoms might not contribute to the catalytic reaction since they are incorporated inside the silica support and can not be exposed to the outer atmosphere. Indeed, more than 20% of Ni atoms were remained inside the silica support forming Ni-O-Si network even after the reduction at 700°C by hydrogen.

The purpose of the present work is to develop the technique which enhances the fraction of Ni atoms existing on the catalyst surface, the Ni particles being still controlled in an even size level. In the alkoxide technique the simultaneous hydrolysis of the mixed alkoxides is an important step to prepare the catalyst which contains the metal particles controlled in a homogeneous size. Instead of the simultaneous hydrolytic decomposition, alumina spheres, the specific surface area being 298 m^2/g, supplied from Sumitomo Aluminium Co., were immersed

in the mixed solution of Ni-ethlene glycolate and ethyl silicate and then placed under water vapor atmosphere in order to make a gel consisting of Ni-O-Si network over the alumina surface. The alumina spheres thus treated were dried at 110 °C in an oven, followed by calcination and reduction at 700 °C in a hydrogen stream. The details of the preparation procedure are given in Table 1. The nickel concentration in the mixed alkoxides solution employed was 20 wt%, measured by an atomic absorption spectroscopy.

When the alumina spheres were immersed in the mixed alkoxides solution for 1 min, the nickel atoms in the catalyst were well concentrated in the vicinity of the outer surface of alumina spheres, as shown in Fig. 1-a. The photographs demonstrated in Fig. 1 are the cross sections of the catalyst spheres. The distributions of Si and Ni atoms in the catalyst spheres were measured by means of EPMA(electron probed X-ray micro-analyser, Hitachi model X-650) operated at an accelerating voltage of 20 kV with an energy dispersive detector (see Fig. 2). After the drying at 110 °C, Ni atoms are rather broadly distributed in the vicinity of the outer surface of alumina spheres while they are concentrated in a narrow band just inside the spheres when the catalyst is calcined at 500 °C for 4 h. The position and width of this narrow band

Table 1. Catalyst preparation procedure



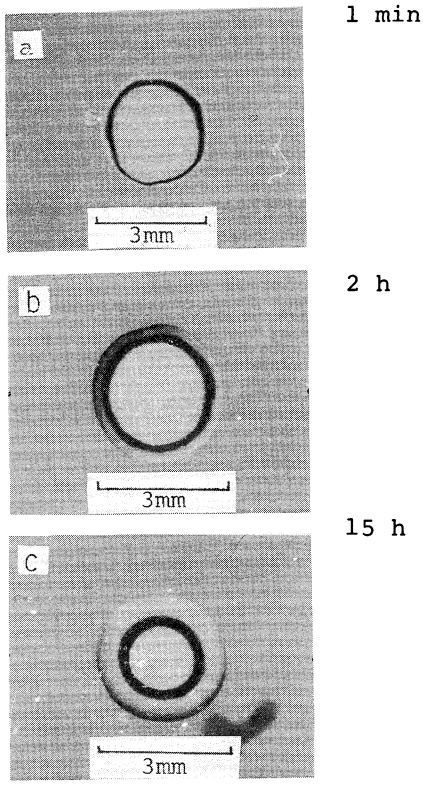


Fig. 1. Distributions of Ni in the catalysts with different immersion periods.

were preserved during the reduction at 700 °C for 4 h under hydrogen stream.

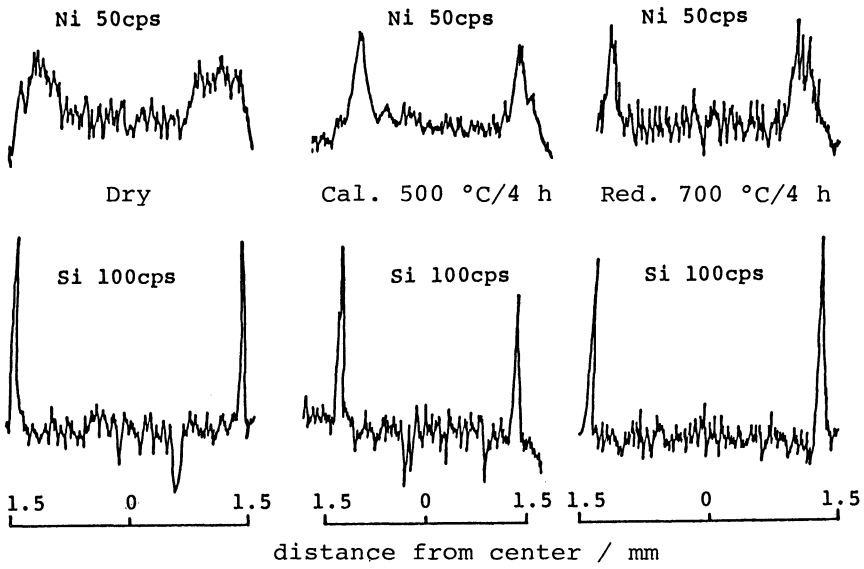


Fig. 2. Distribution of Ni and Si atoms in the catalyst measured by EPMA.
(the catalyst was immersed for 1 min.)

On the contrary, the Si atoms are sharply distributed on the outer surface of the alumina spheres in any steps of the preparation procedure, suggesting that a thin film consiting of SiO_2 covers the whole external surface of every alumina sphere. The thickness of the SiO_2 film was estimated to be about 50 μ in average. The specific surface area of the resulting catalyst was 201 m^2/g, measured by BET method using nitrogen at its liquid temperature. The concentration of Ni in the catalyst was 0.37 wt%, measured by an atomic absorption spectroscopy.

The particle size of the Ni metal in the catalyst was measured using a transmission electron microscope(TEM, Hitachi model H-800), operated at an accelerating voltage of 200 kV with a magnification of $x10^5$. The nickel metal particles are highly dispersed in an even size around 80 Å on the alumina spheres, as is clearly shown in Fig. 3. The hydrogen chemisorption method was also adopted to confirm the Ni particle size in the catalyst. The degree of reduction of Ni ions in the catalyst is necessary for the determination of the metal particle size,[4] and whole Ni ions were proved to be reduced to Ni metal by measuring the saturated magnetic susceptibility after the reduction at 700 °C by hydrogen. The magnetization was measured by a vibrating sample magnetometer (Toei Kogyo Co., Model VSM-2), with a vibrating frequency of 80 Hz and the magnetic field strength up to 20 kOe. The amount of hydrogen adsorbed was 0.095

ml per g of the catalyst, indicating the Ni dispersion expressed in terms of H/M is 0.14. By these measurements the particle size of Ni(assumed to be spherical) was estimated to be 70 Å, being in good agreement with that obtained by TEM. This means that the fraction of Ni atoms trapped inside the SiO_2 support is negligibly small. In order to increase the amount of Ni atoms in the catalyst, the immersing time of alumina spheres in the mixed alkoxides solution was prolonged. In Fig. 1-b and 1-c are shown the photographs of the cross sections of the catalysts with the immersing time of 2 and 15 h, the Ni concentrations being 0.44 and 0.49 wt%, respectively. The position of the narrow band seems to move toward the center of the alumina sphere with immersing time. Thus, the distribution of Ni in alumina support was well controlled by adjusting the immersing time of the support spheres with the mixed alkoxides solution, although the mechanism of the concentration of Ni atoms in a narrow band still remains to be revealed.[5)]

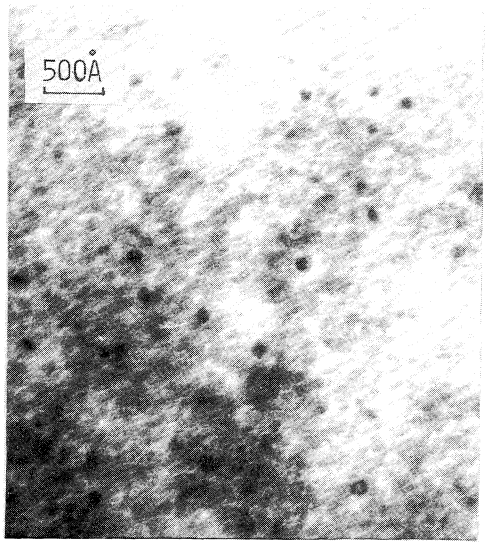


Fig. 3. TEM photograph of Ni in the catalyst reduced at 700 °C for 4 h.

References

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