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Effects of Calcination and Reduction Temperatures upon Particle Size of Ni in Ni/SiO_2 Catalyst Prepared by Alkoxide Technique

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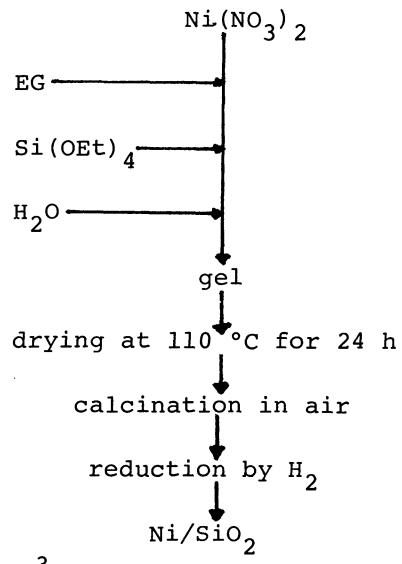
The particle size of Ni in Ni/SiO_2 catalyst prepared by alkoxide technique was proved to be well controlled by setting proper calcination and reduction temperatures even for the constant nickel metal concentration in the catalyst.

In our previous paper[1] it was reported that Ni metal particle size in the silica supported Ni catalyst prepared by alkoxide technique was well controlled by varying the Ni metal concentration in the catalyst. The silica supported Ni catalyst thus prepared was quite free from impurities such as alkaline and alkaline earth metal ions and chroline and sulfur ions, which is one of the most important conditions to study the relationship between metal particle size and the catalysis. One of the disadvantages of the alkoxide technique is, however, in the fact that the control of Ni particle size in the desired levels could not be expected when the Ni concentrations in the catalysts are the same, the Ni particle size being controlled only by the Ni concentration in the catalyst. In most of our works the catalyst was prepared through the calcination and reduction steps, the temperatures being varied in short ranges; between 450 and 500 °C. The purpose of the present work is to control the Ni metal particle size by the calcination and reduction temperatures even when the Ni concentration in the catalyst is the same. It has been reported that the mean particle size

of metal in the supported catalyst prepared by the conventional impregnation technique was ready to be varied by the calcination or reduction temperature employed,[2] but it seems difficult to control the metal particle size in a homogeneous level. The catalyst used in the present work is Ni/SiO_2 prepared by the alkoxide technique according to the preparation procedures given in Table 1. The Ni concentration in the catalyst was 2.5 wt%, revealed by X-ray fluorescence measurements. In Fig. 1 are shown the typical photographs of the catalysts calcined at 500 °C for 4 h, followed by the reduction at 500, 700, and 900 °C, respectively, in flowing hydrogen. The photographs of the catalysts calcined at 500, 700, and 900 °C for 4 h, respectively, followed by the hydrogen reduction at 500 °C are also shown in Fig. 1. The photographs were obtained by a transmission electron microscopy (Hitachi, H-800), operated at an accelerating voltage of 200 kV with a magnification of $x10^5$. The size distribution curves of Ni metals in these catalysts were obtained by measuring the size of more than 10^3 particles in each catalyst and are shown also in Fig. 1. The mean particle sizes of Ni metal in these catalysts were estimated by hydrogen chemisorption measurements at room temperature following the procedures proposed by Hall et al.[3] The resulting surface areas of Ni metals in the catalysts and the mean particle sizes obtained with an assumption for the metal particles of cubic form are listed in Table 2. In order to determine the metal surface area and, hence, the mean particle size, it is necessary to know the degree of reduction from NiO to Ni metal after the reduction by hydrogen at each temperature. The reduction degrees of the catalysts were measured by using a vibrating sample magnetometer (VSM-2, Toei Kogyo) with the magnetic field up to 2 T and the vibrating frequency of 80 kHz. The reduction

Table 1.
Preparation procedure of Ni/SiO_2 catalyst by alkoxide technique; EG represents ethylene glycol



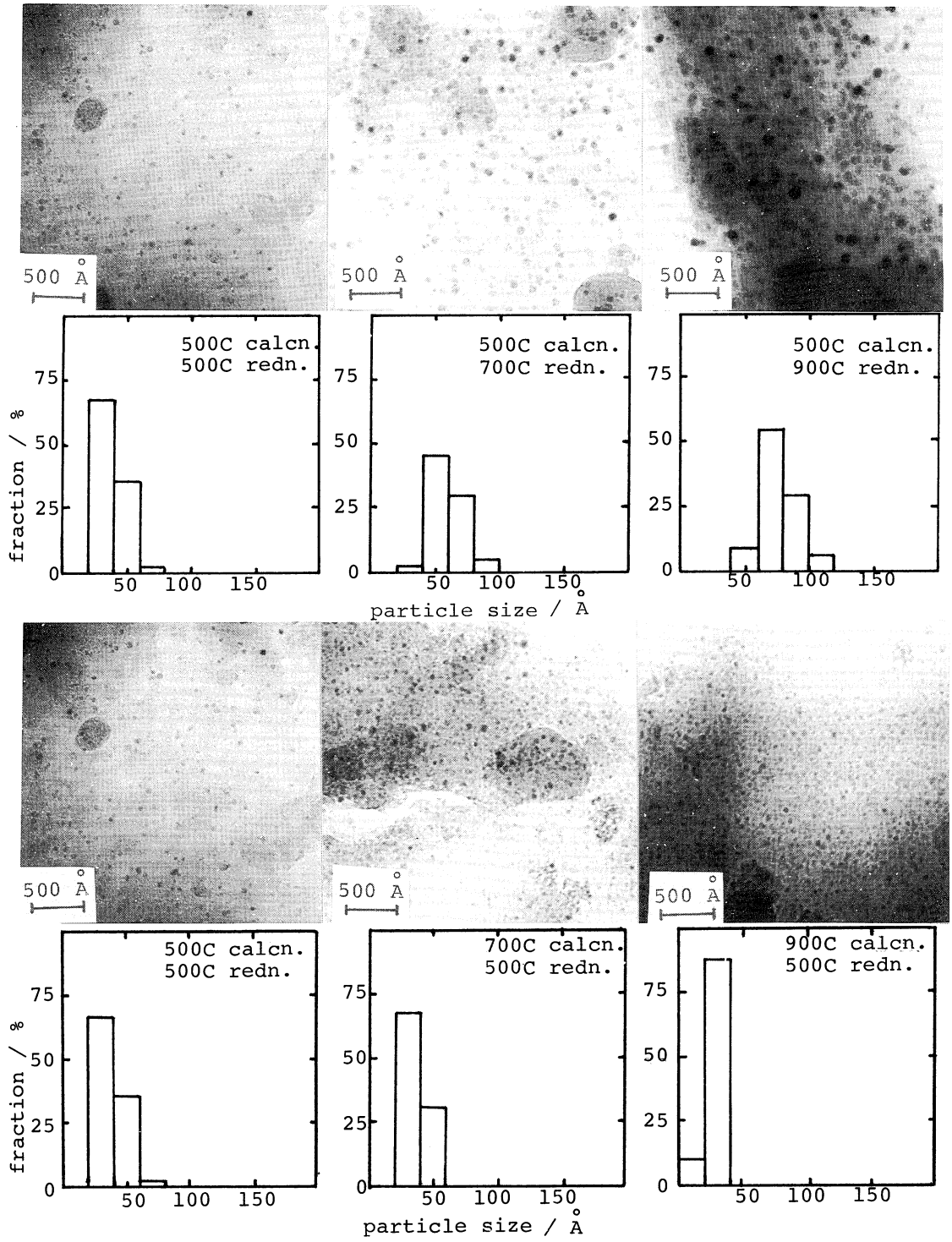


Fig. 1. TEM photographs and particle size distributions of Ni in 2.5 wt% Ni/SiO_2.

degrees were determined by the resulting saturation magnetization since the saturation magnetization of Ni is known to be 54.4 emu·cm^{3}·g^{-1}.[4] In Table 2 are given the reduction degrees, the specific surface areas of Ni and the mean particle sizes of Ni metal particles obtained by TEM and magnetic measurements.

Table 2. Mean particle sizes of Ni in 2.5 wt% Ni/SiO_2 catalysts measured by hydrogen chemisorption and TEM techniques

Calcination temp / °C	500	500	500	500	700	900
Reduction temp / °C	500	700	900	500	500	500
Ni surface area / m^2g^{-1} Ni	88	82	81	88	83	164
$\bar{d}$ by H_2 chemisorption / Å	45	55	71	45	47	24
$\bar{d}$ by TEM / Å	34	58	74	34	32	22
Reduction degree / %	70	80	100	70	69	69

Although the size distribution curves became rather broader with increasing the reduction temperature, the particles were still controlled in a relatively even size level, as shown in Fig. 1. The mean particle size of Ni increased with increasing the reduction temperature, but rather decreased with elevating the calcination temperature. (see Table 2) A few models concerning the sintering and redispersion of metal particles in elevating temperature have been proposed[5] but are still controversial with each other. The mechanisms of sintering and redispersion of the present system will be discussed in successive papers. The control of Ni metal particle size by the reduction and calcination temperatures is achieved here even when the Ni concentrations in the catalysts are the same.

References

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