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Preparation of Fine Fe-Ni Alloy Particles Dispersed in Silica

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Fine Fe-Ni alloy particles dispersed in silica were prepared by hydrolysis of a mixed solution of ethyl silicate and iron and nickel nitrates dissolved in ethylene glycol, the size of the alloy particles being controlled in an even level.

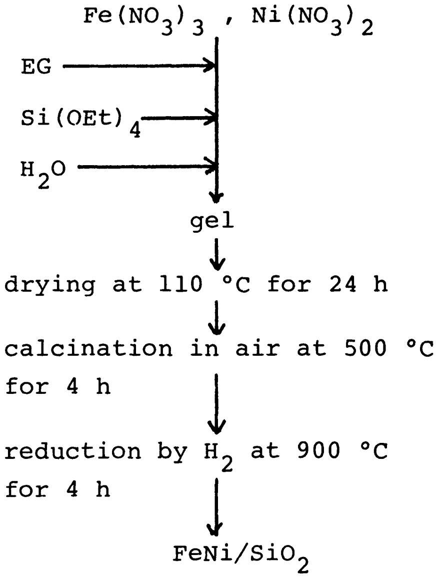
Since a catalytic reaction by a supported metal catalyst takes place over the surface of the metal particles, the electronic property of the particles is often reflected on the catalytic performance. Many attempts have been made to control the electronic property of the metal particles. Alloying, as well as a control of the particle size, have been considered to be one of the promissing candidates to improve the catalysis; the reaction rate and the product selectivity.1) Among the alloy catalysts Cu-Ni and Fe-Ni systems have been extensively studied as bimetallic catalysts because of a lot of knowledge about their structures and electromagnetic properies.2)

In our previous work3) it was revealed that the particle size of Ni in the silica supported nickel catalyst prepared by hydrolysis of a mixed solution of ethyl silicate and nickel nitrate dissolved in ethylene glycol was well controlled in an even level. The purpose of the present work is to prepare the catalyst composed of fine Fe-Ni alloy particles dispersed in silica, the particle size being well controlled in a homogeneous level.

The catalyst was prepared by hydrolysis of a mixed alkoxide solution of ethyl silicate and nickel and iron ethylene glycolates. The metal ethylene glycolates were readily prepared by dissolving the metal nitrates in ethylene glycol at 60 °C, followed by stirring at the same temperature. The hydrolysis was carried out at 60 °C by an addition of distilled water by at least four times moles of the ethyl silicate employed. The gel thus obtained was dried under a reduced pressure at 150 °C. The powder was dried again in an oven at 110 °C for 24 h, followed by a calcination at 500 °C for 4 h. As the final step of the preparation procedures shown in Table 1, the fine powder was placed in a hydrogen stream at 900 °C for 4 h. The loading and the atomic ratio of Ni/Fe in the alloy could be varied by changing the amounts of the metal nitrates employed in the first step of the procedures. In Fig. 1 is shown an X-ray diffraction pattern of the 20 wt% Fe-Ni/SiO_2 catalyst reduced at 900 °C; the atomic ratio of Ni/Fe in the alloy being 1/1. The X-ray diffraction spectrometer was operated at an accelerating voltage of 30 kV with a filament current of 15 mA using Ni filter for Cu Kα radiations. The diffraction peaks observed were assigned to the diffractions from (111) and (200) planes of Fe-Ni alloy. The particle size of the alloy was estimated using Scherrer's equation; $d = 0.9\lambda/\beta\cos\theta$, where λ is the wave length of the incident X-ray and β is the width of the diffraction peak at its half height. The resulting value was 140 Å. The alloy particle size was also monitored by a transmission electron microscope (Hitachi, H-800), operated at an accelersting voltage of 200 kV with a magnification of x10^5. A typical photograph of the silica supported alloy catalyst is shown in Fig. 2.

Table 1.

Preparation procedure of FeNi/SiO_2 catalyst by alkoxide technique; EG represents ethylene glycol



Apparently, the particles are well controlled in an even size and the size distribution was obtained by measuring more than 1000 particles in photographs. (see Fig. 3) The alloy particles in the catalyst reduced at 900 °C became spheres because of their surface tensions. It is well known that the iron rich Fe-Ni alloy has a body centered cubic type structure and with increase in the Ni concentration in the alloy system the crystallographic structure transforms into face centered cubic.4) When the Ni concentration is higher than ca. 25 atomic per cent, the alloy always takes the f.c.c. structure. Thus, the lattice spacing of the Fe-Ni alloy changes with the Ni concentration as is shown in Fig. 4.5)

The atomic ratio of Ni/Fe in the silica supported alloy catalyst was varied from 1/3 to 3 keeping the alloy loadings constant; 20 wt%. The X-ray diffraction patterns of these catalyst reduced at 900 °C are shown in Fig. 5. The (111) diffraction angle of the Fe-Ni alloy particles slightly shifted toward lower angles with increasings in the Ni concentration up to 50 atomic per cent and then moved toward higher angles. From these observations the changes in the lattice spacing of the alloy catalyst were estimated and the results are also shown in Fig. 4. The structural changes of the fine alloy particles dispersed in silica were proved to be very close to those

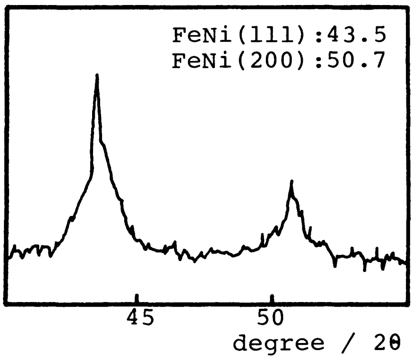


Fig.1.X-Ray diffraction pattern of the reduced catalyst.

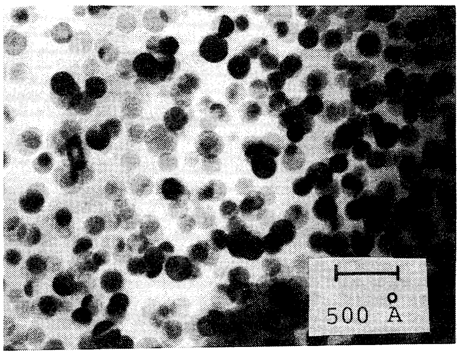


Fig.2.TEM photograph of $FeNi/SiO_2$ catalyst.

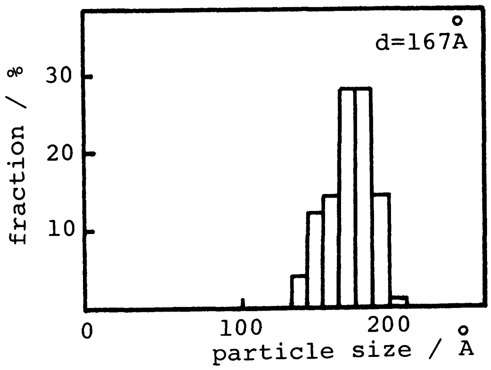


Fig.3.Particle size distribution on $FeNi/SiO_2$ catalyst.

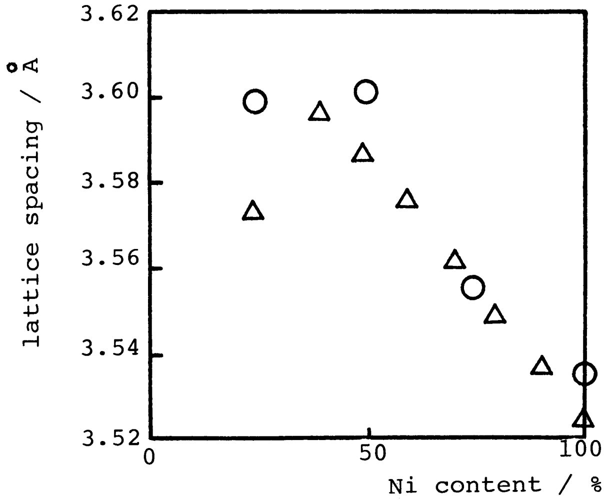


Fig.4.Relationship between lattice spacing and Ni content for FeNi/SiO$_2$ catalyst. (○:exp.value,△:ref.value)

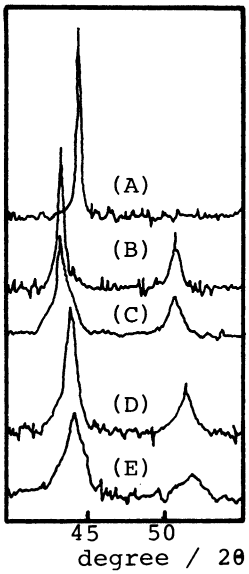


Fig.5.Change in X-ray diffraction patterns of the catalyst. (A)Fe:Ni=100:0,(B)Fe:Ni=75:25 (C)Fe:Ni=50:50,(D)Fe:Ni=25:75 (E)Fe:Ni=0:100.

in bulk Fe-Ni alloy, indicating that the atomic arrangements in the alloy catalyst are the same as those in the bulk alloy. This finding encourages us in studying the size effects of the alloy upon its catalysis. The control of the alloy particle size with the alloy loading on silica and the size effects of alloy on the catalysis will be discussed in a successive paper.

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