STUDY ON THE SIZE DISTRIBUTION OF IRON
PARTICLES DISPERSED IN SiO_2 SUPPORT

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A new method to control the size of iron particles in Fe/SiO_2 catalyst was studied. The catalyst was prepared by drying and then calcining a gel obtained by hydrolysis of the mixed solution of ethyl silicate and iron(III) nitrate dissolved in ethylene glycol. Iron particles were deposited in a controlled size level by reducing the calcined catalyst in a hydrogen stream. EXAFS and IR spectroscopies were employed to see the reason why the size of iron particles was controlled in the catalyst thus prepared.

Although iron is an important element of practical catalysts for ammonia synthesis, Fischer-Tropsch reaction, water-gas shift reaction and partial oxidation of methanol, the size effect of iron particles upon the catalysis has never been studied. This might be due to difficulties to control the iron particles in a desired size distribution. Recently, Dumesic et al.[1] reported the morphological studies on iron particles supported by TiO_2 carrier where the iron particles were deposited by evaporating the metal wire. The purpose of the present work is to develop techniques to control the size of iron particles in Fe/SiO_2 catalyst.

The catalyst employed was prepared by hydrolysis of the mixed solution of ethyl silicate and iron nitrate dissolved in ethylene glycol at 80 °C. A gel thus prepared was first dried at 110 °C in an oven, following by calcination at 450 °C for 4 h. Iron particles deposited by reduction at 450 °C in a hydrogen stream

were observed by a transmission electron microscope (TEM, Hitachi H-300) operated
at an accelerating voltage of 75 kV with magnification of x50000.   Typical photo-
graphs obtained for 5 and 10 wt% Fe/SiO_2 catalysts are given in Fig. 1 and the
size distribution curves of iron particles are obtained by measureing more than
300 particles in each catalyst (see Fig. 2).

   Catalysts were also prepared by a conventional impregnation method.   The
conditions employed for drying, calcination and reduction were the same as
mentioned above.   Apparently, the size of iron particles was not controlled and
the size distribution curve was broad (see Figs. 3 and 4).   The iron loading of
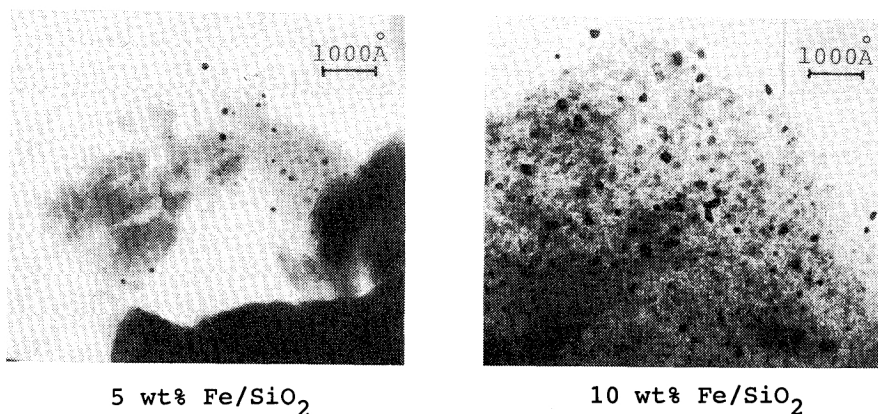this catalyst was also 10 wt%.

5 wt% Fe/SiO_2 10 wt% Fe/SiO_2

Fig. 1. Transmission electron micrographs of Fe/SiO_2 catalyst
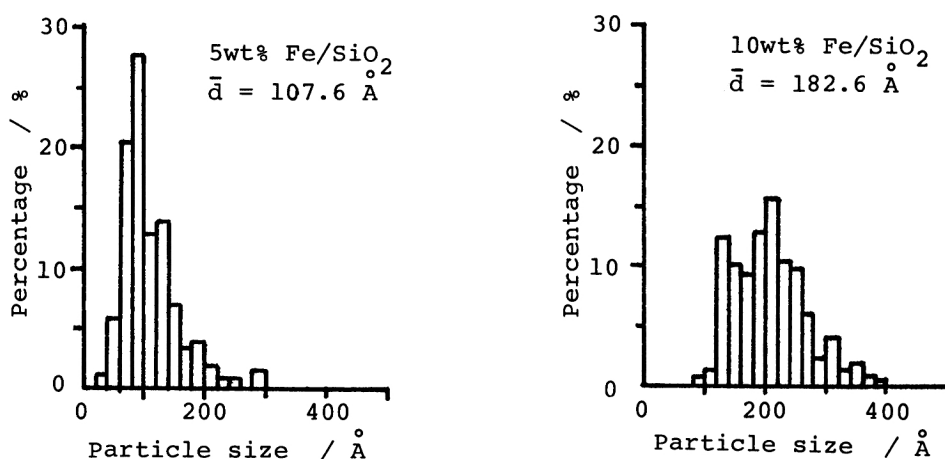prepared by alkoxide technique.

Fig. 2. Particle size distribution of Fe in Fe/SiO_2 catalyst
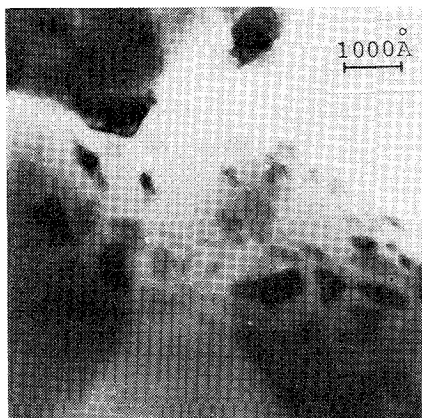prepared by alkoxide technique.

Fig. 3. Transmission electron
micrographs of Fe/SiO$_2$ catalyst
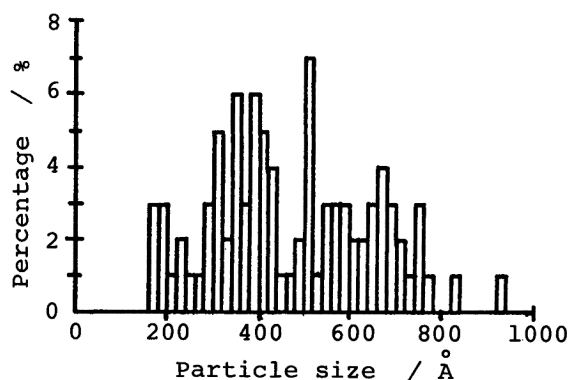prepared by impregnation method.

Fig. 4. Particle size distribution
of Fe in Fe/SiO$_2$ catalyst prepared
by impregnation method.

An attempt was made to see the reason why the size of iron particles was
controlled by the former method (called Alkoxide technique). The local structures
around iron ions in every step of the catalyst preparation procedure were investi-
gated by EXAFS spectroscopy.[2] The spectra were compared with those observed in
every step in the impregnation method. No significant differences were observed
between the spectra after the drying and reducing procedures.

Fourier transforms of EXAFS spectra for these calcined catalysts, FeO, Fe$_3$O$_4$,
and Fe$_2$O$_3$ powders are given in Fig. 5. A comparison of Fig. 5(a) with Fig. 5(c)
informs that the local structure around iron ions in the calcined catalyst
prepared by impregnation is similar to that in bulklike Fe$_2$O$_3$, suggesting that the
crystalline size of Fe$_2$O$_3$ in this catalyst is comparable with that of the bulklike
Fe$_2$O$_3$. On the other hand, Figs. 5(b)-5(e) inform that the surroundings of iron
ions in the catalyst prepared by Alkoxide technique are similar to those in Fe$_3$O$_4$,
but they are dissimilar to those in FeO and in Fe$_2$O$_3$. In addition the size of
iron oxide in this calcined catalyst appears so fine since the peak intensities
decreased with the distance from the central iron atom (see Fig. 5(b)). According
to Lytle et al.[3] a crystalline size can be estimated by measuring the ratio of
$\bar{N}_j/N_j$, where $\bar{N}_j$ is the intensity of the j-th shell in the sample and N_j is that in
the reference material, respectively. Since the present catalyst was calcined in
air, enough numbers of oxygen atoms are in the first shell of the iron ions so
that the value of $\bar{N}_1/N_1$ should be close to unity. The crystalline size of Fe$_3$O$_4$
in the catalyst might be estimated by calculating the value of $\bar{N}_2/N_2$. This value

is around 0.5 from the spectra shown in Figs. 5(b) and 5(d), suggesting that the Fe_3O_4 crystallites in the catalyst might consist of several hundreds of iron and oxygen atoms.[3] Fe_3O_4 has a spinel structure and the unit cell contains 24 iron atoms and 32 oxygen atoms. Accordingly, around 10 unit cells of the spinel are included in a crystallite, indicating the mean crystalline size of Fe_3O_4 in the calcined catalyst might be around 20 Å since the lattice constant of the spinel is about 8 Å.

An infrared spectrum of the calcined catalyst prepared by the Alkoxide technique showed an absorption peak at 980 cm^{-1}. This means that iron ions in the calcined catalyst are bound with Si atoms via the terminal oxygen atoms in the spinel structure since absorption peak due to Si-O-Metal structure appears in the range between 1000 and 900 cm^{-1}.[4]

Thus, in the calcined catalyst prepared by the alkoxide technique iron ions are trapped in SiO_2 network to form fine Fe_3O_4 spinel structure and this might be a cause why the size of iron metal can be controlled by the Alkoxide technique.
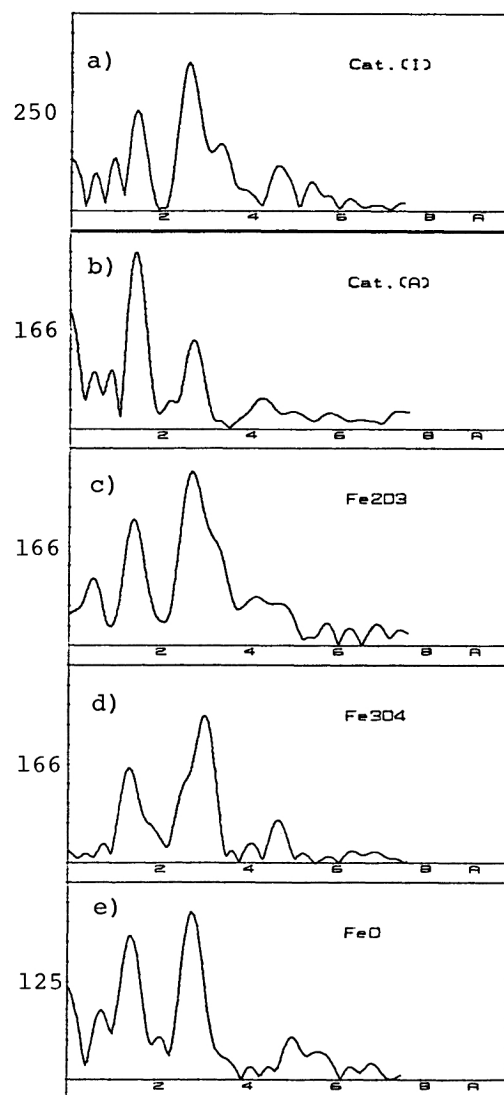

Fig. 5. Fourier transforms of EXAFS spectra for catalyst prepared by impregnation method(a) and Alkoxide technique(b), Fe_2O_3 (c), Fe_3O_4(d), and FeO(e).

References
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4) D.Bradley, R.Mehrotra, and D.Gauer, "Metal Alkoxides," Academic Press, New York, (1978), p. 180.