Mössbauer study of carbon-supported alpha-iron catalysts

Citation for published version (APA):

Christensen, P. H., Moerup, S., & Niemantsverdriet, J. W. (1986). Mössbauer study of carbon-supported alpha-iron catalysts. *Hyperfine Interactions*, 28(1-4), 911-914. <https://doi.org/10.1007/BF02061592>

DOI:

[10.1007/BF02061592](https://doi.org/10.1007/BF02061592)

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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MÖSSBAUER STUDY OF CARBON-SUPPORTED α -Fe CATALYSTS

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Mössbauer spectra of carefully reduced carbon-supported iron catalysts show superparamagnetic α -Fe at 80 K. The results indicate that the particle size depends on the reduction temperature. Effects of evacuation and CO chemisorption are discussed.

1. INTRODUCTION

Recently, Jung *et al.* /1/ have reported that very small particles of metallic iron (α -Fe) with diameters in the 2-3 nm range can be prepared on a carbon support called Carbolac-1 (C-1). Mössbauer spectra of these samples measured by Niemantsverdriet *et al.* confirmed that most of the iron is in the metallic state and revealed that about 60 % of the α -Fe is superparamagnetic at 80 K /2/.

In a subsequent study /3/ we have prepared an Fe/C-1 catalyst in which all α -Fe is superparamagnetic at 80 K and we have estimated the average particle diameter by means of the magnetic field dependence of the Mössbauer spectra.

In this paper we show that the superparamagnetic behaviour of the α -Fe particles depends critically on the reduction conditions. Spectra of the catalysts in H_2 , vacuum and CO show that the Mössbauer spectra are sensitive to the environment.

2. EXPERIMENTAL SECTION

The Fe/C-1 catalysts were prepared by the incipient wetness impregnation, as described earlier /3/. The samples were reduced in flowing hydrogen either at 725 K for 16 h or, in a two-step procedure, at 615 K for 16 h and at 675 K for 16 h. During the measurements the samples were kept in an *in situ* Mössbauer cell, which allows spectra to be obtained at temperatures between 80 K and 725 K with applied magnetic fields up to about 1.0 T /4/.

Mössbauer spectra were measured with a constant acceleration spectrometer. Velocities are given with respect to the isomer shift of α -Fe at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the 80 K spectra of the catalyst after reduction at 675 K. The spectra were obtained in hydrogen and in vacuum after desorption of hydrogen at 510 K. Spectra of this sample measured in applied magnetic fields up to 1.0 T confirmed that the single peak is due to superparamagnetic α -Fe, and, furthermore that the average diameter of the particles is 2.5 ± 0.2 nm /3/.

The lines in the spectra shown in Fig. 1, are rather broad, but the line width decreases when hydrogen is removed, indicating an

increase in the superparamagnetic relaxation frequency. In accordance with previous studies of chemisorption on α -Fe particles /5,6/ we attribute this effect to an increase in the surface contribution to the magnetic anisotropy energy constant when hydrogen is chemisorbed on the surface of the particles.

The spectra of Fig. 1 contain, in addition to the singlet due to superparamagnetic α -Fe, a shoulder at about 2 mm/s , which is attributed to unredoxed iron in the ferrous state /2/.

Figure 2 shows the 80 K spectra of the Fe/C-1 catalyst in vacuum and after CO chemisorption at 190 K, measured in an applied magnetic field of 1.03 T. As a result of CO adsorption the sextuplet is reduced in intensity and the relative area of the line at about -0.2 mm/s has increased. Although a detailed interpretation is not yet possible, we believe that the changes in the spectrum are indicative of a strong interaction between CO and the iron atoms at the surface.

Figure 3 shows the room temperature spectrum of the Fe/C-1 catalyst after the first reduction step at 615 K measured in a 1 T field, and the spectrum after reduction at 675 K in a 0.55 T field. The relative area of the paramagnetic component is larger after reduction at 615 K than after reduction at 675 K. Both spectra are partly magnetically split due to the applied magnetic fields, and the total widths of the superparamagnetic components are quite similar. Since the applied fields differ by a factor of about two we conclude that the volumes also differ by a factor of approximately two. Thus the mean diameter of the particles, prepared by reduction at 615 K, is about 2.0 nm.

Figure 4 shows spectra of the sample which was reduced at 725 K. The spectrum obtained at 300 K in an applied magnetic field of 1.03 T shows that about 50 % of the iron is α -Fe. The remaining iron is

Fig.1. Mössbauer spectra obtained at 80 K of the Fe/C-1 catalyst after reduction in H_2 at 675 K for 16 h, and in vacuum after desorption of the H_2 at 510 K.

Fig.2. Mössbauer spectra of the Fe/C-1 catalyst after reduction at 625 K. The spectra were obtained at 80 K in an applied magnetic field of 1.03 T in vacuum after evacuation at 510 K and after chemisorption of CO at 190 K.

present in iron carbides, possibly Fe_xC and $\chi\text{-Fe}_5\text{C}_2$ /7/. The 650 K spectra contain, in addition to the α -Fe sextet, a singlet, in agreement with $\chi\text{-Fe}_5\text{C}_2$ being paramagnetic above 530 K /7/.

The spectrum, obtained at 300 K in an applied magnetic field of 0.01 T has broader lines than the 1.03 T spectrum and, moreover, a broad central line is present near zero velocity. These features can be explained by the presence of superparamagnetic relaxation effects and collective magnetic excitations /6,8/. A comparison with the spectra shown in Fig. 1 shows that reduction at 725 K leads to a considerably longer relaxation time than reduction at 675 K. The results can be explained by an increase in the average diameter to about 10 nm upon reduction at 725 K. It is, however, also possible that the better resolved magnetic hyperfine splitting in the room temperature spectra in Figure 4 can be explained by an enhancement of the magnetic dipole-dipole interaction between the particles /2,9/.

Fig.3. Room temperature Mössbauer spectra of the Fe/C-1 catalyst after

- a) reduction at 615 K measured in 1.03 T applied magnetic field and
- b) after reduction at 675 K measured in 0.55 T applied magnetic field.

Fig.4. Mössbauer spectra of the Fe/C-1 catalyst after reduction at 725 K. Left: without applied magnetic field; right: with 1 T applied magnetic field. Upper spectra obtained at 650 K and lower spectra obtained at 300 K.

The carburization of the iron, seen from the presence of carbides in Fig. 4, is presumably due to the fact that C-1 is significantly gasified in H_2 above about 675 K /10/. During the gasification CH_4 is formed and these molecules act as carburizing agents for α -Fe.

4. CONCLUSIONS

The present study has shown that careful drying and reduction of carbon-supported iron catalysts results in formation of very small α -Fe particles, which are well suited for studies of surface effects.

The particle size seems to increase with increasing reduction temperature and carbide formation becomes important at reduction temperatures above 675 K.

ACKNOWLEDGEMENTS

The authors acknowledge support from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) and the Danish Council for Scientific and Industrial Research.

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