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In situ Mössbauer spectroscopy of carbon-supported iron catalysts at cryogenic temperatures and in external magnetic fields

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A highly dispersed carbon-supported iron catalyst has been studied with *in situ* Mössbauer spectroscopy at temperatures down to 5 K and with external magnetic fields. It is shown that measurements of spectra in the presence of large magnetic fields considerably improves the information obtained from Mössbauer spectra.

Keywords: Iron catalysts; Mössbauer spectroscopy

1. Introduction

Mössbauer spectra of iron compounds are easily interpreted with the help of three parameters, isomer shift, quadrupole splitting and magnetic hyperfine field. These three parameters are usually specific for a compound. Interpretation of spectra of small particles or well dispersed surface phases as in catalysts is often less straightforward. If the dimensions are small, magnetic hyperfine splittings either collapse as a result of superparamagnetism or decrease with a reduction that depends on particle size. In addition, surface atoms have less symmetric environments than atoms in the interior and this affects particularly the quadrupole splitting and the magnetic hyperfine fields. If the particles in a catalyst do not have uniform size, this presents an additional cause for broadening of the spectra [1–3].

Carbon is a favorable support for making small metallic iron particles. The interaction with the support is weak and therefore it is possible to obtain highly dispersed particles with a degree of reduction that is much higher than in oxide-supported catalysts [4]. Niemantsverdriet et al. [5] and Christensen et al. [6] reported Mössbauer spectra of carbon-supported iron particles which were superparamagnetic at the temperature of liquid nitrogen. Mössbauer spectroscopy studies with external magnetic fields at 80 K [6], or without field at liquid helium temperature [5] were essential to confirm that metallic iron was indeed present. The purpose of this letter is to demonstrate that measuring spectra *in situ* at liquid helium temperature in external magnetic fields at 4 T obtained with a superconducting magnet improves the information content of spectra even further.

2. Experimental

The Fe/C catalyst was prepared by impregnating a carbon support (Ketjen black ED-600 JD, AKZO Chem. Division, 1250 m^2g^{-1}) with an aqueous solution of $Fe(NO_3)_3.9\,H_2O$ (Merck, p.a.) and dissolved ^{57}Fe ($^{56}Fe : ^{57}Fe = 4:1$), followed by drying in air at 295 K for several days, at 325, 345, and 365 K for 1 day and finally at 400 K for 2 days. The dried sample was pressed into a thin self-supporting wafer, mounted in the Mössbauer *in situ* cell and reduced in a flow of purified H_2 according to the following scheme: 350 K for 1 h; 395 K, 1 h; 525 K, 0.5 h; 600 K, 45 h.

Mössbauer spectra were obtained with a constant acceleration spectrometer with a ^{57}Co-in Rh source of approximately 50 mCi. Isomer shifts are reported with respect to that of metallic iron at room temperature. The Mössbauer *in situ* cell is equipped with teflon-coated Kapton windows which can be used in the temperature range of 0-670 K. The cell can be inserted in a liquid helium cryostat, in the center of a superconducting magnet with an external magnetic field of up to 5 T.

3. Results and Discussion

FRESH Fe/C CATALYST

Fig. 1 shows Mössbauer spectra of the fresh Fe/C catalyst after drying at 400 K. The spectra at 295 and 80 K show a quadrupole doublet with the isomer shift and quadrupole splitting of high spin Fe^{3+}. At 5 K, the spectrum consists of a magnetically split component with rather broad lines and a doublet. The fact that the outer lines of the sextet are broader than the inner lines is characteristic of a distribution in magnetic hyperfine fields, as is conceivable for a highly dispersed phase. If we ignore the distribution and fit the sextet with one Lorentzian per line, we obtain an average hyperfine field of 48.0 ± 0.3 T, a vanishingly small quadrupole interaction and an isomer shift of 0.47 ± 0.03 mms^{-1} in agreement with Fe^{3+}. Similar spectra have been observed before and assigned to poorly define iron (III) oxides or oxyhydroxides [7,8].

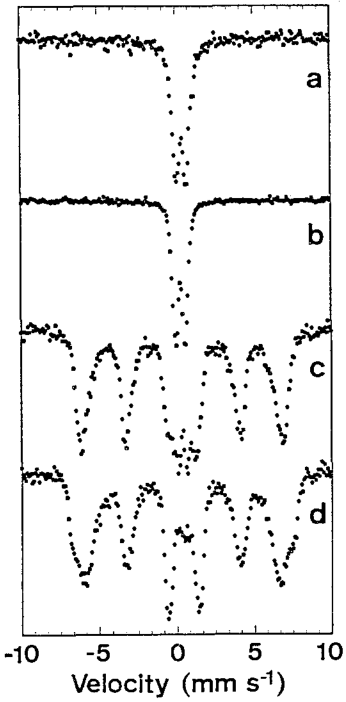

Fig. 1. Mössbauer spectra of the fresh Fe/C catalyst at (a) 295 K, (b) 80 K, and (c) 5 K and at (d) 5 K in an external magnetic field of 4 T applied parallel to the γ-radiation.

When an external magnetic field of 4 T is applied, the doublet in the 5 K spectrum of the fresh Fe/C catalyst splits up, as fig. 1d shows. The important points to note are that the central doublet disappears, that new lines become visible on the outside of the oxide sextet, and that the inner lines of the sextet are stronger, but that no new intensity appears on or near the second and fifth lines of the sextet. These observations indicate that the doublet in the zero field spectrum belongs to a paramagnetic phase. The paramagnetic compound has an isomer shift of 0.33 ± 0.1 mms^{-1}, which, although of limited accuracy, is significantly lower than that of the iron (III) oxide component. Assuming that the average magnetic hyperfine splitting of 52.3 T measured in a 4 T field is at saturation, the corrected average saturation field is 56.3 T. This value is an average over a distribution that extends to about 60 T. Such values are typical for Fe^{3+} coordinated to H_2O molecules [9]. The broad lines may be due to relaxation effects or to a distribution in magnetic saturation fields.

The magnetic splitting of the main component, assigned above to iron (III) oxide or oxyhydroxide, decreases from 48.0 ± 0.5 to 46.5 ± 0.5 T in the external field of 4 T, indicating that the spin moments are to some extent aligned by the field. In addition to this, the lines have become broader. This type of behaviour is expected for speromagnetic or sperimagnetic compounds [10]. The quadrupole splitting is 0.8 mms^{-1} at 295 and 80 K. However, the quadrupole shift is almost zero in the magnetically split spectra at 5 K. This indicates that the directions of the electrical field gradients in a particle are randomly distributed relative to the magnetic hyperfine fields as in a speromagnet.

REDUCED Fe/C CATALYST

Fig. 2 shows *in situ* Mössbauer spectra of the Fe/C catalyst after reduction in H_2 at 600 K. The spectra at 295 and 90 K show broad, overlapping lines and are difficult to interpret. At measurement temperatures of 35 K or lower, the magnetically split spectra sharpen up and start to show a sharp sextet with a magnetic hyperfine field of 34.2 ± 0.2 T. This value is in agreement with the value of 34.5 T expected for isolated, spherically shaped, single-domain metallic iron particles, for which the demagnetizing field of 0.7 T has to be added to the bulk field of 33.8 T of metallic iron. This metallic iron sextet, however, is not the

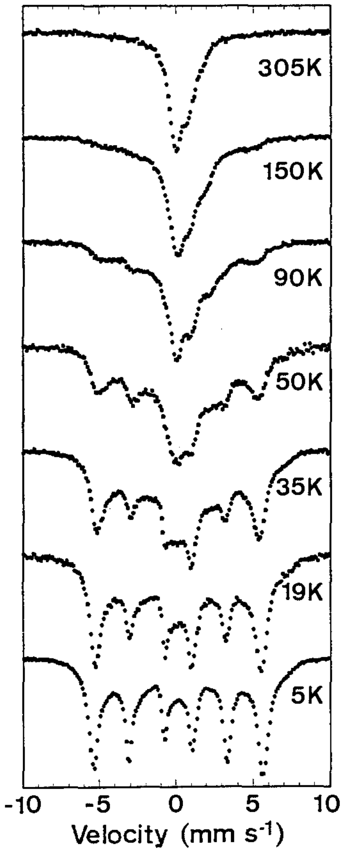

Fig. 2. *In situ* Mössbauer spectra of the reduced Fe/C catalyst at a range of temperatures between 305 and 5 K.

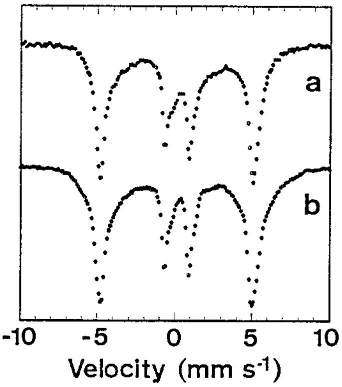

Fig. 3. *In situ* Mössbauer spectra of the reduced Fe/C catalyst at (a) 90 K and at (b) 5 K. Both spectra were obtained with an external magnetic field of 4 T applied parallel to the direction of the γ-radiation.

only spectral component present, as can be inferred from the wide tails on the outer peaks that extend to higher velocities, and from the asymmetry in the central region of the spectrum.

Application of a 4 T magnetic field parallel to the gamma rays again helps to obtain more detailed information as seen in the spectra in fig. 3. The first beneficial effect is that the second and fifth line of the metallic iron sextet disappear from the spectrum, with the result that the shape of the outer lines can be determined more accurately. Second, the components present in addition to metallic iron are somewhat better resolved than in the zero-field spectra.

These spectra can be fitted with a component which corresponds to α-Fe and one with a distribution of magnetic hyperfine fields which accounts for the broad components best visible around the outer lines of the α-Fe sextet in fig. 3b. As explained in detail elsewhere [11], we believe that the distribution consists of two parts, one with magnetic fields smaller and one with magnetic fields higher than that of α-Fe. Both have an isomer shift that is about 0.35 mms^{-1} larger than that of α-Fe. The Mössbauer parameters of the component with the smaller magnetic splittings are in agreement with those of amorphous iron carbides [12–14]. We attribute the component with the larger magnetic hyperfine field to surface atoms on the α-Fe particles. At 90 K, the average magnetic hyperfine field of this component has decreased much more than that of the α-Fe. At 5 K, the spectral intensities of the surface and the α-Fe are in the proportion of about 1:3 which appears in order of magnitude consistent with the dispersion of 3.7 nm particles.

In order to determine the size of the metallic iron particles, spectra of the reduced catalyst at 150 K, where the metallic iron is superparamagnetic, were taken in a range of magnetic fields between 0 and 4 T (not shown). These spectra were used to estimate the average volume of the particles by the Langevin equation in the high field limit [2,3]:

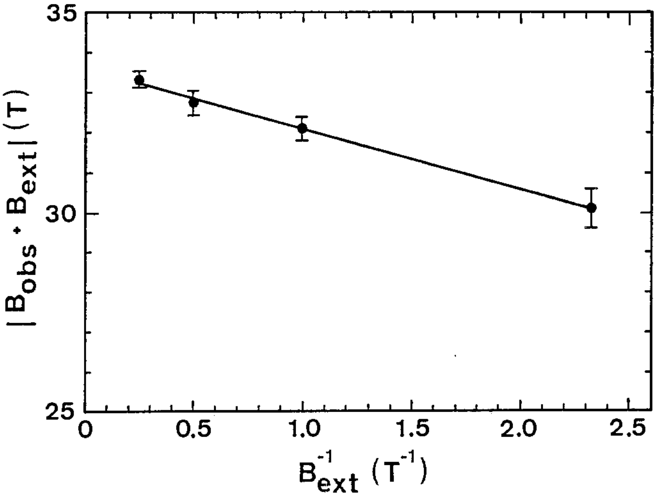

Fig. 4. Magnetic hyperfine fields as a function of the reciprocal external field, according to eq. (1). The slope of the line corresponds to spherical particles with an average diameter of 3.7 ± 0.3 nm.

$$|B_{\mathrm{obs}}+B_{\mathrm{ext}}| \approx B_0\left(1-\frac{kT}{\mu B_{\mathrm{ext}}}\right) \tag{1}$$

in which B_{obs} is the observed magnetic hyperfine field in the Mössbauer spectra, B_{ext} the external applied field, B_0 the magnetic hyperfine field of bulk metallic iron, k Boltzmann's constant, T the temperature and the μ the magnetic moment of the particles. A plot of $B_{\mathrm{obs}}+B_{\mathrm{ext}}$ against $1/B_{\mathrm{ext}}$ for the 150 K spectra of the reduced Fe/C catalyst (see fig. 4) gives a straight line with a slope that corresponds to an average magnetic moment of $(4.6 \pm 1.1) \cdot 10^{-20}$ J/T per particle, which with an atomic moment of 2.2 Bohr magnetons corresponds to spherical particles with an average diameter of 3.7 ± 0.3 nm.

In the zero-field spectra of fig. 2 and at temperatures where the metallic iron particles are not superparamagnetic, the magnetic hyperfine field is reduced by the phenomenon of collective magnetic exitations [2,3,15–17]:

$$B_{\mathrm{obs}}=B_0\left(1-\frac{kT}{2KV}\right) \tag{2}$$

where K is the magnetic anisotropy constant of the particle and V its volume. If we apply this formula to the hyperfine fields in the spectra of fig. 2, we obtain a magnetic anisotropy constant $K=(2.0 \pm 0.5) \cdot 10^5$ J/m^3. As the magnetic anisotropy of small particles is sensitive to the presence of gases, this value is characteristic of 3.7 nm particles in hydrogen. It is interesting to compare the present value with those from previous studies on reduced iron catalysts, see table 1. The increase in the magnetic anisotropy energy constant with decreasing particle size is presumably related to an increasing importance of the surface anisotropy.

Table 1
Magnetic anisotropy energy constants of metallic iron particles in catalysts under hydrogen

Catalyst	Diameter (nm)	K (J/m^3)	Ref.
Fe/SiO$_2$	6.3 ± 0.5	$1.2 \pm 0.3 \cdot 10^5$	[16]
Fe/C	3.7 ± 0.4	$2.0 \pm 0.5 \cdot 10^5$	this work
Fe/C	2.5 ± 0.2	$7.0 \pm 3.0 \cdot 10^5$	[6]

Finally, the temperature dependence of the spectral area of the complete spectra corresponds to an effective Debye temperature of 133 ± 15 K. This value is much lower than the Debye temperature of bulk iron phases, which are on the order of 450–500 K. As explained by several authors, the effective Debye temperature of small particles is not only determined by lattice vibrations, but also by the mobility of the particles themselves [18–20]. In principle the two contributions can be separated by using the second order Doppler shift (the temperature dependence of the isomer shift, which reflects the influence of lattice vibrations) [20]. However, we feel that the isomer shifts of the rather complicated spectra of the present work are insufficiently accurate to warrant such an analysis.

4. Conclusions

In conclusion, we believe that the present work illustrates that the combination of *in situ* Mössbauer spectroscopy at cryogenic temperatures and application of external magnetic fields helps to resolve more details in the spectra of highly dispersed catalysts. A full account which emphasizes the magnetic properties of these and other carbon-supported iron particles will be published elsewhere.

Acknowledgement

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