



# Monodisperse Magnetic Iron Colloids Grafted with Polyisobutene: A Model System for Fischer–Tropsch Catalysts?

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**Abstract.** Iron colloids stabilised with polyisobutene with a radius ranging from 2.1 to 8.2 nm have been prepared and characterised by Mössbauer absorption spectroscopy. Comparison with results reported in the literature on sarcosyl and oleic acid stabilised colloids reveals that the stabilising ligand influences the properties of the colloids. By impregnating an alumina support with a solution of the  $r = 2.1$  nm Fe colloids a model catalyst has been prepared. The first results show that the impregnation was successful. However, due to the low Fe loading, the signal-to-noise ratio is too low to perform good measurements on this model system. Therefore, Fe-colloids will be prepared that are enriched in  $^{57}\text{Fe}$ .

## 1. Introduction

Colloids of mono-disperse ferromagnetic transition metal particles, stabilised with organic ligands, are of interest for a wide range of applications, as well as for fundamental physical and chemical research. Mössbauer spectroscopy has been applied to investigate physical properties of both oleic-acid stabilised iron-colloids and sarcosyl stabilised ones that were prepared from  $\text{Fe}(\text{CO})_5$  solved in decalin [1, 2]. The formation of small  $\alpha$ -Fe particles was expected. However, it turned out that small disordered  $\text{Fe}_{1-x}\text{C}_x$  particles were formed [1, 2] with  $x \approx 0.25$  [3].

The colloids that have been investigated in the present Mössbauer absorption spectroscopy study (MAS) have been stabilised by polyisobutene (PIB) [4]. The aim was to apply mono-disperse small Fe-colloid particles for the preparation of supported Fe model catalysts for Fischer–Tropsch synthesis: the formation of hydrocarbons from CO and  $\text{H}_2$ . This would offer interesting possibilities for catalyst characterisation studies because the preparation procedure of the mono-disperse Fe-colloids would enable us to produce small particles of which the surface layer (where the catalysis takes place) is enriched in  $^{57}\text{Fe}$ .

In a first step the as-prepared Fe-colloids with radii ranging from 2 to 8 nm (radii determined by TEM on the reoxidised samples) have been characterised *in*

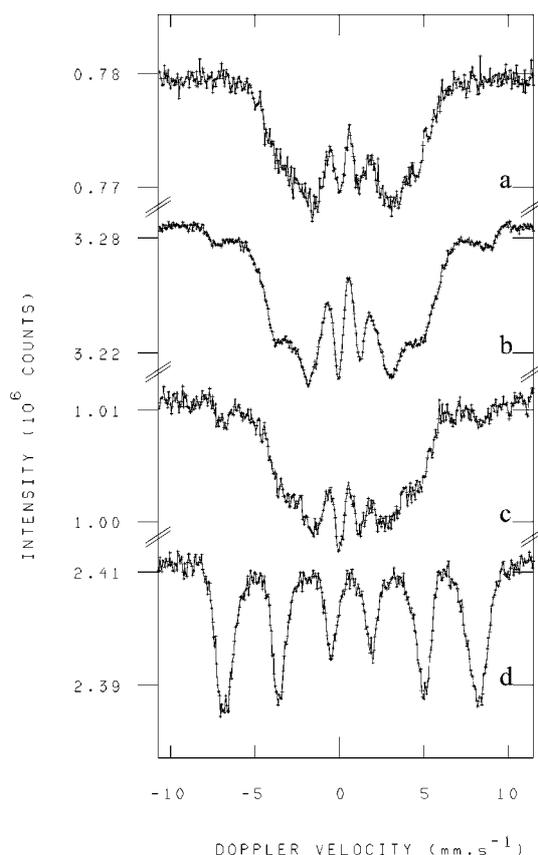


Figure 1. Spectra recorded at 4.2 K on Fe colloids stabilised by PIB with radii of (a) 8.2 nm, (b) 6.9 nm, (c) 5.3 nm and (d) 2.1 nm, as prepared. IS relative to SNP at room temperature.

*situ* (exclusion of air) by MAS at temperatures down to 4.2 K. It turned out that the PIB stabilised colloids show similarities as well as differences in behaviour compared to the sarcosyl and oleic acid stabilised ones [1, 2, 5].

In addition, a first attempt has been made to prepare a model catalyst by impregnating an alumina support with a solution of reoxidised Fe-colloids with a radius of 2.1 nm. The sample has been prepared using the incipient wetness method. The possibility to use these Fe-colloids as model system for the characterisation of heterogeneous catalysts has been investigated by MAS studies on samples that have been subjected to various subsequent reduction and oxidation treatments.

## 2. Results

The preparation of the PIB stabilised iron colloids has been reported previously by Pathmamanoharan *et al.* [4]. The spectra measured at 4.2 K of the colloids with different particle sizes are presented in Figure 1. The spectra of the colloids with

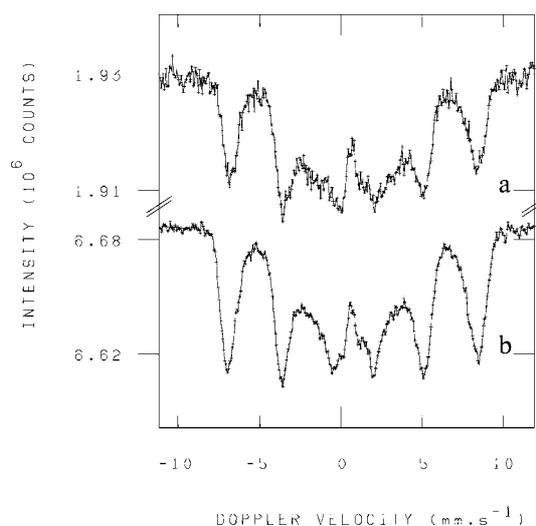


Figure 2. Spectra recorded at 4.2 K on an Fe (8.2 nm) colloid exposed to air during evaporation of the decaline for 1 week (a), respectively for one year (b). IS relative to SNP at room temperature.

$r = 5.3, 6.9$  and  $8.2$  nm are dominated by the broadened sextuplet with  $H_{\text{eff}} = 262$  kOe similar to that found in the sarcosyl and oleic acid stabilised colloids [1, 2]. This hyperfine field characterises  $\text{Fe}_{1-x}\text{C}_x$  species with  $x \approx 0.25$  [3].

As the obtained spectra are rather symmetrical, the observed significant high-spin  $\text{Fe}^{2+}$  contribution in the spectra of the sarcosyl and oleic acid stabilised colloids [5] is absent in our PIB stabilised colloids.

In addition, a small contribution of a sextuplet with  $H_{\text{eff}} = 496$  kOe characterising an Fe(III) oxidic contribution is visible in the spectra of the colloids with  $r = 5.3$  and  $6.9$  nm. This Fe(III) oxidic contribution is absent for the largest colloid with  $r = 8.2$  nm, while the spectrum of the colloids with the smallest radius ( $r = 2.1$  nm) turned out to be completely oxidic.

By exposing the samples to air at room temperature, the  $\text{Fe}_{1-x}\text{C}_x$  species oxidises and a disordered Fe(III) oxidic species is formed, characterised by a sextuplet with  $H_{\text{eff}} \approx 470$  kOe [6, 7]. In Figure 2a it can be seen that the large colloids only oxidise partly. Although a significant contribution of the Fe(III) oxide species could already be observed after exposure of the sample to ambient air for one week, it is clear from Figure 2b that after an exposure time of one year, the spectrum is hardly changed and a significant part of the colloids is still present as  $\text{Fe}_{1-x}\text{C}_x$ .

Treating the colloid sample with  $r = 2.1$  nm by evaporating the decaline in ambient air reveals a sample that has the consistency of a thick paste. Measurements could be performed at 4.2 K, 77 K and 300 K. In Figure 3 it can be seen that at 77 K the magnetic sextuplet has disappeared completely in favor of an  $\text{Fe}^{3+}$  doublet. At room temperature, the doublet is significantly broadened due to Brownian motion of the colloids in the paste [5].

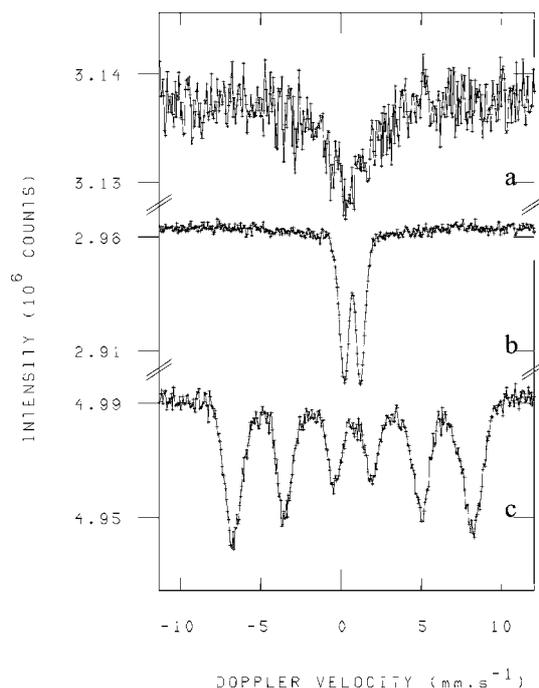


Figure 3. Spectra recorded at 300 K (a), 77 K (b) and 4.2 K (c) on an Fe (2.1 nm) colloid, exposed to air during evaporation of the decaline. IS relative to SNP at room temperature.

In Figure 4 spectra are presented of a model catalyst that has been prepared by incipient wetness impregnation of an alumina support with a solution of 2.1 nm colloids. Although the PIB ligand is supposed to have a strong affinity towards the alumina support, no recoil free fraction is observed in the sample directly after impregnation. Upon evaporation of the decaline in ambient air at 373 K, a doublet of superparamagnetic Fe(III) oxide is observed at 300 K as well as at 77 K. At 4.2 K, the main spectral contribution is a sextuplet with  $H_{\text{eff}} \approx 470$  kOe, characteristic for disordered Fe(III)oxide particles and this spectrum resembles that of the original colloid particles in the solution.

The sample has been subjected to subsequent calcination treatments in ambient air up to 673 K. The measurements at 300 K and 77 K did not show any changes due to the treatments up to 573 K. After a treatment at 673 K, however, sintering of the particles can be derived from the appearance of a small spectral contribution of a sextuplet.

The model catalyst has also been subjected to a stepwise reduction treatment for 1 hour in hydrogen. The temperature of the sample has been increased in steps of 100 K up to 673 K. After each treatment Mössbauer spectra have been recorded at 300 K and 77 K. At 573 K the formation of a high-spin Fe<sup>2+</sup> species is observed indicating that the reduction of the Fe(III) oxide species starts at this temperature. After reduction at 673 K a sextuplet with  $H_{\text{eff}} = 330$  kOe becomes visible in the

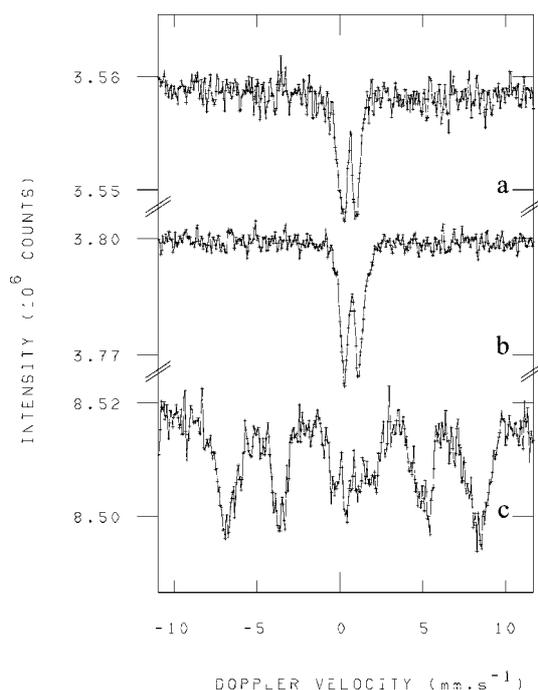


Figure 4. Spectra recorded at (a) 300 K, (b) 77 K and (c) 4.2 K on a model catalyst prepared by incipient wetness impregnation of an alumina support with Fe (2.1 nm) colloids. IS relative to SNP at room temperature.

Mössbauer spectra, indicating that  $\alpha$ -Fe is formed. The contribution of metallic iron increases during extended reduction at 673 K. Subsequent exposure of the sample to ambient air does not lead to re-oxidation of the metallic iron species indicating that the observed  $\alpha$ -Fe particles have become rather large. So, the metallic iron particles turn out to become mobile and sinter at this temperature.

### 3. Conclusions

From the above described preliminary Mössbauer spectroscopic measurements on the Fe (2.1 nm)/Al<sub>2</sub>O<sub>3</sub> sample, it can be concluded that it is promising to produce model catalysts by impregnation of PIB stabilised Fe colloids. However, to avoid sintering of the particles, the temperature of the different applied treatments has to be kept well below 673 K.

To increase the signal-to-noise ratio for a good characterisation study, it will be tried to prepare samples enriched in <sup>57</sup>Fe. Furthermore, as the catalysis takes place at the surface of the catalyst particles and as the larger colloids are prepared in a two step procedure (in a first step small colloids are prepared, than in a second step

Fe(CO)<sub>5</sub> is added to increase the size of the particles) an attempt will be made to prepare small colloids that have a surface that is enriched in <sup>57</sup>Fe.

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