Thermal effects in highly dispersed iron catalysts

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The Mössbauer spectra of three Fe/SiO_2 catalysts with 5 wt% iron content show the presence of several Fe species and display different magnetic behaviours when the precursors are subjected to various thermal treatments. Based on the Mössbauer parameters and CO chemisorption measurements, the average crystal sizes of the catalysts are estimated and discussed in connection with the thermal pretreatment severity and magnetic properties of the samples.

1. Introduction

The activity and selectivity of Fe/SiO_2 catalysts is highly dependent on precursor heating pretreatment. This is responsible not only for the final size of the metal crystallite but also for the magnetic behaviour and metal–support interaction. The precise parameters that control these properties are still a matter of study. With this paper we start a systematic investigation of the influence of the severity of the heating pretreatment on the final crystal size and magnetic behaviour of the catalysts.

2. Experimental

The precursors of the catalysts were prepared as described previously [1] and vacuum dried: pv, calcinated in air at 698 K, 8 h: p8 and 344 h: p344. The catalysts were obtained by reduction of the precursors in H_2 flow at 698 K during 26 h and are called cv, c8 and c344 respectively. CO chemisorption measurements were performed on the catalysts in a conventional static volumetric equipment. The Mössbauer spectra were obtained as described in ref. [1].

3. Results

The Mössbauer spectra of the precursors are shown in fig. 1 and the correspond-
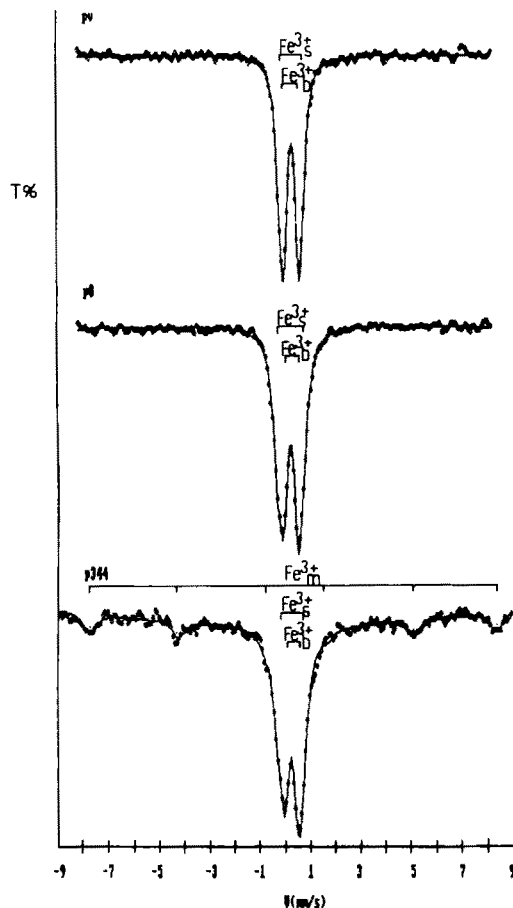
Fig. 1. Mössbauer spectra of the precursors.

ing parameters in table 1. Fig. 2 shows the Mössbauer spectra of the catalysts and table 2 displays the corresponding parameters. The relative number of Fe^0 atoms in each catalyst was calculated assuming equal f factors for all species and their total number was obtained in combination with atomic absorption measurements. The average volumetric-superficial diameters were calculated following the same methodology as in ref. [1] and their values were: 44 ± 6 Å, 43 ± 6 Å and 20 ± 4 Å for cv, c8 and c344 respectively.

4. Discussion

Mössbauer spectra of the precursors (fig. 1) show the presence of two peaks in the central region. These signals were fitted with two doublets with approximately

Table 1
Mössbauer parameters for different precursors.

Species	Parameters[a]	pv	p8	p344
surface Fe^{3+}	IS (mm/s)	0.37 ± 0.01	0.33 ± 0.01	0.31 ± 0.02
	ΔQ (mm/s)	0.92 ± 0.04	0.96 ± 0.05	0.90 ± 0.09
	Γ (mm/s)	0.34 ± 0.03	0.46 ± 0.02	0.53 ± 0.04
	(%)	40 ± 11	50 ± 17	47 ± 23
bulk Fe^{3+}	IS (mm/s)	0.36 ± 0.01	0.35 ± 0.01	0.35 ± 0.02
	ΔQ (mm/s)	0.59 ± 0.02	0.57 ± 0.03	0.49 ± 0.05
	Γ (mm/s)	0.29 ± 0.02	0.36 ± 0.03	0.37 ± 0.06
	(%)	60 ± 11	50 ± 14	32 ± 22
magnetic Fe^{3+}	IS (mm/s)	–	–	0.46 ± 0.03
	ΔQ (mm/s)	–	–	0.06 ± 0.03
	H (kOe)	–	–	500 ± 2
	Γ (mm/s)	–	–	0.54 ± 0.11
	(%)	–	–	21 ± 8

[a] All isomer shifts are referred to α-Fe at room temperature.

equal isomer shifts, δ, and different quadrupole splittings, Δ, and were assigned to α-Fe_2O_3 [2,3]. The p344 sample shows also a magnetically split component which corresponds to α-Fe_2O_3. Its origin might be due to the growth of α-Fe_2O_3 crystallites by sintering. The presence of a new magnetic anisotropy barrier caused by an interaction between crystallites coming close to each other because of the prolonged thermal treatment was also considered. However, rough estimates of anisotropy barriers point towards the first explanation since the calculated magnetocrystalline constant is much higher than the other anisotropies.

The fitting of the central part of the spectra of the catalysts pose the additional problem that the signal originated in atoms embedded in crystallites of different sizes are overlapped. The deconvolution of these spectra would require measurements in different external conditions, i.e., at several temperatures, with applied external magnetic fields, etc., in order to assess the relative contributions of the various Fe species to the total signal. With the present data the hyperfine parameter distributions were simulated with doublets of asymmetric components and large linewidths characteristic of spectra originated in particles of different sizes.

In the three catalysts the broad singlet was assigned to superparamagnetic Fe^0 (Fe^0(sp)) [4,5]. Mössbauer spectra of c8 and c344 show besides, a sextet of magnetic Fe^0 (Fe^0(m)) [3].

The spectra display also the presence of paramagnetic Fe^{2+} compounds. The spectra had to be fitted with one quadrupole doublet (as in ref. [6]) and one singlet for c8 and c344 and only with one singlet for cv similarly to Niemantsverdriet [5].

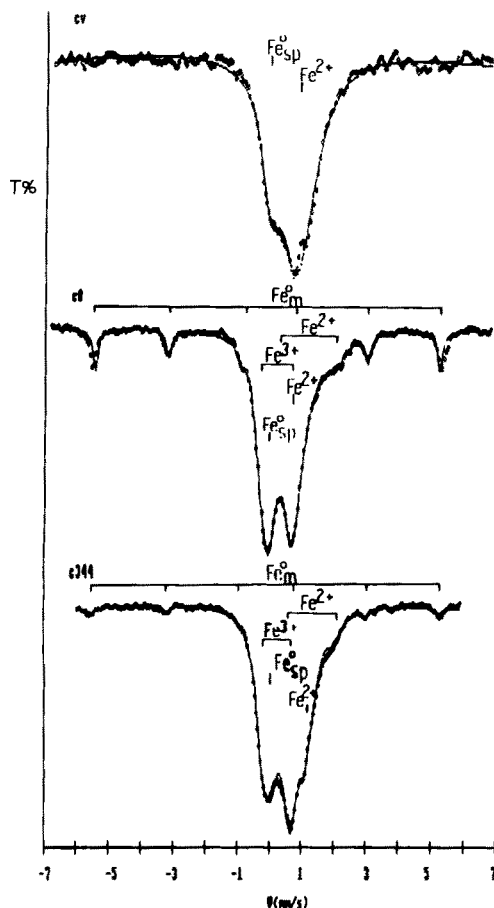Finally, the presence of a third doublet characteristic of Fe^{3+} is observed only

Fig. 2. Mössbauer spectra of the catalysts.

in c8 and c344. This suggests that when the severity of the thermal treatment increased, Fe^{3+} ions were able to migrate inside the support to sites where it is more difficult to undergo reduction.

The fitting of c344 spectrum was particularly difficult because there is a great fraction of Fe^{3+} in the support with significant δ and Δ distributions. Therefore, the fitting was performed by fixing δ of the $Fe^{0}(sp)$ species assuming that their δ distribution resulted only in a larger Γ. Measurements at different temperatures are currently in progress.

The Fe^{0} d_{VA} values obtained from chemisorption of CO and Mössbauer spectroscopy for cv and c8 are equal within errors. However, their Mössbauer spectra are quite different. Considering that in metal supported systems usually there exists a distribution of crystallite sizes, the observed behaviour would be indicative of the growth of the bigger crystallites and the decrease of the smaller ones without a change of the distribution mean value.

Table 2
Mössbauer parameters of reduced catalysts.

Species	Parameters[a]	cv	c8	c344
$Fe^0(sp)$	IS (mm/s)	0.07 ± 0.02	0.06 ± 0.02	0.00 ± 0.00^b
	Γ (mm/s)	0.73 ± 0.06	0.45 ± 0.12	0.59 ± 0.10
	(%)	33 ± 4	22 ± 10	12 ± 3
$Fe^0(m)$	IS (mm/s)	–	0.01 ± 0.01	0.01 ± 0.02
	ΔQ (mm/s)	–	0.01 ± 0.01	0.02 ± 0.02
	H (kOe)	–	331.0 ± 0.3	331 ± 1
	Γ (mm/s)	–	0.20 ± 0.01	0.24 ± 0.00^b
	(%)	–	15 ± 3	4 ± 1
Fe^{2+}	IS (mm/s)	–	1.22 ± 0.08	1.21 ± 0.02
	ΔQ (mm/s)	–	1.72 ± 0.17	1.66 ± 0.05
	Γ (mm/s)	–	0.71 ± 0.13	0.54 ± 0.06
	(%)	–	17 ± 7	12 ± 2
Fe^{2+}	IS (mm/s)	0.92 ± 0.02	0.91 ± 0.10	1.27 ± 0.01
	Γ (mm/s)	1.30 ± 0.04	0.96 ± 0.11	0.65 ± 0.05
	(%)	67 ± 8	17 ± 8	19 ± 4
Fe^{3+}	IS (mm/s)	–	0.27 ± 0.02	0.41 ± 0.01
	ΔQ (mm/s)	–	0.92 ± 0.04	0.76 ± 0.02
	Γ (mm/s)	–	0.45 ± 0.06	0.64 ± 0.04
	(%)	–	29 ± 14	53 ± 5

[a] All isomer shifts are referred to α-Fe at room temperature.
[b] Parameter constrained in fitting.

When the calcination time increases a decrease of Fe^0 d_{VA} is observed for c344 together with a noticeable increase in the amount of Fe^{3+} located inside the support lattice and therefore not available for reduction. The present results are consistent with the fact that for supported materials less iron available for reduction goes with a smaller crystal size [4].

5. Conclusion

The average diameters of Fe^0 particles of cv and c8 are similar, although their particle size distributions are different. The long calcination of p344 led to a strong migration of Fe^{3+} into the support and a growth of α-Fe_2O_3 surface crystallites. The prevalence of the lower concentration of the reducible ions on the support led to a smaller Fe^0 crystal diameter in c344.

References

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