

THE INFLUENCE OF PARTICLE SIZE AND STRUCTURE ON THE MÖSSBAUER
SPECTRA OF IRON CARBIDES FORMED DURING FISCHER-TROPSCH SYNTHESIS

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Introduction

Characterization of the active and stable phase of iron-based Fischer-Tropsch catalysts has been a topic of investigation for several years (1-10). Yet, a great deal of controversy still surrounds the identity of the phase(s) present during synthesis. This stems from the fact that neither x-ray nor Mössbauer studies have proven capable of unambiguously characterizing the metastable carbides formed.

Investigations of the metastable, octahedral carbides (as they have been termed (5)) have been going on for many years (11-18), dating back to at least 1949 (12). The iron structure has been assigned as HCP (or 'nearly' HCP) with the carbon atoms occupying the octahedral holes. The most notable of these are the ϵ and ϵ' carbides. X-ray results have, however, been rather unsatisfactory for many reasons. For instance, the commercial catalysts studied contained many metallic additives and in most cases the small crystallite sizes gave rise to broad, poorly resolved lines.

In recent years, emphasis has shifted toward the use of Mössbauer spectroscopy for in-situ studies of the carburization behavior (1-10, 13-15, 18). Again, a number of conflicting reports have appeared. Many workers suggest that χ and ϵ' are the active phases, with ϵ' being present in smaller particles (4,10). Others have argued that the dominant phases are ϵ and ϵ' (2,8,9). Still others have suggested that the identities of ϵ and ϵ' are actually the reverse of what has been generally reported (5). It should be clear from a careful review of these studies that the ambiguity arises from the difficult interpretation of the spectra obtained. This may be due to the fact that these phases are present as very small particles (ca. 10 nm diameter), which introduces relaxation effects into the spectra. Further, the characteristic peaks attributed to ϵ and ϵ' carbide are, in most cases, present as background lines superimposed on a strong spectral component of α -Fe or Fe-oxide.

It will be shown that if spectra are collected for a single sample over a range of temperatures, and if relaxation effects are properly accounted for, the Mössbauer results can give not only accurate identification of the phase(s) present but also quantitative particle size information and qualitative information regarding particle structure and the nature of particle/support interaction.

Discussion

In this study a Mössbauer modelling routine, described in earlier work (19-21), designed to account for collective magnetic excitations (22,23), superparamagnetic relaxation (24) and quadrupole shift distribution (25,26), was used to generate theoretical iron-carbide spectra which could then be analyzed using a conventional least-squares fitting routine (27). Several parameters (including, temperature, anisotropy energy constant, quadrupole shift distribution, and particle size distribution) were systematically varied to check the effect on the observed spectra. The starting parameters were those of χ -carbide (25).

From the results (shown in Figures 1-4, and Tables I-III) the following conclusions can be drawn:

- 1.) At least one phase of octahedral carbide forms during Fischer-Tropsch synthesis.
- 2.) The partially relaxed spectrum of this phase can be reasonably well fit with a single sextuplet with $H_{hf} \approx 170$ kOe and $\delta_{IS} \approx .25$ mm/s (28). However, due to the clear assymetry of the spectrum, more than one sextuplet is probably present.
- 3.) A wide particle size distribution cannot account for the broadness observed in the peaks attributed to ϵ' -carbide, and the unrelaxed hyperfine field of this phase is probably larger than 170 kOe.
- 4.) The particle sizes reported on the basis of x-ray data cannot be correct (i.e., 35Å particle radius), since it is impossible to obtain a defined sextuplet for a particle size this small. Relaxation effects become overwhelming.

All of these conclusions will be discussed in greater detail.

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TABLE I: Comparison of input and fitted Mössbauer parameters for a bulk χ -carbide phase.

<u>Parameter</u>	<u>Fe Site</u>	<u>Input Values</u>	<u>Fitted Values</u>
H_{hf} (kOe)	I	196.0	196.5
	II	217.0	217.5
	III	118.0	117.5
δ_{IS} (mm/sec)	I	+0.15	+0.149
	II	+0.17	+0.169
	III	+0.15	+0.143
ΔE_Q (mm/sec)	I	0.00	-0.003
	II	+0.027	+0.025
	III	-0.012	-0.021
Relative Intensity	I	3:2:1	3.9:3.2:1.2
	II	3:2:1	4.0:2.1:1.7
	III	1.5:1:0.5	2.0:1.4:0.4
Linewidths (mm/sec)	I	.25:.23:.23	.5:.43:.35
	II	.25:.23:.23	.48:.48:.46
	III	.25:.23:.23	.61:.68:.79

*Other input parameters were (i) anisotropy energy constant = 1,000,000 erg/cm³, (ii) average particle size = 200Å, (iii) temperature = 300 K, (iv) σ = 1.20

TABLE II:
Mössbauer parameters obtained from a 20-peak fit of the spectra in Figure 1.

Spectrum	Spectral Component	H_{rf} (kOe)	δ_{TS} (mm/s)	ΔE_Q (mm/s)	Linewidths (mm/s)	% Area
1a.	X-I	192.3	.146	.020	.57: .62: .67	24.7
	X-II	215.4	.233	.016	.78: .77: .62	24.0
	X-III	106.7	.241	-.027	.61: .62: .61	10.3
	Doublet	--	.157	.590	.76	41.0
1b.	X-I	192.6	.140	.009	.61: .50: 1.4	35.3
	X-II	212.3	.178	.023	.55: .55: .44	28.6
	X-III	110.3	.183	-.019	.72: .88: .51	20.1
	Doublet	--	.152	.533	.60	16.0
1c.	X-I	192.0	.146	-.002	.49: .69: .62	36.6
	X-II	212.4	.165	.027	.57: .53: 1.0	38.8
	X-III	113.9	.162	-.020	.52: .64: .63	19.8
	Doublet	--	.181	.879	.75	4.8

TABLE III: Mössbauer parameters obtained from an 8-peak fit of the spectra in Figure 1 and 2.

<u>Spectrum</u>	<u>Spectral Component</u>	<u>H_{hf}(kOe)</u>	<u>δ_{LS}(mm/s)</u>	<u>ΔE_Q(mm/s)</u>	<u>Linewidths (mm/s)</u>	<u>% Area</u>
1a.	Sextuplet	197.7	0.155	0.014	.77: .70: 1.6	58.4
	Doublet	---	0.158	0.613	.73	41.6
1b.	Sextuplet	200.4	0.155	0.013	.75: .61: 1.7	73.8
	Doublet	---	0.159	0.748	.79	26.2
1c.	Sextuplet	202.0	0.154	0.013	.74: .59: 1.0	92.8
	Doublet	---	0.210	1.209	1.40	7.2
2a.	Sextuplet	199.4	0.155	0.013	.75: .69: 1.19	55.0
	Doublet	---	0.160	0.681	.73	45.0
2b.	Sextuplet	197.6	0.155	0.014	.78: .61: 1.02	79.2
	Doublet	---	0.165	1.594	2.12	20.8
2c.	Sextuplet	198.2	0.157	0.013	.73: .55: .54	91.4
	Doublet	---	0.182	2.300	.632	8.6

FIGURE CAPTIONS

Figure 1. Effect of anisotropy energy constant on spectrum. (a) $K = 750,000$ erg/cm 3 ; (b) $K = 1,500,000$ erg/cm 3 ; (c) $K = 3,000,000$ erg/cm 3 . Other input parameters were (i) average particle size = 55Å; (ii) $\sigma = 1.20$; (iii) $T = 300K$.

Figure 2. Effect of narrowness of particle size distribution on spectrum. (a) $\sigma = 1.25$; (b) $\sigma = 1.10$; (c) $\sigma = 1.05$; (d) log-normal distribution function for several σ values. Other input parameters were (i) average particle size = 55Å; (ii) $T = 300K$; (iii) anisotropy energy constant = 1,000,000 erg/cm 3 .

Figure 3. Effect of a variation of ϵ_0 (equation (3), Ref. 25). (a) $\epsilon_0 = 0$; (b) $-5\text{e} \text{curie} < \epsilon_0 < .5\text{e} \text{curie}$; (c) $-.75\text{e} \text{curie} < \epsilon_0 < .75\text{e} \text{curie}$. Other input parameters were (i) average particle size = 80Å; (ii) $\sigma = 1.20$; (iii) $T = 300K$; (iv) anisotropy energy constant = 1,000,000.

Figure 4. Effect of temperature on spectrum. (a) $T = 350K$; (b) $T = 300K$; (c) $T = 80K$. Other parameters were (i) average particle size = 55Å; (ii) $\sigma = 1.20$; (iii) anisotropy energy constant = 1,000,000 erg/cm 3 . Values of H_{hf} and δ_{IS} were taken from Ref. 25 at each temperature.

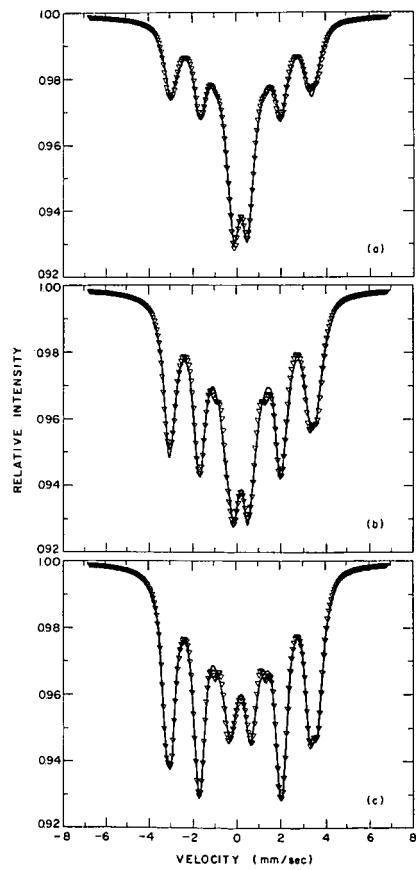
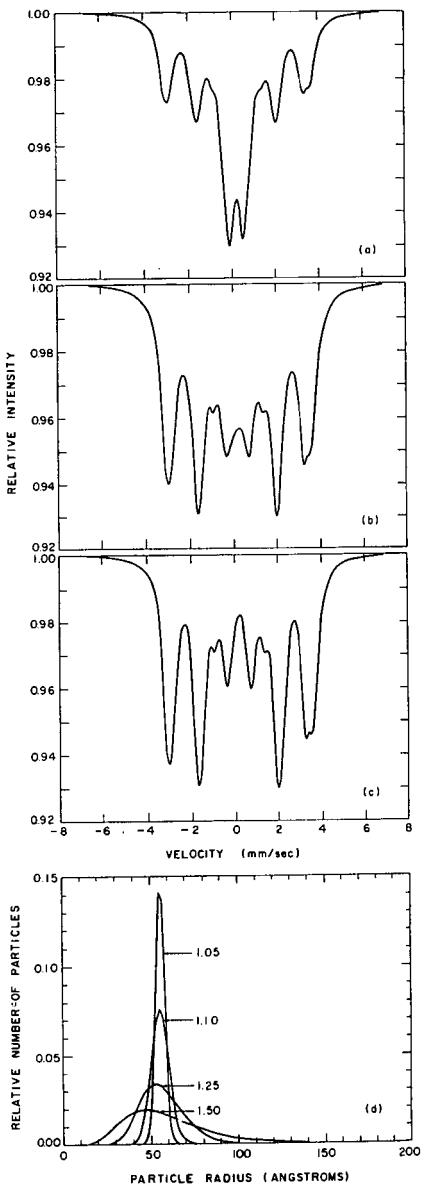


FIGURE 1



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FIGURE 2

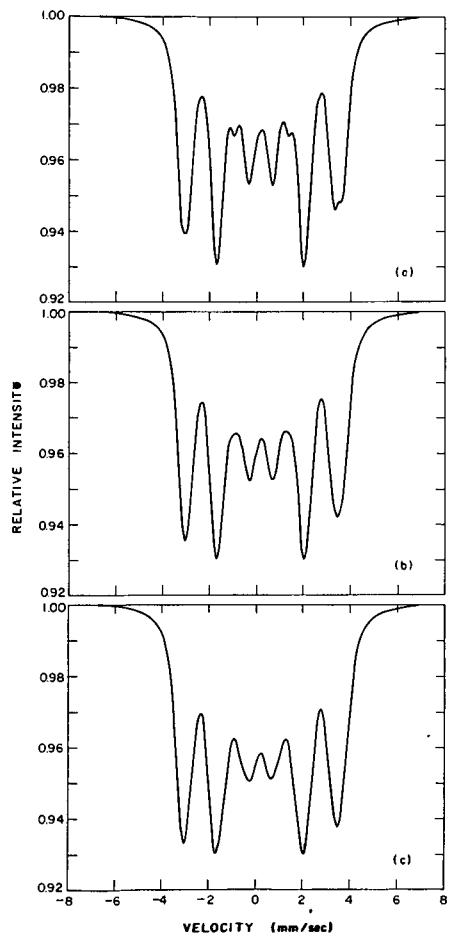


FIGURE 3

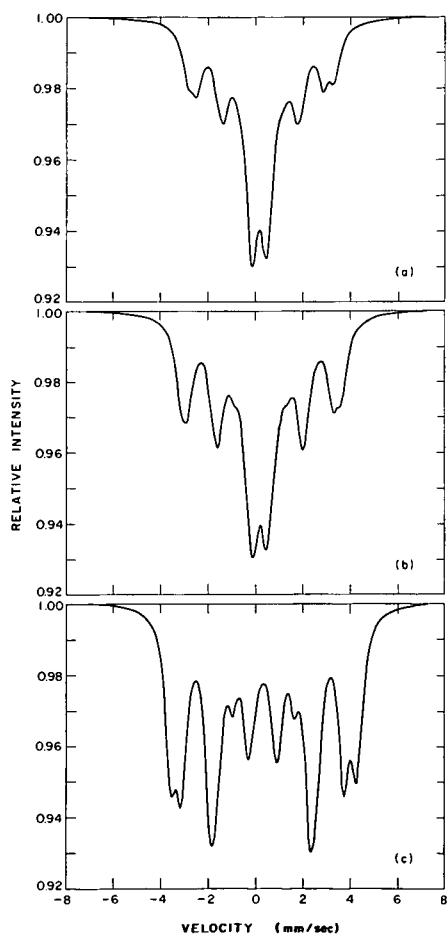


FIGURE 4