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The Structure of a Pseudo-Hexagonal Iron Carbide

BY G. H. BARTON

Physical and Chemical Services Division, Warren Spring Laboratory, Stevenage, Hertfordshire, England

AND B. GALE

Metallurgy Department, National Physical Laboratory, Teddington, Middlesex, England

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This paper describes an X-ray diffraction appraisal of an iron catalyst extracted after use in the Fischer–Tropsch process for the synthesis of hydrocarbons from carbon monoxide and hydrogen. The substance, in which the iron atoms form an approximately hexagonal close-packed array, is monoclinic with cell dimensions $a=b=2\cdot794$ Å, $c=4\cdot360$ Å and $\gamma=120\cdot92°$. It is assumed to be a carbide, with small amounts of associated oxygen. It is not possible, with X-ray powder diffraction, to identify the structure completely, but on the basis of the formula Fe_2C the possibilities are discussed.

Introduction

As part of a programme of research on the structure of Fischer–Tropsch synthesis catalysts, X-ray diffraction studies were made on a catalyst originally charged to the process as a precipitated iron oxide incorporating small amounts of potassium and copper oxides as promoters. After activation and synthesis for 20 hours at 265 °C (Farley & Ray, 1963), the catalyst was withdrawn and exhaustively extracted with benzene and dried *in vacuo*. X-ray diffraction powder photographs of this material showed a marked similarity to the hexagonal iron carbides reported by Hofer, Cohn & Peebles (1949) and by Jack (1950), but the differences, chiefly the doubling of most of the diffraction lines, suggested that some form of distortion was present.

The intensity ratios of the diffraction doublets suggested that the iron atoms had undergone small displacements. These phenomena were investigated.

Experimental

X-ray powder-diffraction photographs were taken in an 11·4 cm diameter Straumanis camera, with Cr $K\alpha$ and Co $K\alpha$ radiations, and several corresponding diffractograms were recorded by means of a Philips PW 1050 X-ray diffractometer.

The broadening of the diffraction lines indicated that the crystallite size was of the order of 300–400 Å.

Values of the lattice spacings and of the line-intensities were derived from the photographs and diffractograms, and the averages of the data for each diffractogram line are given in Table 1.

Table 1. *Values of the lattice spacings and line intensities averaged for each diffraction line*

	Lattice spacing (Å)			Relative intensity	
Indices *hkl*	This study	Hofer's values	Jack's values	Measured	Calculated
100	2·431	2·38	2·36	13	17·6
$1\bar{1}0$	2·402				
002	2·184	2·16	2·16	21	20·7
$1\bar{1}1$	2·125	2·08	2·07	100	100
101	2·103				
$1\bar{1}2$	1·622	1·60	1·60	16	17
102	1·614				
$1\bar{2}0$	1·397	1·37	1·36	13	17·4
110	1·378				
$1\bar{1}3$	1·247	1·24	1·23	13	15·9
103	1·243				
* $\bar{1}22$	1·176	1·16	1·16	20	31·5
* 112	1·165				
* $2\bar{2}1$	1·171				
* 201	1·156				
004	1·088			2·6	3·3
$2\bar{2}2$	1·061			4·4	5·8
202	1·049				
$1\bar{1}4$	0·9946			2·3	3·5
104	0·9922				

* The large overlapping of these lines did not allow their separate intensities to be measured.

The total integrated intensities of the doublets and singlets were measured from the diffractograms, and the results, which are given in Table 1, were expressed as a fraction of the intensity of the strongest line ({101} doublet). Intensity measurements on the {112} and {201} doublets were not reliable because of their close proximity. The relative intensities were also obtained by calculation with the use of the standard relationship for a diffractometer,

$$I \propto |F_t|^2 qG(\theta)$$

where q = multiplicity factor,

$$G(\theta) = \operatorname{cosec}^2 \theta \sec \theta (1+\cos^2 2\theta)^{-1}$$

Table 2. *Degree of shear and comparison of calculated intensity ratios for suggested structure with observed intensity ratios*

		$\Delta\theta$ cot θ		Degree of shear (γ)			Calculated intensity ratio	
Indices hkl	A	Co $K\alpha$	Cr $K\alpha$	Co $K\alpha$	Cr $K\alpha$	Measured intensity ratio	$\varepsilon_z=0$	$\varepsilon_z=0{\cdot}01$
100	-1	0·782	0·778	0·908°	0·900°	1·3 ± 0·2	2	1·5
$1\bar{1}0$	-2					1	1	1
$1\bar{1}1$	-1	0·585	0·619	0·885°	0·937°	1	1	1
101	2					2·1 ± 0·2	2	2·2
$1\bar{1}2$	-1	0·346	0·348	0·894°	0·899°	1	1	1
102	2					1·5 ± 0·2	2	1·5
$1\bar{2}0$	0	1·754	1·705	1·027°	0·998°	1·8 ± 0·2	2	2
110	9					1	1	1
$1\bar{1}3$	-1	0·339	0·407	0·844°	0·887°	1	1	1
103	2					1·9 ± 0·2	2	2·2
$\bar{1}22$	0	0·528	—	0·868°	—	—	—	—
112	9							
$2\bar{2}1$	-4	0·748	—	0·934°	—	—	—	—
201	8							

(Lorentz–polarization factor), and F_t = temperature-dependent structure factor. F_t was calculated assuming that the root mean square amplitudes of vibration of both iron atoms and carbon atoms are approximately 0·12 Å.

The intensity ratios of all but the last two doublet components were measured, and the results are given in Table 2. It was not possible to obtain reliable values in the case of the last two doublets because of their large overlap.

Form of distortion

A general distortion of a unit hexagonal cell would result from a change in the values of the four lattice parameters. If, in this event, the new cell dimensions are a, $a(1+\varepsilon)$ and c, and the new cell angles are $\pi/2+\alpha$, $\pi/2+\beta$ and $2\pi/3+\gamma$, where α, β, γ and ε are small, the volume of the resulting triclinic cell is given by:

$$V=\frac{\sqrt{3}a^2}{2}c\left(1+\varepsilon-\frac{1}{\sqrt{3}}\gamma\right)$$

and the spacing, d, of the lattice planes with indices (hkl) is given by:

$$1/d^2=1/d_0^2+\Delta Q\ ,$$

where

$$(1/d_0^2)=(4/3a^2)(h^2+hk+k^2)+(l^2/c^2)$$

and

$$\Delta Q=(4/3\sqrt{3}a^2)(2h^2+5hk+2k^2)\gamma-(4/3a^2)k(h+2k)\varepsilon + (8l/3ac)[(\alpha+\tfrac{1}{2}\beta)k+(\tfrac{1}{2}\alpha+\beta)h]\ .$$

In powder diffraction, the reflexions having the same values of ΔQ are superimposed, the maximum multiplicity occurring when $h\neq k\neq 0$, and $l\neq 0$, and under these conditions, twelve lines are each formed by the superposition of two reflexions. The multiplicity is reduced in special cases. For example, if $h=k$, $l\neq 0$, or $h\neq k$, $l=0$ or $h\neq 0$, $k=0$ and $l=0$, there will be six components each formed by two reflexions, while if $h\neq 0$, $k=l=0$ or $h=k$, $l=0$, there will be three components each formed by two reflexions. For $h=k=0$, $l\neq 0$ there is only one component from two reflexions. These multiplicities will be further reduced as the number of distortion parameters decrease.

The only distortion consistent with the observed pattern is the one for which $\alpha=\beta=\varepsilon=0$, and for this condition, the angle of shear, γ, can be shown to satisfy the equation

$$\gamma=\frac{3\sqrt{3}a^2\Delta\theta_0\cot\theta_0}{2d_0^2(A_2-A_1)}$$

where $A=2h^2+5hk+2k^2$, θ_0 is the mean Bragg angle of the components of a doublet, and $\Delta\theta_0$ is the difference between the Bragg angles of the components of a doublet. The values of $\Delta\theta_0$ were measured from the several diffraction photographs and diffractograms of the material. Values of $\Delta\theta_0$ cot θ_0 obtained for each line were then calculated, the results being given in Table 2. The values of d_0 were calculated from the sufficiently approximate formula

$$d_0=\frac{A_1d_2-A_2d_1}{A_1-A_2}$$

and these, using the method of least squares, gave the cell dimensions as $a=2{\cdot}794$, $c=4{\cdot}360$ Å. Using this value of a in the above formula for γ, the degree of shear was obtained from each diffraction line, and the results, which are given in Table 2, are essentially constant, having an average value of 0·92° with a probable error of ±0·05°.

Discussion of possible structures

There are several possible structures in which the iron atoms form an approximately hexagonal close-packed array with the carbon atoms distributed in various ways on the two octahedral sites of each cell. Assuming the composition to be Fe_2C, there are three main possibilities. The structure may be of the $C6$ type, space group $P\bar{3}m1$ (D_{3d}^3), in which the carbon atoms occupy only one of the octahedral sites. It may be the L_3^1 type, space group $P6_3/mmc$ (D_{6h}^4), in which the carbon atoms are statistically distributed among the octahedral sites, or the structure may be isomorphous with orthorhombic Mo_2C, space group $Pbcn$ (D_{2h}^{14}), in which the iron atoms are hexagonally close packed and the carbon atoms form a regular array on the two octahedral sites (Parthé & Sadagopan, 1963). These structures can only be completely distinguished by measuring those reflexions for which the structure factor is proportional to the scattering factor for carbon. Such reflexions were too weak to be recorded in this work because the X-ray scattering factor for carbon is very small and also because the diffraction lines were diffuse. Allowing for the difference in cell volume, the strong reflexions have the same structure factor in all three structures except for lines with indices $\{h0l\}$, $h=3n\pm1$, $l=4n\pm1$ and $\{hkl\}$, $l=4n+1$, in which case the modulus of the structure factor is given by $|F|=4\sqrt{3}f_1$ for the orthorhombic structure and $|F|=[\sqrt{3}f_1\pm(2p-1)f_2]$ for the hexagonal structures, where f_1 is the scattering factor for iron, f_2 is the scattering factor for carbon, and p is the probability of finding a carbon atom on a particular octahedral site. In a powder diffraction pattern, the terms $\pm(2p-1)f_2$ cancel out when the reflexions are superimposed, and if the slow angular dependence of the scatter, Lorentz and polarization factors are neglected, the intensity ratio of the Debye ring doublets would be 2:1, independent of the carbon atom arrangement.

The agreement between the calculated and the observed relative intensities of the doublets and singlets (Table 1) was reasonably good and supports an approximate hexagonal close-packing array of iron atoms. However, the observed intensity ratios of the doublet components (Table 2) were not in the ratio of 2:1, and this is considered to be a consequence of small displacements of iron atoms. When referred to the orthorhombic space group, the coordinates of the atoms are $\pm(x, y, z;\ \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}-y, \bar{z};\ \bar{x}, y, \frac{1}{2}-z)$ with $x=\frac{1}{4}$, $y=\frac{1}{8}$ and $z=\frac{1}{12}$. It can be shown that, if x, y and z take increments ε_x, ε_y and ε_z respectively, the first five doublet ratios are as follows:

$$2:(1+6\pi\sqrt{3}\varepsilon_z) \quad \text{for the } (100) \text{ doublet,}$$

$$2:(1+6\pi\sqrt{3}\varepsilon_z) \quad \text{for the } (1\bar{1}2) \text{ doublet,}$$

$$2:\left(1-\frac{6\pi}{\sqrt{3}}\varepsilon_z\right) \quad \text{for the } (1\bar{1}1) \text{ doublet,}$$

$$2:\left(1-\frac{6\pi}{\sqrt{3}}\varepsilon_z\right) \quad \text{for the } (1\bar{1}3) \text{ doublet,}$$

$$2:1 \quad \text{for the } (1\bar{2}0) \text{ doublet.}$$

Only the value of ε_z can therefore be calculated. The measured intensity ratios of the doublet components can be reasonably reproduced by giving to ε_z the value 0·01, and the ratios so corrected are given in Table 2.

Concluding remarks

As far as X-ray diffraction could show, the structure of the iron carbide portion of the catalyst remained unchanged irrespective of the synthesis time, although its proportion in an extracted sample varied with the time on synthesis. The only method of locating the carbon atoms would be by neutron diffraction, although if a single crystal were available it would at least be possible to distinguish between the orthorhombic structure and the hexagonal structure provided that $p\neq\frac{1}{2}$.

The substance was stable at room temperature, but on heating for a few hours at 320 °C in a vacuum of about 10^{-5} mm, the crystalline form became identical with the hexagonal structure reported by Hofer. A few per cent of spinel and of cementite were also detected. On further heading at 420 °C the hexagonal form was completely replaced by cementite and iron, while the spinel disappeared. This behaviour suggests that some oxygen was present in the lattice of the pseudohexagonal structure, but it is not understood why the presence of oxygen should produce the shear observed.

The cell dimensions are significantly different from those reported by Hofer *et al.* and by Jack, who calculate $a=2{\cdot}755$, $c=4{\cdot}349$ Å and $a=2{\cdot}73$, $c=4{\cdot}33$ Å respectively. However, the similarity between all three substances suggests that they may well belong to a continuous family.

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