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Mössbauer Spectra of Ferrite Catalysts Used in Oxidative Dehydrogenation

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Room temperature Mössbauer spectroscopy has been used to examine *bulk* changes which occur in low surface area $CoFe_2O_4$ and $CuFe_2O_4$ catalysts as a result of contact with various mixtures of *trans*-2-butene and O_2 during oxidative dehydrogenation reactions at about 435°C. So long as there was at least *some* O_2 in the gas phase, the $CoFe_2O_4$ spectrum was essentially unchanged. However, the spectrum changed from a *random* spinel in the oxidized state to an *inverse* spinel as it was reduced by oxide ion removal. The steady state catalyst lies very near the fully oxidized state. More dramatic solid state changes occurred as the $CuFe_2O_4$ underwent reduction. Under severe reduction, the ferrite was transformed into Cu^0 and Fe_3O_4, but it could be reversibly recovered by oxidation. An intense doublet located near zero velocity persisted in all spectra of $CuFe_2O_4$ regardless of the state of reduction.

INTRODUCTION

While Mössbauer spectroscopy has been used to study the structure of iron and tin compounds for many years, only recently has the technique been applied to the study of catalysis (*1*). Several studies have been directed toward determining the crystallite size of Fe_2O_3 supported on silica (*2–5*) or toward iron synthetic ammonia catalysts (*6*). The purpose of this work is to report the use of ^{57}Fe Mössbauer spectroscopy to explore *bulk* structural changes that occur in two ferrite catalysts as a result of their use in promoting oxidative dehydrogenation (OXD) of butene to butadiene. Rennard and Kehl (*7*) have recently used similar techniques to study other ferrite catalysts. Kinetic and isotopic tracer studies of the reaction mechanisms that occur over these cobalt and copper ferrites have been previously reported (*8*).

Ferrites are convenient for such investigations, because they generally occur as well-characterized normal, inverse, or mixed spinels with the iron atoms occupying octahedral or tetrahedral holes in the close-packed oxide lattice. Furthermore, the ease of interconversion between Fe^{2+} and Fe^{3+} provides a reasonable oxidation–reduction pathway by which these OXD reactions can occur. Mössbauer spectroscopy is an extremely effective tool for studying these materials since relatively subtle bulk phase changes that are beyond the resolution of such techniques as X-ray analysis can be clearly observed.

EXPERIMENTAL METHODS

Catalysts and Pretreatment. Both $CoFe_2O_4$ and $CuFe_2O_4$ (surface areas 2.0 and 0.12 m^2/g, respectively) were commercially available powers supplied by Alfa Inorganics. A sample of α-Fe_2O_3 (AR grade from Fisher Scientific Co., surface

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area 7.7 m^2/g) was included for comparison. Catalyst samples from 0.5 to 1.0 g were placed in a removable Pyrex reactor that contained a thermocouple well in the center of the catalyst bed. Each fresh catalyst was initially activated at 520°C by (1) evacuation to 10^{-6} Torr, (2) oxidation with a 77°K-trapped, recirculating oxygen stream for 2 h, and (3) reevacuation to 10^{-6} Torr. Following this treatment, the evacuated catalysts were cooled to 435°C and then exposed to a premixed *trans*-2-butene: O_2 mixture (usually 50:25 Torr) in the recirculation system (for conversion into SI units, 1 Torr = 133.3 N cm^{-2}). Samples were periodically removed by expansion for glc analysis (*8*).

After completion of an experiment, each catalyst was evacuated briefly, cooled quickly to room temperature, and exposed to the air before being mounted on a paper slide for Mössbauer analysis.

Mössbauer spectra. The Mössbauer spectra were obtained at room temperature by Austin Science Associates. Laser velocity calibrations were performed for each sample, and peak positions were determined by comparing the multichannel analyzer (512 channels) calibration points with those of a 0.5 mil iron foil. The counting level was about 4×10^6 counts/channel. Because peak minima were found by visual inspection, an error of about ±0.025 mm/sec (±1 channel) might be expected.

RESULTS AND DISCUSSION

Representative Mössbauer spectra are shown in Fig. 1. Since the relative velocity and recording speed varied slightly from one sample to another, the velocity scale shown in Fig. 1 is only approximate. Data points are shown only for curves 1, 4, and 7; individual calibration points are not included. Exact peak positions and Mössbauer parameters are recorded in Table 1. Some general observations and definitions will first be presented, then each individual spectrum will be discussed.

General observations. As expected for mixed spinel structures, all samples showed two 6-line hyperfine splitting patterns; a quadrupole splitting is superimposed on the hyperfine splittings. In addition, some of the spectra showed an intense doublet located near zero velocity.

The 6-line pattern that has the more negative velocity for its first line (numbering from left to right) is arbitrarily called Pattern I; the other is called Pattern II. With the peaks' positions specified by their number (from left to right), the quadrupole interaction (ΔS) within each pattern is defined by the equation (*9*)

$$\Delta S = (2 - 1) - (6 - 5). \qquad (1)$$

Because the quadrupole interaction shifts the position of the two extreme peaks (Nos. 1 and 6) an equal amount but opposite in direction to the shift of the four inner peaks, the isomer shift (IS) for each pattern is calculated as the average center line of the peaks 1 and 6 and peaks 2 and 5. The IS of the doublet is the center line between the two peaks, and ΔS is the separation between them. The effective magnetic field (H_{eff}) at the iron nucleus (kOe) is calculated from the equation (*9*)

$$H_{\text{eff}} = \frac{330}{10.657}(6 - 1), \qquad (2)$$

where 330 is the field at the nucleus of metallic iron and 10.657 mm/sec is the separation between the terminal peaks in the metallic iron sample. The distance (6 − 1) is the separation between peaks 1 and 6 in the unknown sample. Table 1 gives the line positions, the IS relative to iron metal, ΔS, and H_{eff} for the seven samples discussed herein.

$CoFe_2O_4$. The Mössbauer spectrum of cobalt ferrite has been reported by several authors (*10–13*), but the results are not in complete agreement. A likely reason for

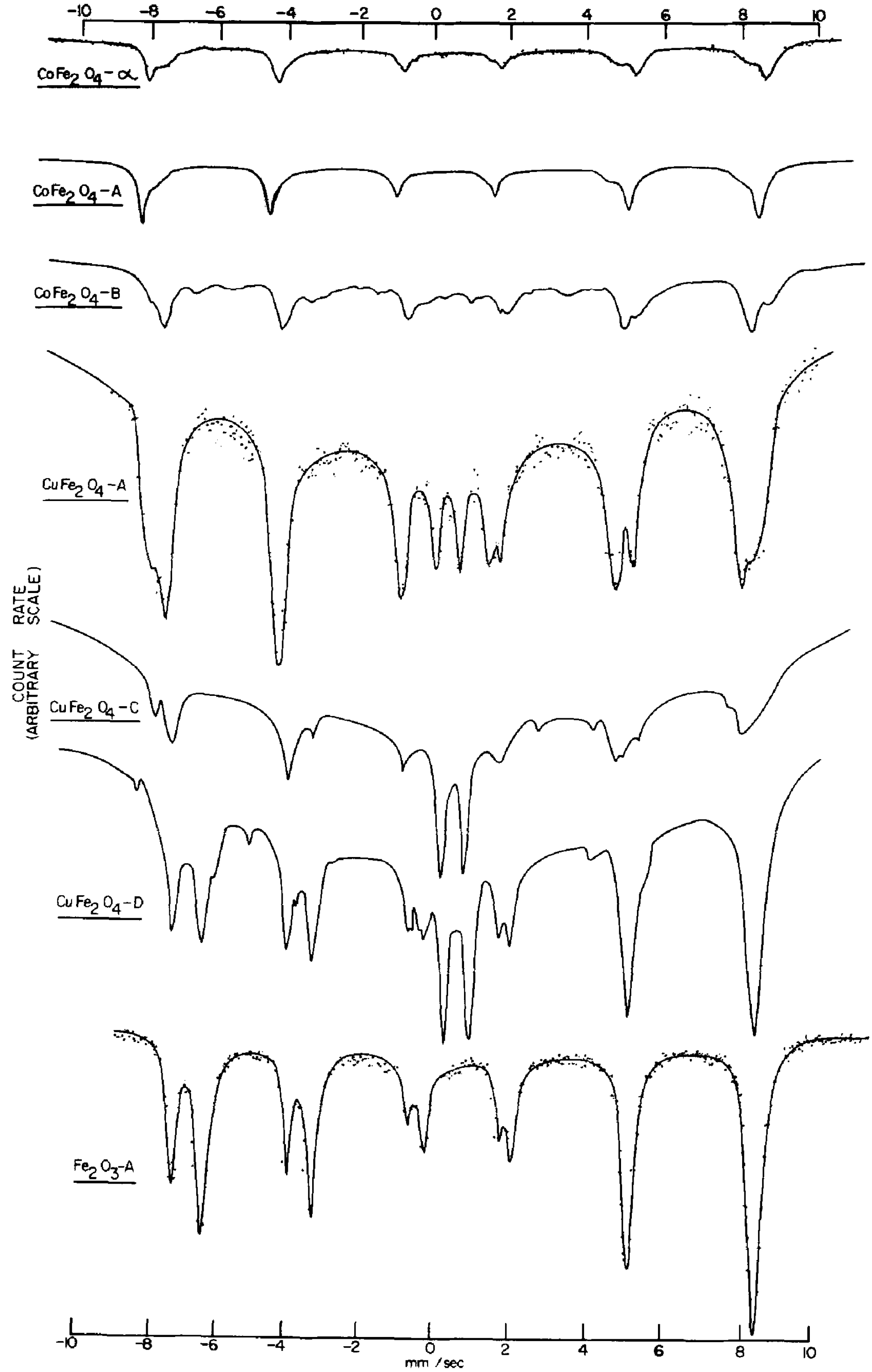

FIG. 1. Room temperature Mössbauer spectra of selected ferrite catalysts after exposure to various mixtures of *trans*-2-butene and O_2 during oxidative dehydrogenation at 435°C. Formulas refer to the starting compositions and may not necessarily describe the solid state composition after the various treatments, as noted in the text.

TABLE 1

MÖSSBAUER PARAMETERS OF FERRITE CATALYSTS AT 300°K

Catalyst	6-Line pattern	Peak positions (mm/sec)[a]						IS[a]	ΔS	H_{eff} (kOe)
		1	2	3	4	5	6			
$CoFe_2O_4$-α	I	−8.09	−4.35	−0.86	+1.76	+5.29	+8.60	0.36	+0.42	517
	II	−7.67	−3.98	−0.51	+1.45	+4.83	+8.10	0.32	+0.41	488
$CoFe_2O_4$-A	I	−8.06	−4.35	−0.86[b]	+1.74[b]	+5.31	+8.61	0.38	+0.41	516
	II	−7.67	−4.03	−0.86[b]	+1.74[b]	+4.81	+8.06	0.29	+0.39	487
$CoFe_2O_4$-B	I	−8.08	−4.5	−0.93[b]	+1.66	+5.13	+8.60	0.29	+0.11	516
	II	−7.68	−4.37	−0.93[b]	+1.53	+4.86	+8.22	0.26	−0.05	492
$CuFe_2O_4$-α	I	−7.76	−4.05[b]	−0.94[b]	+1.71	+5.31	+8.64	0.54	+0.41	508
	II	−7.33	−4.05[b]	−0.94[b]	+1.37	+4.82	+8.37	0.45	−0.27	486
	Doublet			−0.04	+0.61			0.29	+0.65	
$CuFe_2O_4$-A	I	−7.93	−4.28[b]	−0.92[b]	+1.74	+5.23	+8.50	0.38	+0.39	509
	II	−7.52	−4.28[b]	−0.92[b]	+1.44	+4.80	+8.03	0.26	+0.01	482
	Doublet			+0.01	+0.68			0.34	+0.67	
$CuFe_2O_4$-B	I	−7.91	−4.35	−0.90[b]	+1.49[b]	+5.20	+8.01	0.24	+0.75	493
	II	−7.41	−4.11	−0.90[b]	+1.49[b]	+4.68	+7.88	0.26	+0.13	473
	Doublet			+0.01	+0.71			0.36	+0.71	
$CuFe_2O_4$-C	I	−7.97	−4.16[b]	−1.00[b]	+1.62[b]	+4.85	+8.19	0.23	+0.47	500
	II	−7.47	−4.16[b]	−1.00[b]	+1.62[b]	+4.68	+7.89	0.23	+0.11	
	Doublet			−0.03	+0.66			0.32	+0.69	
$CuFe_2O_4$-D	I	−7.46	−4.33	−0.99	+1.42	+4.94[b]	+8.40[b]	0.39	−0.33	491
	II	−6.62	−3.65	−0.60	+1.73	+4.94[b]	+8.40[b]	0.77	−0.49	465
	Doublet			−0.05	+0.65			0.30	+0.70	
Fe_2O_3A	I	−7.43	−4.30	−1.02	+1.46	+4.96[b]	+8.40[b]	0.41	−0.32	490
	II	−6.63	−3.62	−0.56	+1.76	+4.96[b]	+8.40[b]	0.78	−0.43	465

[a] Relative to Fe^0.

[b] Insufficient separation of peaks does not allow individual assignment to Pattern I or II.

these differences is the rate of cooling of a fired sample, which has a marked effect on the distribution of Fe ions between the octahedral and tetrahedral sites (*14*). Furthermore, the distribution patterns change as the material is contacted with various gas mixtures in catalytic reactions, which indicates that *bulk* structural rearrangements occur during catalysis.

The method of preparation of our original catalyst (rapid quenching) would probably lead to a *random* distribution of Fe^{3+} ions between the octahedral and the tetrahedral positions (*14*); the 2:1 intensity ratio between Patterns I and II in the starting sample supports this conclusion. The isomer shifts (~0.4 mm/sec) are characteristic of Fe^{3+} species. Very little change occurred when the catalyst was used for a single OXD experiment, as noted in the $CoFe_2O_4$-A sample in Fig. 1. However, when the catalyst was subjected to depletive reduction through prolonged contact with *n*-butene (lattice oxygen was removed by H_2O, CO, and CO_2 formation), the Mössbauer spectrum ($CoFe_2$-

O_4-B) changed considerably. The octahedral:tetrahedral (Pattern I:II) ratio changed from 2:1 to 2:3. This change may be due to some (~20%) of the Fe^{3+} ions in octahedral sites contributing to the tetrahedral spectrum (*15*). It might also be due to rapid electron exchange between Fe^{2+} and Fe^{3+} in adjacent octahedral sites (*16*), the Fe^{2+} being created by the reduction of the catalyst sample giving a cobalt substituted magnetite type crystal structure.

The insignificant changes which accompany the OXD reaction are consistent with the observation that the state of the catalyst *in the presence of* O_2 is very near complete oxidation. The previous electrical conductivity measurements are consistent with this conclusion (*8*). However, when the gaseous O_2 is removed, the conductivity increases markedly, and the Mössbauer spectrum is changed. The increased electrical conductivity of the reduced sample supports a cobalt-substituted, magnetite-type structure for the reduced $CoFe_2O_4$-B. Since the surface area is quite small, the fraction of total iron ions near the surface is small, and thus the observed changes must have occurred in the *bulk*.

$CuFe_2O_4$. Even more dramatic bulk changes occurred in the $CuFe_2O_4$ as it was subjected to various reaction conditions, and these changes were paralleled by changes in catalytic behavior.

The Mössbauer spectra of the initial, untreated sample ($CuFe_2O_4$-α) and of an extensively used sample which had been reoxidized at 520°C (Curve $CuFe_2O_4$-A in Fig. 1), were both very similar to the spectrum of the tetragonal modification of the inverse spinel material reported by Evans and Hafner (*15*), with one glaring exception—theirs did not show the obvious doublet near zero velocity. Both sets of spectra showed two 6-line hyperfine splitting patterns, with Pattern I being assigned to Fe^{3+} in octahedral sites and Pattern II to Fe^{3+} in tetrahedral sites. Furthermore, not all the iron atoms in these two patterns were equivalent, for about 30% of the octahedral iron contributed to the tetrahedral pattern (*15*). This accounts for the *observed* I:II intensity ratio of about 2:3 in spite of the fact that a pure inverse material should show a ratio of 1:1. As will become apparent, the cation distribution is strongly dependent on the history of the sample and upon small changes in the O^{2-} and Cu^{2+} stoichiometry.

When the catalyst was simply evacuated and cooled to room temperature following a run at 435°C (samples B and C), the Mössbauer spectra showed some significant intensity changes, as may be seen in curve $CuFe_2O_4$-C in Fig. 1. The relative integrated intensity of the doublet was markedly increased (from about 1/15th of the total in the oxidized sample to about 1/2 in the reduced sample) by this treatment. However, the peak positions (see Table 1) were not significantly different in the samples B and C from those in the samples α and A.

A small pressure of O_2 remained at the end of the previous experiments. Another sample, $CuFe_2O_4$-D, was similarly treated, but this time the gas phase O_2 was completely depleted before the run was terminated and the catalyst evacuated and quenched; the spectrum corresponding to this condition is also shown in Fig. 1 with the peak positions given in Table 1. In addition to intensity changes, new peaks developed which indicated a much greater reduction than previously observed. Supporting this assessment was a color change from gray-black to reddish, and there was a copper mirror plated on the reactor wall. Apparently when the O_2 gas is removed, the bulk reduction occurs quite rapidly.

The two 6-line hyperfine patterns in sample $CuFe_2O_4$-D corresponded very closely to a spectrum of Fe_3O_4, which is the last spectrum shown in Fig. 1. This spectrum, Fe_2O_3-A, was obtained from a

TABLE 2

Fe_3O_4 MÖSSBAUER PARAMETERS AT 300°K

Ref.	Pattern	H_{eff} (kOe)	IS (mm/sec)	ΔS
(*16*)	I	500 ± 20	0.36 ± 0.10[a]	0.0 ± 0.1
	II	450 ± 20	0.61 ± 0.1[a]	0.0 ± 0.1
(*17*)	I	495 ± 20	0.31 ± 0.10[b]	0.1 ± 0.2
	II	470 ± 20	0.72 ± 0.10[b]	−0.1 ± 0.2
This study	I	490	0.41	−0.32
	II	465	0.78	−0.43

[a] Corrected to Fe^0 from ^{57}Co in stainless steel.

[b] Corrected to Fe^0 from ^{57}Co in Cr.

sample of α-Fe_2O_3 that had been partially reduced by a butene:O_2 run in which the O_2 was completely depleted before the run was terminated. Table 2 compares the Mössbauer constants for this material with those reported for Fe_3O_4 (*16, 17*); the agreement is quite good. Further evidence that the sample was indeed Fe_3O_4 is the observation that the "reduced" catalyst reacted with exactly that amount of O_2 which would be required to convert the sample from Fe_3O_4 back to the original Fe_2O_3.

Apparently the copper ferrite catalyst undergoes extensive reduction to form Cu^0 and Fe_3O_4 when the oxidizing atmosphere is removed. However, the original ferrite can be reconstituted (see curve $CuFe_2O_4$-A in Fig. 1) simply by roasting at 520°C in O_2, providing the reduction has not continued to the point that Cu^0 has been distilled from the catalyst.

The origin of the doublet in the spectra is not understood. Such doublets have been observed before and are most frequently attributed to superparamagnetism (*2–6*). However, this implies that the crystallites do not exceed a few hundred angstroms, or the effect would not be observed at room temperature (*2–6, 18*). The low surface area of the $CuFe_2O_4$ fixes the mean particle diameter at about 10 μ—three orders of magnitude too large for this effect to be important. Of course each large particle may contain many small crystallites fused together, but it is difficult to envision crystallites this small surviving the drastic reduction (~20%) and extensive bulk structural changes that obviously occurred during the oxidation–reduction cycles. This is a strong argument against the superparamagnetism explanation.

Mössbauer parameters for a number of iron oxides and oxyhydroxides that give room temperature doublets have recently been reported (*19*); however, there is no reasonable agreement between the reported parameters and our values. Furthermore, the hydroxides would be decomposed to Fe_2O_3 under the present reaction conditions (*20*), which discounts this suggestion.

Another possible origin of the doublet is metallic iron. Dilute solutions of iron in copper or copper–nickel alloys have been reported to exhibit "a number of poorly resolved lines, extending over 1 mm/sec or less, in which a 'doublet' is evident" (*21*). Metallic iron is indeed present in the extensively reduced sample $CuFe_2O_4$-D, as indicated by the two small adsorption peaks at ±5.36 mm/sec. While this may explain the doublet in the reduced sample D, it is not reasonable to assume that as much as 7% (1/15th) of the iron is present as Fe^0 in the oxidized sample A.

Still another explanation for the doublet is the formation of $CuFeO_2$ through a series of solid state reactions. Mössbauer parameters of ±0.40 mm/sec for the isomer shift and +0.32 mm/sec for the quadrupole splitting have been reported for $CuFeO_2$ at 300°K (*22*). This isomer shift value compares favorably with those determined here for the doublet. The formation of $CuFeO_2$ may be envisioned to occur through the following series of reactions:

1. Reduction of $CuFe_2O_4$

$$9CuFe_2O_4 \rightarrow 9Cu + 6Fe_3O_4 + 6O_2. \quad (3)$$

2. Reaction of additional $CuFe_2O_4$ with the produced Fe_3O_4 and the subsequent

decomposition of the product at 400°C (*23*)

$$6CuFe_2O_4 + 6Fe_3O_4 \rightarrow 12Cu_{0.5}Fe_{2.5}O_4, \quad (4)$$

$$12Cu_{0.5}Fe_{2.5}O_4 \xrightarrow{400°C} 6CuFeO_2 + 12Fe_2O_3. \quad (5)$$

3. Immediate reduction of the formed Fe_2O_3

$$12Fe_2O_3 \rightarrow 8Fe_3O_4 + 2O_2. \quad (6)$$

The net result of these reactions can be written as:

$$15CuFe_2O_4 \rightarrow 9Cu + 6CuFeO_2 + 8Fe_3O_4 + 8O_2 \quad (7)$$

A direct conversion of $CuFe_2O_4$ may also be postulated

$$3CuFe_2O_4 \rightarrow 3CuFeO_2 + Fe_3O_4 + O_2. \quad (8)$$

The conversion of an entire $CuFe_2O_4$ catalyst sample according to Eq. (7) would yield a Mössbauer spectrum showing 20% of the iron atoms in the $CuFeO_2$ doublet and 80% of the iron atoms in the Fe_3O_4 spectrum. This distribution closely matches that of sample $CuFe_2O_4$-D; however, both Eqs. (7) and (8) indicate the presence of Fe_3O_4 which is not observed in sample $CuFe_2O_4$-C.

Suffice it to say that whatever its origin, the doublet is sufficiently stable that it survives many oxidation–reduction cycles that involve considerable structural rearrangements.

Correlations with catalytic activity. As previously reported (*8*), the $CoFe_2O_4$ is difficult to reduce, and the catalytic activity is reproducible so long as there is some gaseous O_2 present. Electrical conductivity measurements have shown that the active catalyst lies near the completely oxidized state and is relatively independent of the oxygen pressure, so long as there is *some* gaseous O_2. The Mössbauer spectra reported herein also indicate that the catalyst does not change except when subjected to relatively drastic reduction conditions.

The solid state changes were much more marked with the copper ferrite, and catalytic activity apparently reflected these changes. Even after being given the standard oxidation pretreatment, a fresh catalyst sample always showed an "induction" effect. Apparently some "sensitization" of the material had to occur before it became active; unfortunately, these effects were not pinpointed by the Mössbauer work. They were likely surface phenomena, which would have gone undetected because of the low surface/bulk iron ratio. However, extensive *bulk* changes did indeed occur quite readily in the material as the catalytic conditions were altered, but the catalyst could be returned to the initial state by reoxidation.

CONCLUSIONS

These Mössbauer studies have demonstrated that rather drastic bulk alterations take place when copper and cobalt ferrites are subjected to gas mixtures during catalytic reactions. Significant reduction can occur in both catalysts if the O_2 is removed from the gas phase during OXD reactions. In the cobalt system, this results in a change in the numbers of Fe^{3+} ions in the tetrahedral and octahedral sites. In the copper ferrite, the reduction leads to Cu^0 and Fe_3O_4.

Unfortunately, it was not possible to run the Mössbauer spectra *in situ* under reaction conditions, nor was it possible to avoid exposure to air before the measurements were made. We have no way of assessing what changes may have occurred within the solids as a result of this exposure; however, we feel that the effects were not too significant because the reactions were carried out at 435°C and exposure to air occurred only after quenching to room temperature.

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