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Mössbauer Spectra of Ferrite Catalysts used in
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Abstract

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 420°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 of the reported studies have been directed towards determining the crystallite size of Fe_2O_3 supported on silica (2-5). The purpose of this work is to report the use of ^{57}Fe Mössbauer spectroscopy to explore bulk structural changes which occur in two ferrite catalysts as a result of their use in promoting oxidative dehydrogenation (OXD) of butene to butadiene. Rennard and Kehl (6) have recently used similar techniques to study other ferrite catalysts. Kinetic and isotopic tracer studies of the reaction mechanisms which occur over these cobalt and copper ferrites have been previously reported (7).

Ferrites are convenient for such investigations, since 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.

Experimental

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 powders supplied by Alfa Inorganics. A sample of $\alpha\text{-Fe}_2\text{O}_3$

(AR grade from Fisher Scientific Company, surface area $7.7 \text{ m}^2/\text{g}$) was included for comparison. Catalyst samples from 0.5 to 1.0 g were placed in a removable Pyrex reactor which 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 two hours, and (3) re-evacuation to 10^{-6} Torr. Following this treatment, the evacuated catalysts were cooled to the desired reaction temperature (usually 435°C) and then exposed to a pre-mixed trans-2-butene: O_2 mixture (usually 50:25 Torr) in the recirculation system. Samples were periodically removed by expansion for GLC analysis (7).

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. Lazer 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. Peak minima were found by visual inspection; thus an error of about $\pm 0.025 \text{ mm/sec}$ (± 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 the figure 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 (8)

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

Because the quadrupole interaction affects the position of the two extreme peaks, numbers 1 and 6, the isomer shift (IS) for each pattern is calculated as the average center line of the internal peaks 2 and 5 and peaks 3 and 4. 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) at the iron nucleus, in kOe, is calculated from equation (8)

$$H = \frac{330}{10.657} (6 - 1) \quad (2)$$

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, IS relative to iron metal, ΔS , and H for the seven samples discussed herein.

CoFe_2O_4 - Two authors (9-10) have reported the Mössbauer spectra of CoFe_2O_4 , and the results are not in complete agreement. A likely reason for 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 (11). Furthermore, it was found that 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 the original catalyst (rapid quenching) would probably lead to a random distribution of Fe^{3+} ions between the octahedral and the tetrahedral positions (11); the 2:1 intensity ratio between Pattern I and II in the starting sample bears this out. Moreover, the isomer shifts (~ 0.4 mm/sec) are indicative 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_2O_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 ($\sim 20\%$) of the Fe^{3+}

ions in octahedral sites contributing to the tetrahedral spectrum (12). It might also be due to rapid electron exchange between Fe^{2+} and Fe^{3+} in adjacent octahedral sites (13), although the constancy of the peak positions with degree of reduction tends to discount this possibility.

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 support this conclusion (7). However, when the gaseous O_2 is removed, the conductivity increases markedly, and the Mössbauer spectrum is changed. 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 ($\text{CuFe}_2\text{O}_4 - \alpha$) and of an extensively used sample which had been reoxidized at 520°C (Curve $\text{CuFe}_2\text{O}_4 - \text{A}$ in Fig. 1), were both very similar to the spectrum of the tetragonal modification of the inverse spinel material reported by Evans and Hafner (12), with one glaring exception--theirs did not show the obvious doublet near zero velocity. Both sets of spectra showed two six-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 (12). 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 O_2 gas phase 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 this case there were not only intensity changes, but also new peaks developed which indicated a much greater reduction than previously observed. Supporting this assessment was a color change from grey-black to reddish, and there was a copper mirror plated on the reactor walls. Apparently when the O_2 gas is removed, the bulk reduction occurs quite rapidly.

The two six-line hyperfine patterns in sample -D corresponded very closely to a spectrum of Fe_3O_4 , which is the

last spectrum shown in Fig. 1. This spectrum was obtained from a sample of α -Fe₂O₃ which had been partially reduced by a butene:O₂ run in which the O₂ was completely depleted before the run was terminated. Table 2 compares the Mössbauer constants for this material with those reported for Fe₃O₄ (13,14); the agreement is quite good. Further evidence that the sample was indeed Fe₃O₄ is the observation that the "reduced" catalyst reacted with exactly the amount of O₂ which would be required to convert the sample from Fe₃O₄ back to the original Fe₂O₃.

Apparently the copper ferrite catalyst undergoes extensive reduction to form Cu⁰ and Fe₃O₄ when the oxidizing atmosphere is removed. However, the original ferrite can be re-constituted (see curve CuFe₂O₄-A in Fig. 1) simply by roasting at 520°C in O₂, providing the reduction has not continued to the point that Cu⁰ has been distilled from the catalyst.

The origin of the doublet in the spectra is not understood. Such doublets have been observed before, and they are most frequently attributed to superparamagnetism (2-6). However, this implies that the crystallites do not exceed a few hundred Å⁰, or the effect would not be observed at room temperature (2-6,15). The low surface area of the CuFe₂O₄ fixes the mean particle diameter at about 10μ --three orders of magnitude too large. 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 which 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 which give room temperature doublets have recently

been reported (16). 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 (17), 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" (18). Metallic iron is indeed present in the extensively reduced sample CuFe_2O_4 -D, as indicated by the two small absorption 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. Suffice it to say that whatever its origin, the doublet is sufficiently stable that it survives many oxidation-reduction cycles which involve considerable structural rearrangement.

Correlations with Catalytic Activity - As previously reported (7), 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 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. After about one hour of relative inactivity when exposed to a butene:O₂ mixture, the reaction rate suddenly increased markedly. Additional reactions (either with or without re-oxidation between runs) on the same sample never exhibited this 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 re-oxidation.

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 O₂ is removed from the gas phase during OXD reactions. In the cobalt system, this results in a change in the occupancy ratio of Fe³⁺ in the tetrahedral and octahedral sites. In the copper ferrite, the reduction leads to Cu⁰ and Fe₃O₄.

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 since the reactions were carried out at 435°C and exposure to air occurred only after quenching to room temperature.

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REFERENCES

1. Delgass, W. N., and Boudart, M., Catal. Revs. 2, 129 (1968).
2. Hobson, M. C., Jr., and Campbell, A. D., J. Catal. 8, 294 (1967).
3. Kündig, W., Bommel, H., Constabaris, G., and Lindquist, R. H., Phys. Rev. 142, 327 (1966).
4. Kündig, W., Ando, K. J., Lindquist, R. H., and Constabaris, G., Czech. J. Phys. B17, 467 (1967).
5. Hobson, M. C., Jr., and Gager, H. M., J. Catal. 16, 254 (1970).
6. Rennard, R. J., and Kehl, W. L., J. Catal. 21, 282 (1971).
7. Cares, W. R., and Hightower, J. W., J. Catal. 22, xxx (1971).
8. Greenwood, N. N., Chem. in Britain 3, 56 (1967) and References Therein.
9. Dézsi, I., Hrynkiewicz, A. Z., and Kulgawczuk, D. S., Acta Physica Polonica 24, 283 (1963).
10. Sawatzky, G. A., Van Der Woude, F., and Morrish, A. H., J. Appl. Phys. 39, 1204 (1968).
11. Rieck, G. D., and Thijssen, J. J. M., Acta Cryst. B24, 982 (1968).
12. Evans, B. J., and Hafner, S. S., J. Phys. Chem. Solids 29, 1573 (1968).
13. Bauminger, R., Cohen, S. G., Marinov, A., Offer, S., and Segal, E., Phys. Rev. 122, 1447 (1961).
14. Ito, A., Ono, K., and Ishikawa, Y., J. Phys. Soc. Japan 18, 1465 (1963).

15. Schuele, W. J., Shtrikman, S., and Treves, D., Appl. Phys. 36 (2), 1010 (1965).
16. Terrell, J. H., and Spitjkerman, J. J., Appl. Phys. Lett. 13, 11 (1968).
17. Potvin, W. J., Jr., and Greenblatt, S., J. Phys. Solids 30, 2792 (1969).
18. Swartzendruber, L. J., and Bennett, L. H., Phys. Lett. 27A, 141 (1968).

TABLE 1

MÖSSBAUER PARAMETERS OF FERRITE CATALYSTS AT 300°K

Catalyst	6-Line Pattern	Peak Positions, mm/sec ^(a)						I.S. (a)	S	H, kOe
		1	2	3	4	5	6			
CoFe ₂ O ₄ ^{-α}	I	-8.09	-4.35	-0.86	+1.76	+5.29	+8.60	0.46	+0.42	517
	II	-7.67	-3.98	-0.51	+1.45	+4.83	+8.10	0.45	+0.41	488
CoFe ₂ O ₄ ^{-A}	I	-8.06	-4.35	-0.86*	+1.74*	+5.31	+8.61	0.46	+0.41	516
	II	-7.67	-4.03	-0.86*	+1.74*	+4.81	+8.06	0.42	+0.39	487
CoFe ₂ O ₄ ^{-B}	I	-8.08	-4.5	-0.93*	+1.66	+5.13	+8.60	0.34	+0.11	516
	II	-7.68	-4.37	-0.93*	+1.53	+4.86	+8.22	0.27	-0.05	492
CuFe ₂ O ₄ ^{-α}	I	-7.76	-4.05*	-0.94*	+1.71	+5.31	+8.64	0.51	+0.41	508
	II	-7.33	-4.05*	-0.94*	+1.37	+4.82	+8.37	0.30	-0.27	486
	Doublet			-0.04	+0.61			0.29	+0.65	
CuFe ₂ O ₄ ^{-A}	I	-7.93	-4.28*	-0.92*	1.74	5.23	8.50	0.44	+0.39	509
	II	-7.52	-4.28*	-0.92*	1.44	4.80	8.03	0.26	+0.01	482
	Doublet			+0.01	+0.68			0.34	+0.67	
CuFe ₂ O ₄ ^{-B}	I	-7.91	-4.35	-0.90*	+1.49*	+5.20	+8.01	0.36	+0.75	493
	II	-7.41	-4.11	-0.90*	+1.49*	+4.68	+7.88	0.29	+0.13	473
	Doublet			+0.01	+0.71			0.36	+0.71	

TABLE 1 (Cont'd)

Catalyst	6-Line Pattern	Peak Positions, mm/sec ^(a)						I.S. ^(a)	S	H, kOe
		1	2	3	4	5	6			
CuFe ₂ O ₄ -C	I	-7.97	-4.16*	-1.00*	+1.62*	+4.85	+8.19	0.33	+0.47	500
	II	-7.47	-4.16*	-1.00*	+1.62*	+4.68	+7.89	0.28	+0.11	475
	Doublet			-0.03	+0.66			0.32	+0.69	
CuFe ₂ O ₄ -D	I	-7.46	-4.33	-0.99	+1.42	+4.94*	+8.40*	0.26	-0.33	491
	II	-6.62	-3.65	-0.60	+1.73	+4.94*	+8.40*	0.61	-0.49	465
	Doublet			-0.05	+0.65			0.30	+0.70	
Fe ₂ O ₃ -A	I	-7.43	-4.30	-1.02	+1.46	+4.96*	+8.40*	0.28	-0.32	490
	II	-6.63	-3.62	-0.56	+1.76	+4.96*	+8.40*	0.64	-0.43	465

*Insufficient separation of peaks does not allow individual assignment to Pattern I or II.

^aRelative to Fe⁰.

TABLE 2

 Fe_3O_4 MÖSSBAUER PARAMETERS AT 300°K

Reference	Pattern	H_{EFF} (kOe)	I.S. (mm/sec)	S
7	I	500 \pm 20	0.36 \pm 0.10 ^(a)	0.0 \pm 0.1
7	II	450 \pm 20	0.61 \pm 0.1 ^(a)	0.0 \pm 0.1
8	I	495 \pm 20	0.31 \pm 0.10 ^(b)	0.1 \pm 0.2
8	II	470 \pm 20	0.72 \pm 0.10 ^(b)	-0.1 \pm 0.2
This Study	I	490	0.28	-0.32
This Study	II	465	0.64	-0.43

(a) Corrected to Fe° from ^{57}Co in Stainless Steel.

(b) Corrected to Fe° from ^{57}Co in Cr.

FIGURE CAPTION

Figure 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 420°C.

