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Oxidative Dehydrogenation of Butenes over Magnesium Ferrite

Catalyst Deactivation Studies

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Magnesium ferrite ($MgFe_2O_4$) is a moderately selective catalyst for butadiene formation from *n*-butenes via oxidative dehydrogenation (OXD). However, both the activity and selectivity decrease irreversibly as the catalyst ages, and these changes have been correlated with bulk phase solid-state changes that occur in reducing atmospheres at temperatures above 300°C. The fresh catalyst contained a 5% α-Fe_2O_3 impurity phase whose disappearance paralleled the activity/selectivity decline. These conclusions were confirmed by X-ray, Mössbauer, and magnetic susceptibility measurements. In addition, TGA (thermogravimetric analysis) experiments suggested that oxygen equivalent to about 6.4 layers could be slowly removed by evacuation at elevated temperatures in the range of 530°C. This labile oxygen is probably related to the OXD activity. A proposed deactivation mechanism attributes the loss of selectivity to an increased population of Fe^{2+} sites at the expense of Fe^{3+} sites. A process that would stabilize the Fe^{3+} population in the $MgFe_2O_4$ matrix would presumably decrease the deactivation and result in a more stable catalyst.

INTRODUCTION

In the preceding paper (*1*) isotopic tracers were used in kinetic studies to examine the mechanism of oxidative dehydrogenation of butenes to 1,3-butadiene over a magnesium ferrite catalyst. The formation of butadiene in some microcatalytic experiments in the absence of gas-phase oxygen clearly indicated the participation of adsorbed and/or lattice oxygen in the OXD reaction. As the surface becomes reduced, the activity falls to a very low value. Another observation was an irreversible decay in both the activity and selectivity for butadiene formation as a fresh catalyst sample is "aged" in successive runs. This decay suggests that bulk solid-state changes may have occurred, and the purpose of this paper is to examine these changes and relate them to the observed catalytic performance. The combination of special magnetic features and the possibility of multiple valence states of the iron atoms makes this material quite interesting from a solid-state viewpoint. Furthermore, there is a wealth of information on the solid-state properties of $MgFe_2O_4$ in the literature (*2–7*) with which these results may be compared.

EXPERIMENTAL METHODS

The catalyst, gases, and glc equipment were described in the previous paper (*1*). The techniques that were used to examine the solid-state properties include thermogravimetric analysis (TGA), magnetic susceptibility, X-ray diffraction, and Mössbauer spectroscopy. The TGA and some of the magnetic measurements were carried

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out with a Cahn RH electrobalance and an Alpha Scientific electromagnet. The balance was enclosed in an all-glass gas-handling system that could be operated as a flow, static atmosphere, or high vacuum system. The magnet, equipped with Faraday pole pieces, provided a field strength of about 3000 G at the sample. A special resistance furnace made by electrodepositing a platinum coating on a quartz tube (Instatherm, Ace Glass Co., Vineland, N. J.) fitted easily between the magnet pole pieces and produced negligible axial and transverse magnetic fields. The catalyst sample, whose temperature was measured by a fine thermocouple, was contained in a small quartz bucket suspended in the furnace's heated zone and in a constant force sector of the Faraday pole pieces.

A Philips Electronic Instruments unit provided CuK_α radiation for the X-ray diffraction analyses. Room temperature patterns were made with powdered samples in a flat plate holder. Patterns made at elevated temperatures were obtained with a Materials Research Corporation diffraction furnace that allowed control of both the temperature and contacting atmosphere.

Mössbauer spectroscopy (*8*) equipment included a laser beam-calibrated source driver (Austin Science Associates) and a 1024 channel analyzer (Ortec) with related control electronics. The ^{57}Co source was embedded in copper; its isomer shift was 0.438 mm/sec relative to sodium nitroprusside. A high vacuum furnace with beryllium windows was used as a sample holder for spectra at elevated temperatures.

Saturation magnetization versus temperature data were measured in Princeton Applied Research equipment using the vibrating sample method (*9*) and an external field of 5000 G.

Samples for the magnetic measurements, the Mössbauer spectra, and the room temperature X-ray diffraction patterns were portions of catalysts that had been previously exposed to systematically varied temperatures and atmospheres. Additional experimental details are available elsewhere (*10*).

RESULTS

Thermogravimetric Analysis Experiments (TGA)

Evacuation for varying times and temperatures was the final step in the pretreatment used for catalyst samples in the microcatalytic experiments (*1*). To determine what (if any) species may be removed during such pumping, two TGA experiments were carried out, each with a fresh catalyst sample. The first was in vacuum ($P < 10^{-5}$ Torr; 1 Torr = 133.3 N/m^2 for conversion to SI units); the second was in the presence of 760 Torr static oxygen. The use of a "blank" sample permitted appropriate corrections for buoyancy and aerodynamic forces due to natural convection in the heated zone to be made in the latter case. In both experiments the samples were heated in steps to 530°C with pauses for 15 min at several intermediate temperatures. When 530°C was reached, the sample weight was measured and continuously monitored for 15 hr while the temperature was maintained at 530°C.

In the vacuum experiment 1.20% of the catalyst weight was lost in going from 25 to 530°C; 0.78% of the weight was lost in the intermediate temperature range between 25 and 350°C. During the 15-hr isothermal treatment at 530°C, the catalyst lost about 0.04%/hr. In the second experiment in 1 atm of oxygen, no weight loss was observed either during the rising or constant temperature segments of the run.

These results suggest that oxygen is the species being removed during the evacuation, but it does not occur when oxygen is present in the gas phase. If this is the case, the weight loss during the increasing temperature part corresponds to removal of an equivalent of about 6.4 layers (based on each oxygen atom occupying 10 $Å^2$).

Magnetic Susceptibility Experiments

These measurements were made to obtain information about solid-state changes that parallel the observed changes in catalytic activity and selectivity. The temperature range used for the OXD reactions, 300–450°C, includes values reported for the Neel temperature (T_N) of $MgFe_2O_4$ (*2*). To obtain data on such a material in its fully paramagnetic state, it is necessary to operate at least 70–100°C above the Neel temperature. Since 530°C satisfies this criterion (it is 90°C higher than the highest reported value of T_N) (*2*), this was the temperature used in these experiments.

The first two runs were carried out in static atmospheres of 100 Torr consisting of 100% O_2 and 20% O_2 in helium, respectively. In both cases the paramagnetic susceptibility of the catalyst remained constant at 5.7×10^{-3} cgs units/g mol for 24 hr. This susceptibility corresponds to a value of 0.045 magnetic force units/sample weight.

In a third experiment the catalyst was heated from 25 to 530°C in a static atmosphere of 760 Torr *cis*-2-butene. When 530°C was reached, the magnetic force/sample weight ratio was 1.3, and water condensate was observed on the hangdown tube, thus indicating that reduction had occurred. Figure 1 shows how the magnetic susceptibility changes when the atmosphere is varied at 530°C from pure He, 10% *cis*-2-butene in He, He, to 20% of O_2 in He, the total pressure being 760 Torr and the flow rate about 2.5 cm^3/sec in each case. Noteworthy is the slow increase in the susceptibility when the hydrocarbon is present and the rapid return to near the original value in the presence of oxygen. Since the amount of gas present in the reactor was large, a small trace of oxygen impurity in the helium cannot be ruled out as a possible explanation for the susceptibility drop in the presence of He.

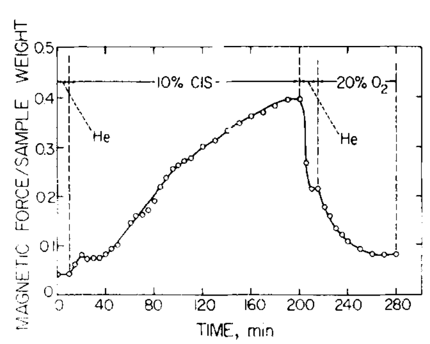

Fig. 1. Dependence of magnetic order on gas-phase composition for a fresh sample of magnesium ferrite held at 530°C.

Other experiments showed that both the rate of susceptibility increase and the highest value obtained were functions of the partial pressure of the hydrocarbon. The rate of increase was slower and the maximum value obtained was lower as the partial pressure of hydrocarbon was decreased.

X-Ray Diffraction Experiments

Phases to be considered in the Mg–Fe–O system include Mg, Fe, FeO, MgO, Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3, and $MgFe_2O_4$. Of these $MgFe_2O_4$, Fe_3O_4, γ-Fe_2O_3, and MgO all have nearly identical diffraction peak positions. This happens because the first three are all cubic spinels with almost identical lattice parameters, while magnesia belongs to the same symmetry group and has exactly half the lattice parameter of the spinels. The other phases have diffraction patterns distinct from the spinels and from each other. Thus X-ray analysis is capable of providing information about some but not all these phases.

Three types of diffraction experiments were conducted. The first type consisted of aging a catalyst in presence of a stoichiometric butene/O_2 mixture (2:1) in the recirculation reactor (*1*) for various

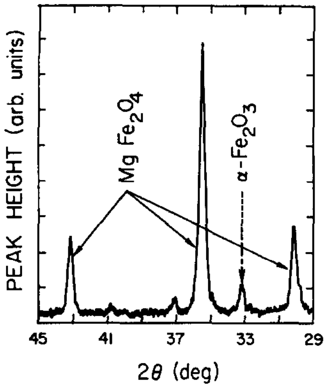

FIG. 2. X-ray diffraction pattern of fresh magnesium ferrite sample at room temperature.

lengths of time at different temperatures. After each, the catalyst was cooled to room temperature in vacuum and transferred in air to the X-ray machine where the diffraction patterns were taken. Figures 2 and 3 compare portions of spectra on a fresh sample and one that had been subjected to four 1-hr OXD runs at 350°C. The main difference between the two is the presence of a small peak at about 33° in the fresh sample. This is the strongest peak due to α-Fe_2O_3 (d = 2.70 Å) and may be compared with the strongest $MgFe_2O_4$ peak at 35.5° (d = 2.53 Å), the intensity ratio being approximately proportional to the concentration ratio of the two phases. In several other experiments where the reaction temperature (or aging time) was systematically increased, the α-Fe_2O_3 peak monotonically decreased and disappeared after about 4 hr at 350°C. These data clearly indicate that bulk solid-state changes were occurring during the reaction. No additional peaks corresponding to any phases except the spinels, MgO, and α-Fe_2O_3 were observed in any sample.

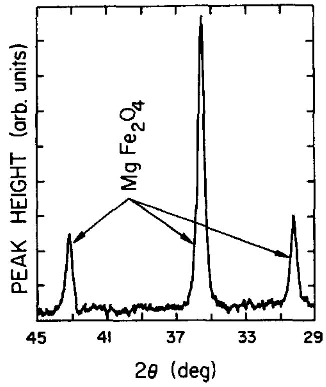

FIG. 3. X-ray diffraction pattern of deactivated magnesium ferrite catalyst after two 4-hr OXD experiments at 350°C in a recirculation reactor.

The second set of diffraction measurements were made on catalyst samples used in the magnetic susceptibility experiments in order to obtain information about structural changes accompanying the increased magnetic order during contact with butenes at 530°C. After the catalyst had been exposed to *cis*-2-butene at 760 Torr and 530°C, it was rapidly quenched in presence of the butene to room temperature before being exposed to air. The observed diffraction patterns in this and all similar experiments were similar to those in Figs. 2 and 3. No new lines appeared, e.g., due to FeO, Fe, or Mg, and all peaks could be assigned to the spinel–MgO group or to α-Fe_2O_3.

A third set of experiments consisted of *in situ* diffraction measurements using the furnace described in the experimental section. In an atmosphere of 150 Torr *cis*-2-butene, a catalyst sample was held 4 hr at 350°C, 2 hr at 400°C, and 2 hr at 500°C. X-ray scans were taken every 30 min, and the results confirmed those obtained in the previous experiments. Specifically, the α-Fe_2O_3 peak decreased systematically with exposure time at a rate that increased with temperature. Again, no new lines appeared at any temperature, indicating that FeO, Fe, and Mg were not formed as separate phases in sufficient quantity to be detected by X-ray diffraction.

Mössbauer Spectroscopy Experiments

Seven of the same samples examined by X-ray diffraction in the preceding section were also subjected to analysis by Mössbauer spectroscopy at room temperature. Typical spectra are shown in Fig. 4 (fresh catalyst sample) and in Fig. 5 (after 3 hr in 76 Torr *cis*-2-butene at 350°C). The only significant difference between the two spectra is the presence of shoulders (due to α-Fe_2O_3) on the outer peaks in the fresh catalyst; these shoulders were absent in spectra of all appropriately aged samples. As in the X-ray measurements, samples exposed to the hydrocarbon (with or without oxygen) for shorter times showed spectra intermediate between these extremes. A fresh sample that was exposed to 150 Torr of oxygen at 530°C for up to 22 hr gave a spectrum very similar to that of the fresh sample, i.e., the shoulders on the external peaks were not affected by oxygen treatment alone even at 530°C.

Attempts to obtain computer-calculated, optimum-fit Lorentzian parameters for the peak systems represented in these figures proved unsuccessful. The number of peaks (6 moderate ones for α-Fe_2O_3 and 6 or 12 strong ones for $MgFe_2O_4$) and the strong overlap between many peaks prevented convergence. Estimates of parameters were therefore made by preparing accurate computer-drawn plots of the multichannel analyzer data and utilizing the laser calibration as the velocity axis. For the ferrite spectra, the isomer shifts of all samples were in the range of 0.5–0.6 mm/sec relative to sodium nitroprusside; these values are typical of Fe^{3+} (*3*). The internal magnetic fields were estimated from the outer, broad ferrite peaks to be in the range 455–460 kG. Only in one case when the catalyst had been severely reduced in 1 atm of butene at 530°C was the internal magnetic field outside the range reported by Wieser *et al.* (*3*) for iron in octahedral and tetrahedral sites, 440 and 465 kG, respectively. The large value (476 kG) in the highly reduced sample is consistent with the large increase in the magnetic force shown in Fig. 1 as the sample became reduced.

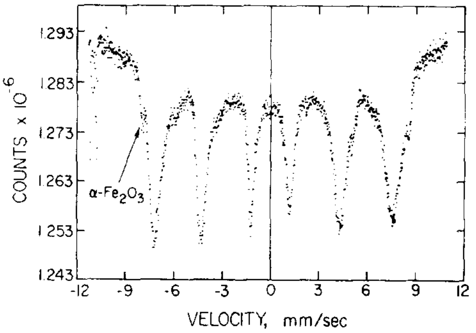

FIG. 4. Room temperature Mössbauer spectrum of fresh magnesium ferrite catalyst.

As was true in the X-ray experiments, no Mössbauer structure assignable to Fe_3O_4, FeO, or Fe appeared in any of the spectra. Of course, neither of these results precludes the possible reduction of Fe^{3+} to Fe^{2+} of Fe^0 in a thin layer on or near the surface. Only about 0.7% of the total iron was present at the surface, and this amount would not have been identified by either technique. However, bulk conversion of α-Fe_2O_3 to one of these bulk phases can be ruled out by these observations.

Magnetization versus Temperature Experiments

To supplement the room temperature Mössbauer measurements, curves of magnetization versus temperature were obtained on several catalyst samples using

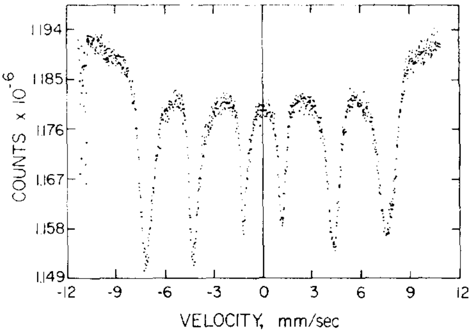

FIG. 5. Room temperature Mössbauer spectrum of deactivated magnesium ferrite catalyst after reduction for 3 hr at 350°C in 76 Torr of *cis*-2-butene.

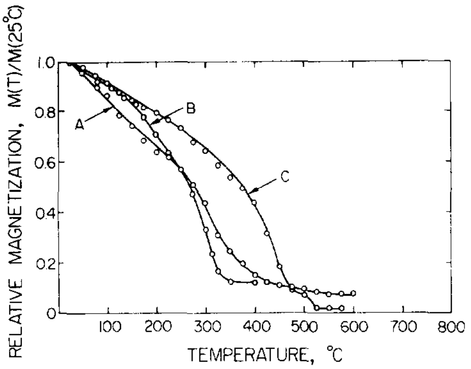

FIG. 6. Relative magnetization of magnesium ferrite after various pretreatments: Curve A, fresh catalyst; curve B, deactivated by reduction for 3 hr at 350°C in 76 Torr of *cis*-2-butene; curve C, strongly reduced for 1 hr at 530°C in 76 Torr of *cis*-2-butene.

the vibrating sample method (*9*) with a Princeton Applied Research Company instrument. The samples were maintained in a vacuum of 10 μm; the external applied field was 5000 G.

The three curves in Fig. 6 are typical of the data obtained on a virgin catalyst (curve A), after 3 hr in 76 Torr of *cis*-2-butene (curve B), and after severe reduction in 1 atm of butene at 530°C (curve C). Extrapolation of the downward breaking part of curve A gives a Curie (Neel) temperature of 325–350°C (typical of $MgFe_2O_4$), but the curve does not break sharply as expected for a pure substance, probably due to the weak parasitic ferromagnetism in the minor α-Fe_2O_3 phase ($T_N = 680°C$). The mild reduction in curve B caused a much sharper decrease in the magnetism, which extrapolates to a T_N of about 325°C. There was no evidence of a species (e.g., α-Fe_2O_3) with a higher Curie temperature. Finally, the severely reduced sample in curve C shows a much higher Curie temperature (425–450°C) than either of the two other samples, and there is a suggestion of a small quantity of material having an even higher Curie temperature. While no ready explanation is attached to this increase, it cannot be due to α-Fe_2O_3 since this phase was destroyed during the strong reduction, as confimred by both X-ray and Mössbauer analysis.

Elevated Temperature Mössbauer Spectroscopy

Mössbauer spectra of virgin and strongly reduced (530°C in butene) catalyst samples were measured at 400°C in a vacuum of about 8 μm. The samples were held between beryllium foils in a water-jacketed furnace with beryllium windows. To minimize errors due to sample oxidation, a 100-mCi ^{57}Co in Cu source was substituted for the 50-mCi source used in the room temperature experiments, and the counting times were decreased to 6–7 hr.

Figure 7 shows the spectrum of the virgin catalyst. As expected, the major magnesium ferrite phase was paramagnetic at 400°C and gave only a single broadened line centered at zero velocity. The remaining structure (four outer peaks) is due to the α-Fe_2O_3 minor phase. Supporting this is the internal magnetic field calculated from the outermost peaks to be 374 ± 10

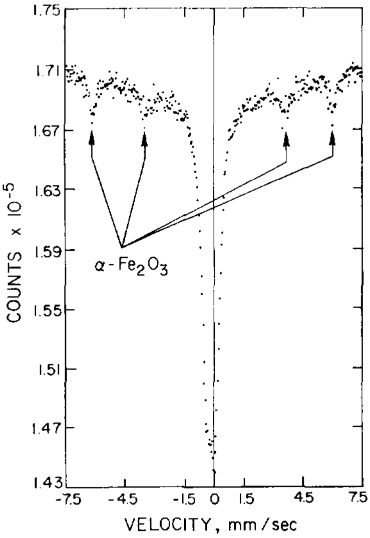

FIG. 7. Mössbauer spectrum of fresh magnesium ferrite taken at 400°C under vacuum. Arrows indicate positions of four of the six peaks due to ferromagnetic α-Fe_2O_3.

kG, which is in good agreement with literature values of 380 kG measured at 400°C (*4*, *5*). The two inner hyperfine splitting lines from the α-Fe_2O_3 are masked by the much more intense central peak from the $MgFe_2O_4$. Spectra on reduced samples not containing the α-Fe_2O_3 phase showed mainly a single broad peak at zero velocity and gave no evidence of satellite peaks that could be attributed to that species, as illustrated by Fig. 8. There was, however, a hint of a small amount of ferromagnetic material indicated by the arrows in Fig. 8 but the peak positions did not correspond to those attributed to α-Fe_2O_3 in Fig. 7.

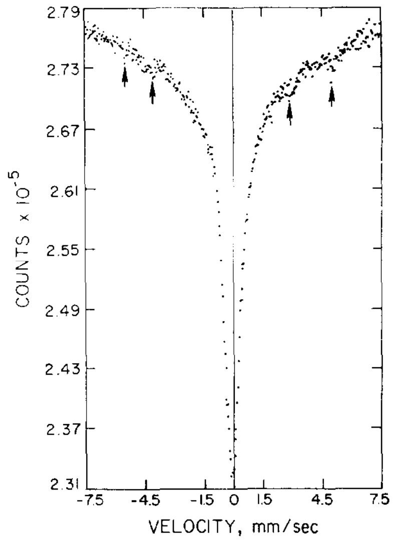

FIG. 8. Mössbauer spectrum at 400°C of deactivated magnesium ferrite after strong reduction for 1 hr at 530°C in 76 Torr of *cis*-2-butene. Arrows indicate positions of possible ferromagnetic materials remaining after (or formed during) reduction.

DISCUSSION

Based on the solid-state measurements made in this work and the data published by Aksel'rod *et al.* (*6*), a deactivation model for the $MgFe_2O_4$ catalyst may be proposed. The observed loss in selectivity is also accounted for by this deactivation process in a way that is consistent with the Rennard–Massoth mechanism (*1*, *11*). It is proposed that deactivation and selectivity loss proceed by formation of anion vacancies in layers on and just below the catalyst surface. These vacancies are not refilled by gas-phase oxygen either under reaction conditions or upon calcining in oxygen at temperatures up to 530°C, the maximum used in this work. If the accompanying reduction $Fe^{3+} \rightarrow Fe^{2+}$ takes place on octahedral sites, the process may be represented by (*6*)

$$Mg_x^{2+}Fe_{1-x}^{3+}[Mg_{1-x}^{2+}Fe_{1+x}^{3+}]O_4 - (Z/2)O \rightarrow Mg_x^{2+}Fe_{1-x}^{3+} \times [Mg_{1-x}^{2+}Fe_Z^{2+}Fe_{1+x-z}^{+3}]O_{4-z/2}\square_{z/2}.$$

Aksel'rod *et al.* (*6*) have shown by several independent methods that the vacancy-containing species above is stable as a single ferrite phase only below O^{2-} vacancy concentrations of 0.6 atomic percent. Above this value the ferrite decomposes to a spinel solid solution of Fe_3O_4 in $MgFe_2O_4$; excess Mg^{2+} cations are precipitated as a separate MgO phase. All of the anion vacancies remain in the solid solution spinel phase.

As might be expected, detection of a small quantity of anion vacancies and Fe^{2+} ions resulting from this process operating within only a few atomic layers of the catalyst surface was not possible with the techniques used. Because of this, more severe reduction (530°C, 76 Torr butene) was necessary to obtain detectable amounts of reduced material. However, in the microcatalytic experiments (*1*) with butene at 350°C, lattice oxygen was consumed which required production of Fe^{2+} ions and anion vacancies. This shows that the reduction process does occur at reaction temperatures. The crucial factors for catalyst stability appear to be maintenance of sufficient oxygen partial pressure to insure surface coverage by oxygen and/or diffusion of oxygen into the catalyst lattice.

All of the measurements made on the severely reduced catalyst are in agreement with this deactivation mode. The X-ray diffraction patterns have lines assignable only to α-Fe_2O_3 or the spinel–MgO group. The magnetic force measurements (Fig. 1) show the production of increased magnetic order at constant temperature as the reduction by butene proceeds. This is consistent with increasing concentration of Fe_3O_4 in the Fe_3O_4–$MgFe_2O_4$ solid solution because the Curie point of pure Fe_3O_4 is 585°C. The increased internal field exhibited by the highly reduced sample (Fig. 5) also points to a phase with greater magnetic order (higher Curie temperature) than the virgin catalyst.

The Mössbauer measurements at 400°C show the reduced catalyst is converted to a mixture of a small amount of magnetically ordered material (at 400°C) and a remainder of paramagnetic material. This strongly supports the idea that a small quantity of ferrite, presumably near the catalyst surface, is converted into the Fe_3O_4–$MgFe_2O_4$ solid solution whereas the remainder, not near the surface, is not reduced. The extent of reduction would be expected to vary with depth into a catalyst particle, and the Curie point of the Fe_3O_4–$MgFe_2O_4$ solid solution is a strong function of the solution composition (*6*), which is determined by the extent of reduction. Because of this, it is probably not valid to interpret the magnetization curve, "C," in Fig. 6 as produced by a well-defined mixture of two phases each with a distinct Curie point. Instead, the reduced catalyst probably consists of unreduced $MgFe_2O_4$, MgO, some single phase ferrite with anion vacancies, and a range of compositions of $MgFe_2O_4$–Fe_3O_4 solid solutions. In Fig. 6 the magnetizations of all these components are superposed. The resultant, however, shows a large increase in magnetic ordering over the virgin catalyst.

A final piece of evidence, the *in situ* electrical conductivity data of Cares and Hightower (*12*) lends support to this deactivation mechanism, although it was obtained with a different ferrite. These measurements show that low frequency (1592 Hz) conductivity of a $CuFe_2O_4$ catalyst pellet increases two orders of magnitude during a 2-hr reduction in butene at 350°C; this increase is rapidly reversed by heating at 350°C in pure oxygen. $Fe^{3+} \leftrightarrows Fe^{2+}$ electron hopping is a well-documented (*13, 14*) means of charge transport in magnetite and would serve to explain the observed increase in conductivity.

In the proposed reaction mechanism (*1*), the loss of selectivity and increased isomerization rates are natural consequences of increased population of Fe^{2+} sites at the expense of Fe^{3+} sites. High selectivity is maintained only in the presence of a high p_{O_2} such that Fe^{2+} is quickly reoxidized to Fe^{3+}.

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REFERENCES

1. Gibson, M. A., and Hightower, J. W., *J. Catal.* Previous paper (1975).
2. Goodenough, J. B., "Magnetism and the Chemical Bond." Interscience, New York, 1963.
3. Weiser, A., Povitskii, V. A., Makarov, E. F., and Kleinstuck, K., *Phys. Status Solidi* **25**, 607 (1968).
4. Freier, S., Greenspahn, M., Hillman, P., and Scheckter, H., *Phys. Lett.* **2**, 191 (1962).
5. Ono, K., and Ito, A., *J. Phys. Soc. Jap.* **17**, 1012 (1962).
6. Aksel'rod, E. I., Alapin, B. G., Vishnevsky, I. I., and Sukharevsky, B. Ya., *J. Phys. Chem. Solids* **32**, 1627 (1971).
7. Bertaut, E. F., Challeton, D., Coeure, P., and Marefchal, I., "Preparation et Etudes de Monocristaux d'Orthoferrites, Terves Rares

pour Circuits Logiques et Memoires Magnetiques." CNRS, Paris, 1970.

8. Goldanskii, V. I., and Herber, R. J. (Eds.), "Chemical Applications of Mössbauer Spectroscopy." Academic Press, New York, 1968.
9. Schieber, M. M., "Experimental Magnetochemistry," p. 135. North-Holland, Amsterdam, 1967.
10. Gibson, M. A., "Oxidative Dehydrogenation of Butenes over Ferrite Catalysts," Ph.D. thesis, Rice University, Houston, Tex., 1972.
11. Rennard, R. J., and Kehl, W. L., *J. Catal.* **21**, 282 (1971); Massoth, F. E., and Scarpiello, D. A., *J. Catal.* **21**, 294 (1971).
12. Cares, W. R., and Hightower, J. W., *J. Catal.* **23**, 193 (1971).
13. Verwey, E. J. W., Haayman, P. W., and Romeijn, F. C., *J. Chem. Phys.* **15**, 181 (1947).
14. Ito, A., Ono, K., and Ishikawa, Y., *J. Phys. Soc. Jap.* **18**, 1465 (1963).