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Ferrite Spinels as Catalysts in the Oxidative Dehydrogenation of Butenes

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Both $CoFe_2O_4$ and $CuFe_2O_4$ spinels are active catalysts for oxidative dehydrogenation of *n*-butenes to butadiene. However, both suffer from their tendency to catalyze total oxidation as well. Neither is an effective *n*-butene isomerization catalyst, even at high temperatures. Surface and lattice oxygen atoms participate in the reactions, and the steady state in the presence of gaseous oxygen, at least for $CoFe_2O_4$, is near the totally oxidized state. Selectivity for the dehydrogenation reaction is strongly dependent on the presence of gaseous oxygen in the case of the Co catalyst, although the selectivity over the Cu catalyst is not a strong function of gaseous oxygen. The kinetics are not simple; the pressure dependencies are less than first order in both butene and oxygen pressures and the reactions are inhibited by the presence of butadiene. C—H bond cleavage is probably involved in the rate-determining step of all reactions, although the reactions showed some characteristics of both inter- and intramolecular mechanisms.

INTRODUCTION

Since the early 1960's there has been much interest in the oxidative dehydrogenation and ammoxidation of mono-olefins to diolefins, aldehydes, and nitriles (*1–3*). Although most work reported in the open literature deals with the use of bismuth oxide–molybdenum oxide systems (bismuth molybdates), many pure metals, single-metal oxides, or mixed-metal oxides have also been mentioned as catalysts for these reactions. Mechanistic studies (*2, 4*) have demonstrated that the initial step is an allylic hydrogen abstraction from the olefin and that some type of oxidation–reduction reaction occurs in the catalyst structure itself (*5*). It was thought that the use of a mixed-oxide catalyst having a known crystal structure and incorporating metallic ions of variable oxidation state might lead to an effective catalyst and shed additional light on the reaction mechanism.

Various ferrite spinel structures seemed well suited for such studies, as the cation distributions in the spinels are fairly well established and the ferric ions offer the availability of a reducible cation. Moreover, one study (*6*) showed that Fe_2O_3 gives the greatest yield of butadiene from pure 1-butene of any of a group of transition metal oxides; as expected, the ferrites are active catalysts for these reactions (*7, 8*). The ferrites chosen for these studies were $CoFe_2O_4$ and $CuFe_2O_4$, both of which have an inverse spinel structure (*9, 10*). The inverse spinel structure has the $+2$ oxidation-state metal cations (Co and Cu in these cases) occupying octahedrally coordinated positions, whereas half of the $+3$ cations (Fe) occupy octahedrally coordinated positions while the other half of the $+3$ cations occupy tetrahedrally coordinated positions.

EXPERIMENTAL

The samples of cobalt ferrite and copper ferrite were obtained from Alfa Inorganics and were their normal commercial preparations. Both were used as black powders. Surface areas of the ferrites were deter-

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mined by the BET technique with CH_4 at −195°C (CH_4 area taken as 16.0 Å^2). Specific areas are: $CoFe_2O_4$, 2.0 m^2/g; $CuFe_2O_4$, 0.12 m^2/g. The zinc aluminum spinel (69 m^2/g) was a preparation kindly supplied by Esso Research and Engineering Laboratory; the fine, white, homogeneous powder was used as supplied.

Small amounts of catalysts were placed between glass wool plugs and sealed into a glass reactor which was then attached to a high-vacuum recirculation system having a volume of 382 ml. Each catalyst sample was given the following initial pretreatment at 520°C: (1) evacuation to 10^{-6} Torr, (2) treatment with a circulating, 77°K trapped O_2 stream for 2 hr, and (3) re-evacuation to 10^{-6} Torr. The temperature of the reactor was then lowered to the desired reaction temperature where the catalysts were usually treated with O_2 for 10 min, followed by evacuation, before admission of the premixed reactants. After each experimental run, the catalyst sample was normally "reactivated" by O_2 treatment either at 520°C or at reaction temperature. The reactor contained a thermocouple well to enable continuous monitoring of the catalyst temperature on a potentiometric, stripchart recorder. Temperature rises measured in this manner are necessarily minimum values, as any transient temperature increases must be transmitted through the glass wall of the thermocouple well.

Dried O_2 was used for both the activation of the catalyst samples and as reactant. All butene samples (Phillips Research Grade) were subjected to several freeze at 77°K-pump-thaw cycles before being used as reactants.

The gas chromatographic system consisted of a $\frac{3}{8}$-in. × 25-ft column of 25% propylene carbonate on $^{80}/_{100}$ mesh AW Chromosorb W thermostatted at 0°C, a Gow-Mac JDC-133 detector, and a Hewlett–Packard Model 7100 BR recorder with a Disc integrator. A second recorder pen measured the output from a thermocouple positioned in the catalyst bed. Analyses of carbon-containing components were based upon C_4 equivalents (i.e., using only one-fourth of the observed CO or CO_2 peak areas). Percentage compositions reported for carbon-containing components are based upon a carbon material balance only, whereas percentages of oxygen reported are based upon the entire reacting mixture.

Deuterium exchange studies of the reactions were carried out with perdeuterio-*trans*-2-butene prepared in our laboratory (*11*). The individual butene isomers were trapped at 77°K as they emerged from the chromatograph and were analyzed for deuterium content on a CEC 21-104 mass spectrometer operated at low ionizing voltage. The usual fragmentation and C-13 corrections were made.

Electrical conductivity measurements were conducted in the reactor shown in Fig. 1. The catalyst samples were prepared by packing a short length of fritted glass tubing with an aqueous slurry of the cobalt ferrite catalyst. Platinum gauze electrodes, to which platinum lead wires had been welded, were positioned at each end of the tube and held in place with additional catalyst paste. The pellet assembly was allowed to dry in air for several days; it was then installed in the reactor where it was activated by the same procedure used for the powdered catalyst samples. The platinum leads issuing from the reactor assembly were connected to a Wayne–Kerr Universal Bridge, Model B221A, which operated at 1592 Hz. Conductance measurements were made by manually balancing the bridge. Tests on a fully oxidized, a fully reduced, and a moderately reduced cobalt ferrite pellet showed identical ac and dc resistances throughout the temperature range of the catalytic experiments.

For all types of experiments, the reaction mixtures were prepared by pressure measurements on a Texas Instruments Model 141 Servo Pressure Gauge; they were thoroughly mixed before being introduced to the catalyst at time $t = 0$. Samples were periodically removed for glc analysis by expansion into a doser. Usually a stoichiometric butene:O_2 = 2:1 mixture was used. A sample of the initial mixture was first taken for chromatographic analysis before the reaction mixture was diverted over the

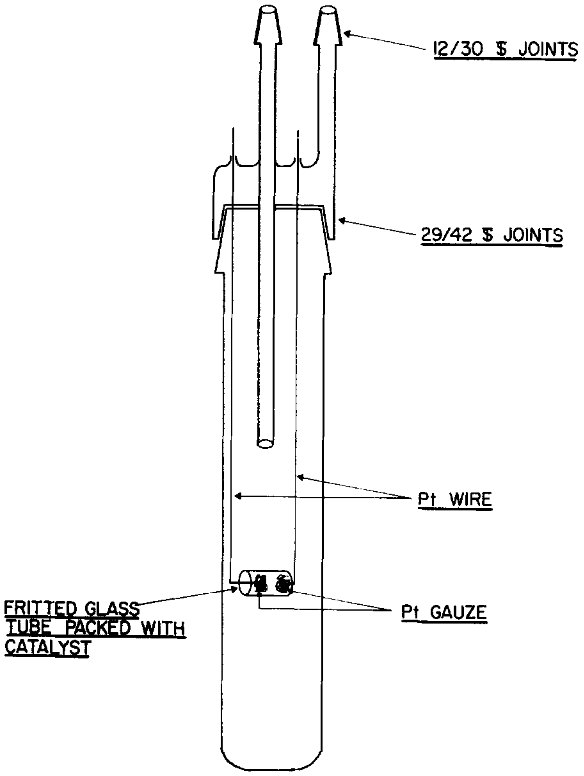

FIG. 1. Reactor assembly for electrical conductivity measurements.

catalyst sample. A trap thermostatted at 0°C in the recirculation loop allowed the vapor pressure of water, produced in the reaction, to increase from zero at zero time to a maximum of about 4.6 Torr.

RESULTS

Cobalt Ferrite

Reactions in the Recirculation Reactor System

Four samples of $CoFe_2O_4$, designated $CoFe_2O_4$-A–D weighed 0.54, 0.10, 1.00, and 0.50 g, respectively; the reactants were usually butene:O_2 = 100:50 Torr mixtures. The reactions were normally slow, lasting from 30 min to a few hours. Isomerization to other *n*-butenes, partial oxidation to butadiene, and oxidation to CO and CO_2 were the only reactions observed in the temperature range 300–530°C. As the temperature increased, the selectivity for the various products varied such that the ratio (partial oxidation)/(total oxidation) and the ratio (isomerization)/(oxidation) both decreased. At 400°C the partially oxidized products about equalled the butene suffering total oxidation, and the isomerization products were considerably less than the oxidized products at any given reaction time.

Direct kinetic measurements were difficult to obtain for several reasons. First, a significant temperature rise (usually a few degrees Centigrade) occurred when the reactants were first admitted to the catalyst. However, the temperature returned to its initial value within a few minutes. No attempt was made to moderate this exotherm by addition of an inert gas. Second, there was extensive poisoning by the product butadiene, as addition of 16% butadiene to a standard reaction mixture at 360°C decreased the rates of all reactions by about a factor of 8. Third, the partial pressure of water varied in the reactor system from zero to 4.6 Torr before becoming constant. The effect of water in this pressure range was, however, not investigated. Finally, explosion hazards limit the butene:O_2 ratio which may be safely employed.

Despite these experimental difficulties, certain qualitative observations can be made regarding the reaction orders. An initial O_2:butene = 10:50 Torr mixture was allowed to react over $CoFe_2O_4$-B at 360°C until the rate became slow (there was still considerable O_2 present in the gas phase). More O_2 (10 Torr) was added to the reacting mixture after 1 hr and again after 2 hr; the results are shown in Fig. 2. The breaks in the curves indicate that the reaction is somewhat greater than zero order in oxygen. Other experiments (see Fig. 3) indicated a reaction order also less than unity in butene, while there is an inverse order effect of the butadiene partial pressure. The isomerization is *cis* selective, as the initial *cis*/*trans* ratio from 1-butene is about 1.8.

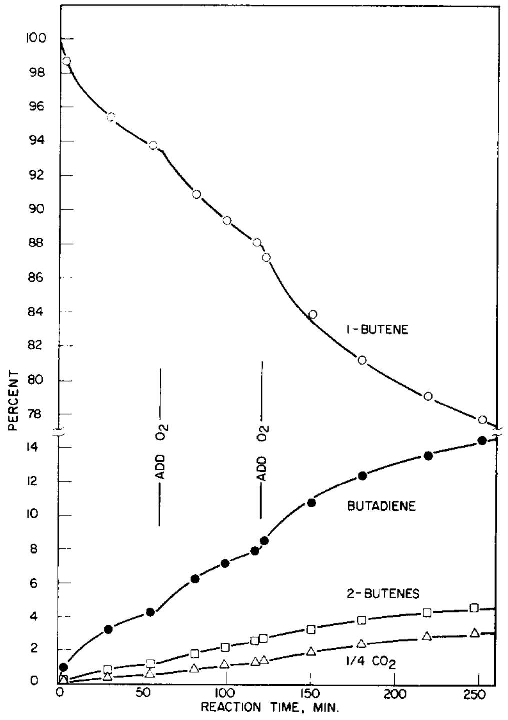

FIG. 2. Periodic addition of 10 Torr O_2 to a 10 Torr O_2/50 Torr 1-butene reactant mixture over 0.10 g $CoFe_2O_4$ at 360°C.

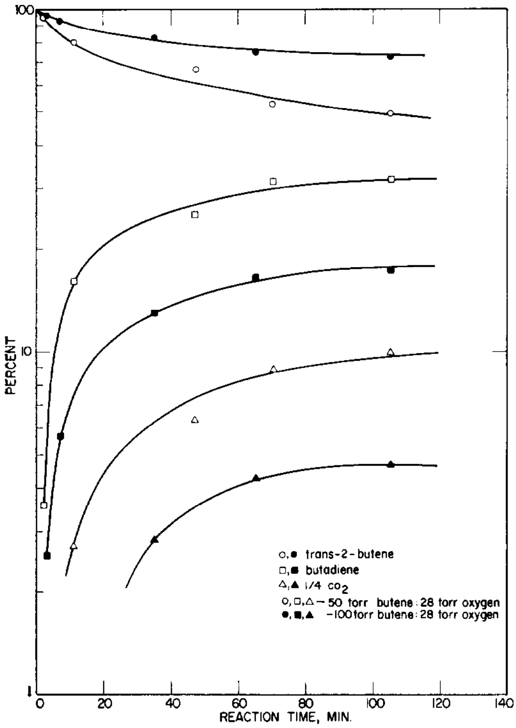

FIG. 3. Reactivities of 50 Torr *trans*-2-butene/28 Torr O_2 and 100 Torr *trans*-2-butene/28 Torr O_2 mixtures over 0.50 g $CoFe_2O_4$ at 436°C.

During regeneration with oxygen between experiments, a large exotherm was observed in the catalyst bed, presumably due to removal of a carbonaceous residue and/or reoxidation of the partially reduced catalyst. Accumulation of CO_2 in the recirculation trap thermostatted at 77°K provided evidence for the former.

Copper Ferrite

The reactions of *trans*-2-butene were studied at 435°C over three different 0.5-g $CuFe_2O_4$ samples. Unlike the $CoFe_2O_4$ catalysts, the first experimental run over each $CuFe_2O_4$ showed an induction period before significant reaction was observed (see Fig. 4). The induction period was not observed on subsequent experimental runs on the $CuFe_2O_4$ samples following reactivation.

Figure 5 illustrates the typical results for the reaction of a 50 Torr *trans*-2-butene/28 Torr O_2 mixture on a reactivated

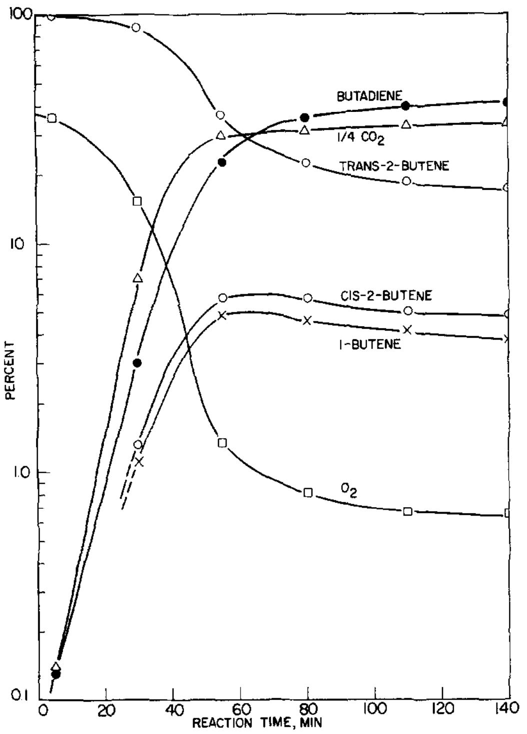

FIG. 4. Induction period observed on reaction of a 50 Torr *trans*-2-butene/28 Torr O_2 mixture over 0.50 g of fresh $CuFe_2O_4$ at 435°C.

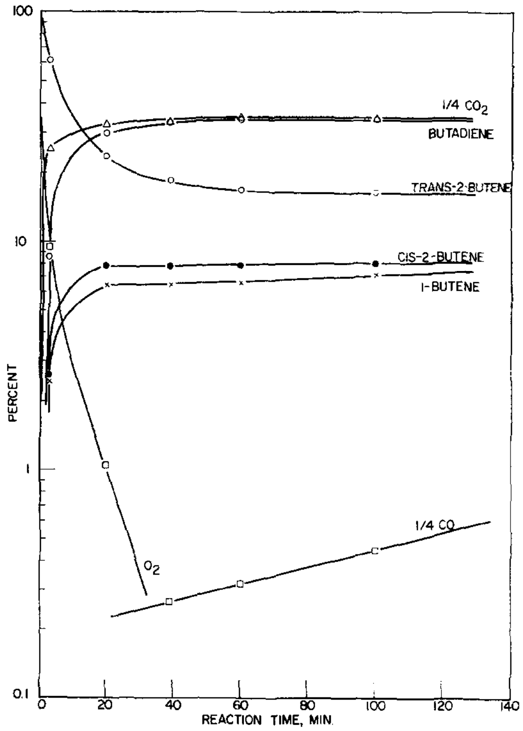

FIG. 5. Reactivity of a 50 Torr *trans*-2-butene/28 Torr O_2 mixture over 0.50 g of reactivated $CuFe_2O_4$ at 435°C.

$CuFe_2O_4$ sample. The 1-butene and *cis*-2-butene products of this reaction are produced in equilibrium amounts at all times (*12*).

Figure 6 illustrates the reaction of 50 Torr *trans*-2-butene with the reactivated catalyst sample, but without any added oxygen gas. The initial rate of *trans*-2-butene disappearance is very similar to the rate shown in Fig. 5, where O_2 gas is present. Also, the initial rate of formation of each product from the *trans*-2-butene reactant is similar in the two cases. The absence of gas-phase oxygen becomes evident only after the reaction has proceeded to a considerable extent. Total oxidation of the *trans*-2-butene becomes less important while partial oxidation to butadiene becomes the dominant reaction; the isomerization reaction also increases in importance and actually exceeds that of the reaction with gas-phase oxygen.

In contrast to these reactions on a fully oxidized $CuFe_2O_4$ sample, the results of the reaction of a 50 Torr *trans*-2-butene/27 Torr O_2 on a reduced $CuFe_2O_4$, i.e., a $CuFe_2O_4$ sample which had not been reactivated following an experimental run, are shown in Fig. 7. In this case much less reaction occurs and the initial reaction rates are less than those on the oxidized catalyst with or without gaseous oxygen. The loss of oxygen from the reaction mixture, however, is faster than that for the oxidized sample. The fact that the CO_2 yield for the reduced catalyst is much less than that for the oxidized catalyst indicates that the faster loss of oxygen is not due primarily to the combustion of a carbon residue from the reduced catalyst.

Zinc Aluminum Spinel (ZAS)

The ZAS sample isomerized 1-butene to *cis*- and *trans*-2-butene at room temperature but it did not catalyze the oxidative dehydrogenation reaction. Increasing the reaction temperature to 265°C caused total oxidation of the butenes to CO_2, but no

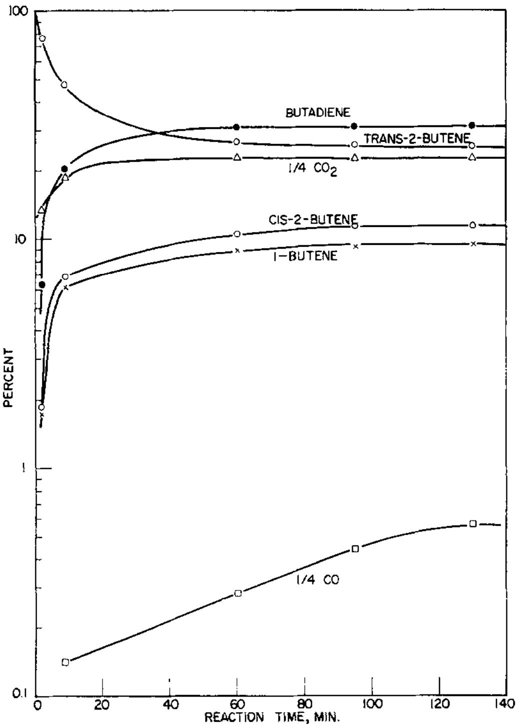

FIG. 6. Reactivity of 50 Torr *trans*-2-butene over 0.50 g of reactivated $CuFe_2O_4$ at 435°C.

partial oxidation product, butadiene, was detected. At room temperature the isomerization was highly *cis* selective, and the product ratios strongly resembled the ratios obtained under similar conditions with γ-, η-Al_2O_3 (*13*).

Deuterium-Exchange Studies in Trans-2-Butene Oxidation

The distribution of deuterium in the product butadiene and butenes was investigated over both $CoFe_2O_4$ and $CuFe_2O_4$ at 435°C. Approximately 25 Torr each of *trans*-2-butene, perdeuterio-*trans*-2-butene and O_2 were reacted over each reactivated catalyst in the circulation reactor system. Table 1 gives the deuterium distributions observed for the initial *trans*-2-butene reactant and for the products over $CoFe_2O_4$-D and $CuFe_2O_4$ catalysts.

For the butenes the average number of hydrogen/deuterium atoms exchanged per molecule can be expressed by the equation (13) where N_i represents the mole fraction

$$\text{atoms exch/molecule} = \sum_{i=0}^{3} iN_i + \sum_{i=4}^{8} (8-i)N_i - C,$$

of each isotopic species containing i deuterium atoms. This formulation assumes that all product molecules containing three or fewer deuterium atoms originated from the d_0 species; all containing more than four deuterium atoms originated from the d_8

TABLE 1

TRACER RESULTS DURING OXIDATION OF *trans*-2-BUTENE d_0, d_8 MIXTURES

Species	% by gc	Isotopic composition (%)								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
$CoFe_2O_4$[a]										
Initial *trans*-2-Butene	100.0	49.9					0.2	2.0	12.9	35.0
Product *trans*-2-Butene	63.6	40.3	0.2				0.1	1.9	14.6	42.8
cis-2-Butene	3.2	55.0	3.6				0.4	3.9	15.0	22.0
1-Butene	1.2	58.9	5.9	0.1			0.6	4.9	15.8	13.8
Butadiene	23.2	69.3	1.3	0.1		0.6	6.5	22.2		
$\frac{1}{4}$ CO_2	8.8									
$CuFe_2O_4$[a]										
Initial *trans*-2-Butene	100.0	57.2					0.1	1.5	11.3	29.9
Product *trans*-2-Butene	53.6	38.1	0.8	0.0			0.2	2.4	16.0	42.4
cis-2-Butene	3.9	50.8	8.2	0.4		0.1	1.3	7.0	19.3	12.8
1-Butene	3.5	50.5	9.7	0.5	0.1	0.1	1.3	7.3	19.1	11.5
Butadiene	10.2	64.5	5.3	0.4	0.3	1.9	8.9	18.8		
$\frac{1}{4}$ CO_2	28.8									

[a] Catalyst weight, 0.50 g; reaction temperature, 435°C, $P_{d_0} = P_{d_8} = P_{O_2} = 25$ Torr.

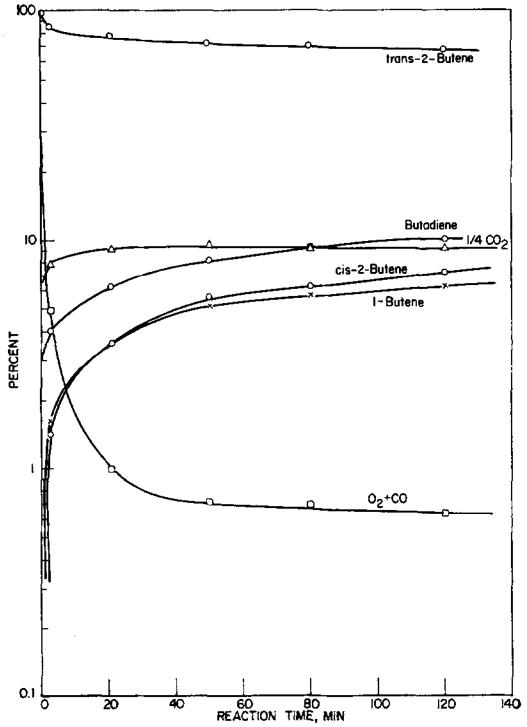

FIG. 7. Reactivity of a 50 Torr *trans*-2-butene/27 Torr O_2 mixture over 0.50 g of nonreactivated $CuFe_2O_4$ at 435°C.

material. Those with four deuterium atoms were assumed to stem equally from both directions. The C term represents a correction for the d_5, d_6, and d_7 species present in the original perdeuterio starting material. The correction term C was calculated by the equation

$$C = \left[\sum_{i=4}^{8} (8-i)N_i\right]_{\text{reactant}} \frac{\left[\sum_{i=4}^{8} N_i\right]_{\text{product}}}{\left[\sum_{i=4}^{8} N_i\right]_{\text{reactant}}}.$$

Thus, it represents a correction useful in relating the total amount of heavy material in the product to that in the reactant. Isotope effects may be estimated from the relative reactivities of the light and heavy species as judged from the ratio of light material,

$$\sum_{i=0}^{3} N_i + \tfrac{1}{2}N_4,$$

to heavy material,

$$\sum_{i=5}^{8} N_i + \tfrac{1}{2}N_4,$$

in the products and normalized to the similar ratio for the reactants. The average isotope effect for formation of all products may be obtained from the light/heavy ratio of the reacted *trans*. For the butadiene product, the isotope effect may be estimated from the ratio of light-to-heavy material in the product

$$\left[\tfrac{1}{2}N_3 + \sum_{i=0}^{2} N_i\right] \bigg/ \left[\tfrac{1}{2}N_3 + \sum_{i=4}^{6} N_i\right].$$

This formulation assumes that the d_3 material comes equally from the light and heavy starting materials. This ratio must also be normalized to the light-to-heavy ratio of the starting butene. The calculation of the average number of hydrogen/deuterium atoms exchanged per molecule of butadiene formed is more difficult due to the loss of two hydrogens/deuteriums from the molecule. The formula,

$$\text{atoms exch/molecule} = \sum_{i=0}^{2} iN_i + \sum_{i=3}^{6} (6-i)N_i - C_2,$$

which is analogous to that for the butenes, may be used. The form of the correction term C_2 is uncertain; however, its value may be estimated fairly accurately as lying between two limits. For $C_2 = 0$ an upper limit is obtained for the number of exchanged atoms/molecule. Alternatively,

$$C_2 = \left[\sum_{i=4}^{8} (8-i)N_i\right]_{\text{reactant}} \times \frac{\left[\tfrac{1}{2}N_3 + \sum_{i=4}^{6} N_i\right]_{\text{butadiene}}}{\left[\sum_{i=4}^{8} N_i\right]_{\text{reactant}}}$$

should give a lower limit to the exchange since the observed isotope effect will cause a slight increase in the mole fractions of the heavy species in the product, thus making the $[\frac{1}{2} N_3 + \Sigma_{i=4}^{6} N_i]$ term greater than it should be, relative to that term of the reactants. Perhaps a more correct method for evaluating the number of atoms exchanged per molecule in the butadiene is to calculate the expected deuterium distribution in the butadiene by statistical methods using the known distribution of the starting butene and the isotope effect found above for the butadiene formation. Such a calculation leads to a value of atoms exchanged per molecule which is to be expected if no actual exchange occurs, that is, to a value for C_2. Values reported for butadiene are calculated by this latter method.

It is possible to calculate the amount of carbon dioxide which has been formed from light and heavy reactant from a material balance on the H and D atoms. The ratio of CO_2 from light material to that from heavy material gives an isotope-effect value for CO_2 production. These isotope-effect values were 1.4 for the $CoFe_2O_4$ and 4.5 for the $CuFe_2O_4$ on a total basis or 1.04 and 1.18, respectively, on a per hydrogen removed basis. Table 2 gives the values of the isotope effects observed and the corrected values of the number of atoms exchanged per molecule.

TABLE 2

Isotope Effects and Hydrogen Exchange During Oxidation of *trans*-2-Butene d_0, d_8 Mixtures

Catalyst[a]	Products	Isotope effect	Atoms exchanged per molecule
$CoFe_2O_4$	*trans*-2-Butene	2.0	—
	cis-2-Butene	1.4	0.13
	1-Butene	1.9	0.11
	Butadiene	2.4	0.02
	CO_2	1.4	
$CuFe_2O_4$	*trans*-2-Butene	2.7	—
	cis-2-Butene	1.1	0.33
	1-Butene	1.1	0.36
	Butadiene	1.8	0.20
	CO_2	4.5	

[a] Catalyst weight, 0.50 g; reaction temperature, 435°C; $P_{d_0} = P_{d_8} = P_{O_2} = 25$ Torr.

Electrical Conductivity Studies of $CoFe_2O_4$

Figure 8 represents the ac electrical conductivities measured through a $CoFe_2O_4$ catalyst held in a porous glass cylinder during (a) its reaction with 52 Torr *trans*-2-butene, (b) its reoxidation with a 77°K trapped 108 Torr O_2 stream, and (c) its reaction with a 49 Torr *trans*-2-butene/24 Torr O_2 stream. Such data are typical of results obtained on this "pellet"; the shapes of the curves are reproducible. Since the exact pellet geometry is not known, only absolute conductivity readings are reported. The conductivity values observed for the totally oxidized pellet following each of several reaction cycles vary by about ±25% of the average absolute reading; however, this variation is small when compared with the order of magnitude changes that are observed upon performing reduction–oxidation reactions over the catalyst. Prolonged reduction of the pellet with *trans*-2-butene led to a conductivity of about 62 mmho after 4 day's reaction time. The energy gap for a reduced pellet, $\sigma = 11.8$ mmho at 420°C, was found by fitting conductivity vs temperature data to the equation

$$\sigma = A \exp\left[-E/2kT\right]$$

The value of 0.30 eV was determined for E. For the fully oxidized pellet a value of 0.65 eV was observed.

DISCUSSION OF RESULTS

It is not surprising that the zinc aluminum spinel is not an active catalyst for the oxidative dehydrogenation of butene to butadiene. This immediately suggests that the spinel structure itself is not a sufficient criterion for catalytic activity and that the presence of a reducible cation is necessary for partial oxidation. Neither Zn^{2+} nor Al^{3+} is easily reducible, whereas Fe^{3+} can be readily reduced to Fe^{2+}. This reduction of Fe^{3+} to Fe^{2+} by butene in a Fe_2O_3 catalyst has recently been confirmed by the authors through the use of Mössbauer spectroscopy. Investigations of other

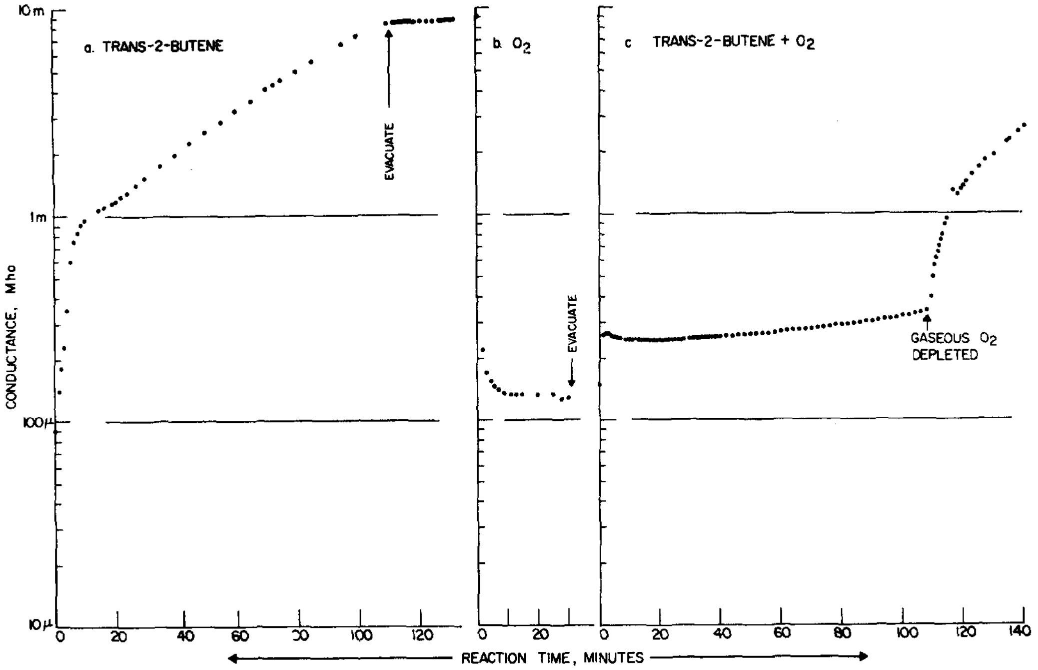

Fig. 8. Electrical conductivities measured at 416°C through a $CoFe_2O_4$ "pellet" during its sequential reaction with (a) a 52 Torr *trans*-2-butene stream, (b) a 77°K trapped, 108 Torr O_2 stream, and (c) a 49 Torr *trans*-2-butene/24 Torr O_2 stream.

ferrites (e.g., $MgFe_2O_4$) are currently underway in our laboratories.

The kinetics of the *n*-butene reactions over both cobalt and copper ferrites are not simple. Strong inhibition of the reactions by butadiene is indicated. Figure 2 suggests that the dependence of the oxidation rates on the oxygen concentration is close to zero, yet definitely not zero. The similarity of the initial loss of butene shown in Figs. 5 and 6 (one with, the other without gaseous O_2) indicates that the catalyst oxygen has a major effect on the reaction rates, whereas the gas-phase oxygen may serve only in reoxidizing the catalyst itself. The much lower reaction rates shown in Fig. 7 (reduced catalyst) confirm this participation by catalyst oxygen and that gas-phase oxygen serves to reoxidize the reduced catalyst.

The copper ferrite is about 10 times more active on a weight basis and about 170 times more active on a surface area basis than is the cobalt ferrite. However, the selectivity of the oxidation reaction to butadiene is much poorer on the copper ferrite. Additionally, the isomerization of the starting *trans*-2-butene over the copper ferrite yields the equilibrium ratio of *cis*-2-/1-butenes, whereas over cobalt ferrite there is a small preference for forming 1-butene over the *cis* isomer. The greater reducibility of the copper ion relative to the cobalt may be the major factor in the difference in activity of the two catalysts.

The electrical conductivity study of the cobalt ferrite shows that a definite steady state of the catalyst exists during the oxidative dehydrogenation reaction. This steady-state conductivity indicates a partial reduction of the catalyst to a level which is relatively close to its fully oxidized state. For example, if one assumes an empirical linear dependence of conductivity on degree of reduction (the true situation may be much more complicated than this, cf. (*14*)), a rough estimate of the steady-state reduction can be calculated. Based on a conductivity of 100 μmho for a fully oxidized pellet and 62 000 μmho for a catalyst reduced as completely as possible with *trans*-2-butene, one obtains a value of only 0.2% reduction in the steady state which showed a conductivity of 250 μmho.

The correspondence between the ac and dc conductivities indicates that the measurements represent mainly effects of the surface boundary layers of the particles.

The shape of the conductivity vs time plot in Fig. 8a seems to indicate a fast reaction of butene with the surface oxygen of the $CoFe_2O_4$ followed by a slower reaction with oxygen located deeper in the particles. Figure 8b shows that reoxidation of the reduced catalyst with pure oxygen is quite fast. Superposition of the data of Figs. 8a and 8b yields a point of intersection of the two graphs at about 200 μmho. This point could then be predicted as the approximate steady-state conductivity that would be observed if a butene–oxygen mixture had been added to the reactor. The steady-state conductivity of about 250 μmho shown in Fig. 8c confirms this prediction. The break point of the conductivity-time curve at about 800–900 μmho shown in Fig. 8a may represent the point where surface oxygen is completely removed. If that is true, the steady state observed during reaction at 250 μmho indicates that the catalyst *surface* is about 20% reduced at its operating steady state. Somewhat similar studies (*15*) have been carried out during propylene oxidation over bismuth molybdate.

The co-reaction of normal and perdeuterio-*trans*-2-butene can lead to information concerning the nature of the reaction. Isotope effects observed for butadiene and butene production over cobalt ferrite are higher than those observed over the copper ferrite; values range from about 1.4 to 2.4 vs 1.1 to 1.8. On the other hand, values found for the number of atoms exchanged per molecule are lower on the cobalt than on the copper ferrite; the values range from 0.02 to 0.13 and from 0.20 to 0.36, respectively. Neither catalyst showed any exchange into the reactant *trans*-2-butene. If each isomerization reaction were accompanied by the exchange of one hydrogen atom, then for the 1:1 light-to-heavy-reactant mixture used, the value of 0.5 would be expected for the number of atoms exchanged per molecule as one-half of the reactions would be between like molecules, which would produce no observable exchange. The exchange of ca. 0.34 molecules into both *cis*-2- and 1-butene over $CuFe_2O_4$ may indicate two separate reaction pathways. The first pathway involves an intermolecular hydrogen exchange, whereas the second pathway involves an intramolecular mechanism. The relative importance of the two routes would be about 2 to 1. Over the $CoFe_2O_4$, the isomerization reaction proceeds by a predominantly intramolecular path. Butadiene is produced with essentially no hydrogen exchange over $CoFe_2O_4$, whereas over $CuFe_2O_4$ about two-fifths of the molecules have undergone exchange. The hydrogen exchange into the butadiene over the more active $CuFe_2O_4$ may take place *after* the actual butadiene formation reaction through a subsequent scrambling reaction.

Assuming that there is a difference in activation energy for hydrogen vs deuterium containing species of about 1 kcal/mole, the observed isotope effects may be approximately corrected to room-temperature isotope effects. These room-temperature isotope effects are in the range of 4–5 for product formation over $CoFe_2O_4$ and 3–4 over $CuFe_2O_4$. These values indicate a primary isotope effect over both catalysts, and that C—H bond cleavage is probably involved in the rate-determining step. An allylic hydrogen abstraction is in agreement with these data, as previously reported for propylene oxidation on bismuth molybdate or on cuprous oxide (*2*). The isotope effect per hydrogen removed for the butadiene (1.6 on $CoFe_2O_4$ and 1.3 on $CuFe_2O_4$) indicates that the removal of each hydrogen could be a slow step in the reaction pathway. The sequential removal of hydrogen atoms may also be indicated by the total isotope effects observed over each catalyst for carbon dioxide formation. The value of 1.36 over $CoFe_2O_4$ could be accounted for by a single hydrogen abstraction. The value of 4.54 over $CuFe_2O_4$ appears to be high; its determination is subject to the compounding of errors in the individual analyses and may be as low as 2.3, which would again be reasonable for a single hydrogen abstraction. The average isotope effects observed in the disappearance of the *tran*-2-butene reactant also leads to a primary effect that is compatible with a hydrogen removal in the rate-determining step.

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