

Oxidative Dehydrogenation of Butenes over Magnesium Ferrite Kinetic and Mechanistic Studies

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Deuterium and ¹⁴C-labeled isotopic tracers were used in kinetic experiments to study the oxidative dehydrogenation (OXD) of *n*-butenes to 1,3-butadiene over a MgFe₂O₄ catalyst in the temperature range 300–400°C. The OXD reaction is approximately zero order in O₂ when O₂ is in excess, and it is near first order in butene when the partial pressure of the hydrocarbon is relatively low. OXD occurs even in the absence of gaseous O₂ over an oxidized catalyst, but the reaction becomes quite slow when the surface is reduced. Use of [¹⁴C]butadiene confirmed that both butene and butadiene are directly oxidized to CO₂ and water. Large kinetic isotope effects ($k_H/k_D \sim 2$) indicate that both OXD and *n*-butene isomerization involve C–H cleavage in the rate-limiting step, but there is no H/D scrambling in the product molecules when the butene reactant is an equimolar mixture of C₄H₈ and C₄D₈. Most of the observations can be accounted for by a modified Rennard–Massoth mechanism involving an oxidation–reduction cycle between Fe²⁺ and Fe³⁺ with C₄H₇, C₄H₆[–], and OH species on the surface.

INTRODUCTION

Magnesium ferrite is a member of the spinel ferrite class of catalysts effective for the oxidative dehydrogenation (OXD) of hydrocarbons containing four to six carbon atoms. Its first use for this process was reported in a patent granted to Bajars, Croce, and Gabliks (1). Since then a number of studies (2–7) have been reported that deal with kinetics and mechanisms of the several reactions that occur over ferrites, and some of them have been aimed at improving the selectivity and extending the activity maintenance for desired reactions.

Over most ferrite catalysts there are three principal reactions: OXD to 1,3-butadiene, overoxidation to CO and CO₂,

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and isomerization of the olefin reactants. Considering these three reactions, the work described herein has three primary objectives: (a) to examine the kinetics and reaction order of OXD and carbon oxide formation; (b) to define more precisely the surface reaction mechanisms on MgFe₂O₄ by use of deuterium and ¹⁴C-labeled compounds; and (c) to determine the extent to which catalyst lattice oxygen participates in both OXD and carbon oxide formation.

EXPERIMENTAL

The magnesium ferrite was used as received from the Columbian Carbon Co. It had a particle size of approximately 100 mesh and a BET surface area of 7.1 m²/g, which did not change appreciably during any of the experiments described in this study. Its phase composition

as determined by X-ray diffraction, Mössbauer spectroscopy, and elemental analysis was about 90% MgFe_2O_4 , 5% $\alpha\text{-Fe}_2\text{O}_3$, and 5% MgO . Various pretreatments were employed as will be discussed later.

The research grade butene isomers and butadiene were kindly supplied by the Phillips Petroleum Co. Each was distilled from -78 to -195°C before use. Cylinder oxygen (99.9% pure) was passed through a trap at -78°C before use. Helium (99.995% pure) was used without further purification as a glc carrier gas. When used as a carrier stream in the microcatalytic experiments, the helium was further purified by passage through a heated quartz thimble.

The deuterium-labeled reagent was prepared by exchange of C_4H_8 over an alumina catalyst (8); the separated *trans*-2-butene isomer had an isotopic composition of about 13 mol% $\text{C}_4\text{D}_7\text{H}$ and 87 mol% C_4H_8 . The radioactive 1,3-butadiene was labeled with ^{14}C in the 1 and 3 positions. Purchased from Mallinckrodt Nuclear, Orlando, Fla., it had a specific activity of 1.6 mC/mmol. Before use it was purified by three fractionations in a preparative-scale propylene carbonate glc column at 0°C .

The kinetic, deuterium-label, and ^{14}C -label experiments were carried out in a Pyrex recirculation loop with a total volume of 382 cm^3 . A magnetically driven pump provided the circulation. The experiments without gas-phase oxygen were conducted in a dual-stream microcatalytic system (9). Butene pulses from a 2.39-cm^3 doser (7.74×10^{16} molecules/Torr reactant pressure in the doser, where 1 Torr = 133.3 N m^{-2} for conversion to SI units) were swept over the catalyst in a stream of ultrapure helium at a measured flow rate. Reaction products were trapped at -195°C , vaporized by heating, and diverted into a second He stream for glc analysis. In both systems reaction temperatures were maintained with a muffle

furnace powered by a proportional temperature controller. Both reactors were connected to an all-glass, high vacuum gas handling system; liquid nitrogen traps protected the catalyst from contamination by mercury.

Component analyses were provided by gas chromatographic columns packed with 25% propylene carbonate on 60–80-mesh Chromosorb W and thermostated at 0°C . Deuterium distribution data for each compound were obtained by trapping the component at -195°C as it eluted from the glc column, removing the gaseous He, and expanding the sample into a CEC 21-104 mass spectrometer. Specific activities in the ^{14}C experiments were measured by counting each compound separately in a Nuclear-Chicago Ultrascaler ratemeter for which appropriate dead times corrections had been made. The counter was separated by a thin mica window from the sample container, and specific activity values were expressed as counts per minute per Torr in the sample container.

Further details of experimental procedures are contained elsewhere (10).

The isotopic compositions of butadiene and of each *n*-butene isomer were determined for each sample. The methods and assumptions of Hightower and Hall (11) and of Cares and Hightower (6) were used to calculate approximate isotope effects and the amount of exchange (or H/D scrambling) that occurred during both isomerization and OXD. Their procedures were also used to correct the data for small amounts of d_7 present in the perdeuterated *trans*-2-butene reactant. The calculated isotope effects are averaged over light and heavy fractions; no attempt was made to calculate relative rates for reaction of each d_i species.

RESULTS

General Behavior

Several experiments were carried out in the recirculation reactor to examine the

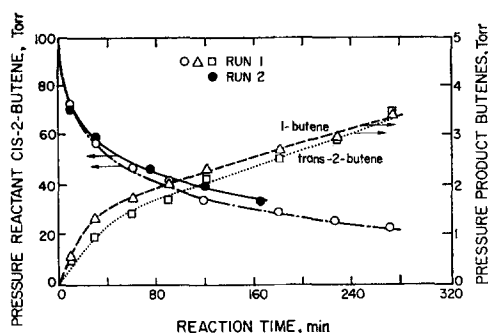


Fig. 1. Disappearance of reactant *cis*-2-butene and formation of other *n*-butene isomers during OXD over a 0.5 g of MgFe_2O_4 catalyst at 360°C . Two consecutive runs were made on a fresh catalyst with an oxygen pretreatment between them.

kinetic sensitivity to changes in gas composition, temperature, and catalyst weight. The performance was strongly dependent upon the pretreatment given the catalyst, and the selectivity for butadiene formation decreased as the catalyst sample was aged in consecutive runs.

Figures 1 and 2 compare results obtained using a 0.5-g sample of fresh catalyst for two successive runs. In each case the reaction temperature was 360°C , and the initial reaction mixture contained 100 Torr *cis*-2-butene and 100 Torr O_2 (twice the stoichiometric amount required for OXD). Before being contacted with the $\text{O}_2\text{-C}_4\text{H}_8$ mixture prepared for each run, the catalyst was pretreated for 1 hr in recirculating O_2 at 150 Torr and 525°C , evacuated 1.5 hr at the same temperature, and cooled to reaction temperature. While carbon dioxide production (and, hence, O_2 consumption) was faster on the used catalyst, butadiene production was markedly slower in Run 2. This means the selectivity for butadiene had decreased in the second run. As can be seen in Fig. 1, the rate of *n*-butene isomerization was quite slow. After over 70% of the *n*-butenes had disappeared in reaction 1, less than 25% of the remaining *cis*-2-butene reactant had become isomerized. Furthermore, the rates of double-bond migration

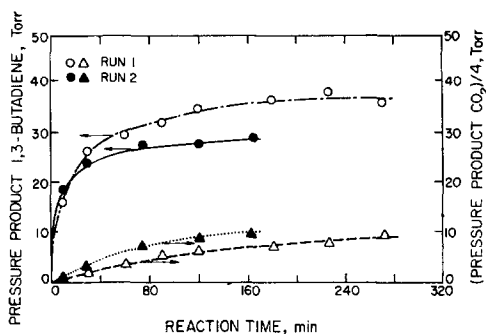


Fig. 2. Formation of 1,3-butadiene and CO_2 during OXD of *cis*-2-butene over 0.5 g of MgFe_2O_4 catalyst at 360°C . Two consecutive runs were made on a fresh catalyst with an oxygen pretreatment between them.

(1-butene formation) and *cis-trans* rotation (*trans*-2-butene formation) were comparable even though the thermodynamic equilibrium favors formation of the *trans* isomer by three to one over the 1-butene isomer. The slow isomerization rate continued even after the OXD and total oxidation reactions essentially stopped when the O_2 partial pressure became quite low.

Similar experiments at 300 and 400°C yielded comparable results. The selectivity decline was faster at the higher temperatures, and at a given temperature it declined more rapidly as the butene/oxygen ratio was increased.

Reaction Orders

The reaction orders were estimated from a series of experiments carried out at the same temperature in which the initial partial pressures and reaction times were varied over a catalyst sample that had been aged to a constant activity level; the results are shown in Table 1. For a given reaction time the conversion of *n*-butenes was independent of O_2 partial pressure (which was always in large excess with O_2 conversion being always less than 5%) from 400 to 800 Torr; this indicates zero order in oxygen. The selec-

TABLE 1

Reaction Order Determination of OXD and Total Combustion of *cis*-2-Butene over MgFe_2O_3 at 300°C^a

Initial oxygen: <i>cis</i> -2-butene (Torr:Torr)	Butene conversions (%)	Reaction time (min)	1,3-Butadiene partial pressure (Torr)	Carbon dioxide partial pressure (Torr)
400:20	32.1	15	2.6	2.0
800:20	33.3	15	2.6	2.1
600:20	54.3	30	6.7	6.2
800:20	54.6	30	6.7	5.8
600:20	53.8	30	7.0	6.0
800:20	56.4	30	6.8	5.6

^a Recirculation system, catalyst mass = 0.500 g. Initial pretreatment: 1 hr, 520°C, 150 Torr O_2 , followed by 1 hr evacuation at 520°C.

tivity was also not affected by changes in the initial pressure of O_2 , which implies zero order for the total combustion reaction as well. Analytical sensitivity limitations at low olefin concentrations and problems with catalyst poisoning at high olefin partial pressures made it difficult to obtain reliable conversion data at different initial olefin partial pressures. However, the increase in conversion from 15 min (32.7% \pm 0.6) to 30 min (54.8% \pm 1.5) is exactly what would be expected from a *linear* dependence on butene partial pressure, although inhibition by product butadiene (12) could also account for this result if the butene order were less than first. Without considering this possibility, it appears that the reaction is approximately zero order in oxygen and probably near first order in butene. It should be pointed out, however, that as the oxygen partial pressure becomes quite low, the rate may in fact become dependent upon the pressure since the data in Fig. 1 indicate that the OXD reaction became quite slow *before* all the O_2 had been consumed.

Effect of Pretreatment

Table 2 summarizes data from a set of recirculation experiments at 350°C each with a stoichiometric mixture containing

100 Torr *cis*-2-butene and 50 Torr O_2 . The same catalyst sample (0.250 g) was used throughout, and the experiments were conducted in the order listed. The first column describes the pretreatment given the catalyst before each run. Following each pretreatment the catalyst was evacuated to 10^{-5} Torr and brought to reaction temperature. The butene conversions, selectivities, and 1,3-butadiene yields were all taken after 30-min reaction time. Selectivity is defined as

$$\text{Selectivity} = \frac{P_{\text{butadiene}}}{P_{\text{butadiene}} + \frac{1}{4}P_{\text{CO}_2}} \quad (1)$$

and the yield is simply the product of the selectivity and the fractional conversion. Both the activity (percentage of conversion) and selectivity for butadiene showed their highest values for the fresh catalyst. Even relatively severe pretreatments such as lengthy heating in O_2 at 530°C could not restore these values. In fact, there was some indication that too strong O_2 treatment was actually detrimental to the performance. This was confirmed by pretreating a fresh catalyst sample for 1 hr (instead of 15 min as given the fresh catalyst in Table 1) at 530°C in 150 Torr O_2 ; after a 30-min reaction time the conversion was 19.6% and the selectivity was

TABLE 2
Effect of Pretreatment on Performance of MgFe₂O₄
during OXD of *cis*-2-Butene at 350°C*

Pretreating conditions	Overall conversion (%)	Selectivity (%)	Butadiene yield (%)
Virgin catalyst, 150 Torr O ₂ , 530°C, 15 min	24.2	92.4	22.4
No pretreatment	22.3	78.4	17.5
No pretreatment	22.4	74.3	16.7
150 Torr O ₂ , 530°C, 1 hr	18.0	83.8	15.1
150 Torr O ₂ , 530°C, 1 hr	19.1	81.4	15.5
150 Torr O ₂ , 530°C, 2 hr	18.8	79.3	14.4
150 Torr O ₂ , 350°C, 1 hr	21.1	74.0	15.6
150 Torr O ₂ , 530°C, 1 hr	19.3	77.8	15.0
150 Torr O ₂ , 530°C, 12 hr	13.5	82.8	11.1

* Recirculation system, catalyst mass = 0.250 g. Initial mixture: 100 Torr *cis*-2-butene, 50 Torr oxygen. Reaction time = 30 min.

91%. Both these values are lower than those obtained for the first run in Table 2.

Deuterium-Label Experiments

To test for intermolecular exchange of hydrogen atoms and for kinetic isotope effects, experiments were carried out at 300, 350, and 400°C with mixtures of perdeuterated and undeuterated *trans*-2-butene and a stoichiometric partial pressure of O₂, e.g., C₄H₈:C₄D₈:O₂ = 50:50:50 Torr. Table 3 contains the isotopic composition of each of the reactant and product hydrocarbons from the run at 300°C. The OXD reaction was essentially complete within a few hours (due to depletion of gaseous O₂ caused by formation of CO₂ and H₂O), but the mixture was circulated over the 0.25-g catalyst sample for 23 hr to allow the *n*-butene isomerization reaction to proceed far enough for

accurate isotopic analysis of the product isomers. It is clear from the data that essentially no intermolecular H/D exchange occurred in either the OXD or the *n*-butene isomerization reactions. Rapid exchange would have produced statistical isotopic distributions similar to the binomial distributions calculated for an H/D ratio of unity shown in the last two lines. Instead of such a distribution showing a maximum at *d*₄ (species with four D atoms) for the butenes (or *d*₃ for butadiene), the observed distributions were completely free of the intermediate deuterated products for all the hydrocarbons.

The data in Table 3 also indicate that both the OXD and isomerization reactions involved kinetic isotope effects. The ratio of lightweight (*d*₀- $\frac{1}{2}$ *d*₄) to heavy ($\frac{1}{2}$ *d*₄-*d*₈) molecules decreased in the unreacted *trans*-2-butene (from 1.15 initially to 0.81), whereas all of the products have higher lightweight/heavy ratios than were present in the reactant. Both of these facts indicate that the lightweight molecules reacted more rapidly than did the heavy molecules.

Similar results were obtained at 350 and 400°C. There was almost no intermolecular H/D scrambling, and relatively large kinetic isotope effects were obtained at all temperatures. Table 4 summarizes data from averages of several analyses at each temperature where the "isotope effect," i.e. the *k*_H/*k*_D ratio, was calculated by the equation of Cares and Hightower (6), viz. for isomerization,

IE_{isom}

$$= \frac{(\sum_{i=0}^3 N_{ip} + \frac{1}{2}N_{4p}) / (\sum_{i=5}^8 N_{ip} + \frac{1}{2}N_{4p})}{(\sum_{i=0}^3 N_{ir} + \frac{1}{2}N_{4r}) / (\sum_{i=5}^8 N_{ir} + \frac{1}{2}N_{4r})}, \quad (2)$$

where *N*_{*i**p*} is the mole fraction of a product isomer containing *i* D atoms and *N*_{*i**r*} is

TABLE 3
Isotopic Analysis of Products from Reaction of $\text{C}_4\text{H}_8:\text{C}_4\text{D}_8:\text{O}_2$ over MgFe_2O_4 at 300°C^a

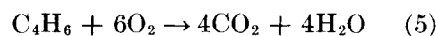
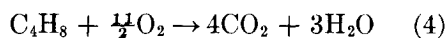
Component	Mole percent								
	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
<i>Trans</i> -2-butene									
(reactant)	53.5	0.0	0.0	0.0	0.0	0.0	0.0	6.9	39.6
<i>Trans</i> -2-butene	45.3	0.0	0.0	0.0	0.0	0.0	0.0	7.2	47.5
1-Butene	69.8	0.0	0.0	0.0	0.0	0.0	0.0	6.0	24.2
<i>Cis</i> -2-butene	60.6	0.0	0.0	0.0	0.0	0.0	0.0	6.5	32.9
1,3-Butadiene	74.7	0.0	0.0	0.0	0.0	2.4	22.9	—	—
Binomial distributions for initial H:D = 1:1									
Butenes	0.39	3.12	10.95	21.9	27.4	21.9	10.95	3.12	0.39
Butadiene	1.56	9.37	23.45	31.25	23.45	9.37	1.56	—	—

^a Recirculation system, catalyst mass = 0.250 g. Pretreatment: 1 hr, 520°C , 150 Torr O_2 , followed by 1-hr evacuation at 520°C .

the mole fraction of remaining reactant that contains i D atoms. A similar expression can be written for the OXD reaction, only the product has six H or D atoms instead of eight. Note that in Table 4 the isotope effects decrease as the reaction temperature is increased, and at each temperature the butadiene (product of OXD) has the largest IE, followed in order by 1-butene (product of double-bond migration) and *cis*-2-butene (product of *cis-trans* rotation). The near absence of H/D exchange indicates that all reactions proceed through intramolecular pathways involving only one butene molecule, but all reactions involve C-H cleavage to some degree in the rate-determining step.

Carbon-14 Tracer Experiments

Experiments designed to test whether the CO_2 was formed through butadiene as an intermediate or directly from the *n*-butene involved the use of a trace of ^{14}C -labeled butadiene in mixture with *trans*-2-butene (100 Torr) and O_2 (50 Torr). The reactions were carried out in the recirculation batch reactor, and aliquots were periodically separated by glc and the components individually analyzed for radioactivity. The specific activity of each was expressed as counts per minute per Torr pressure in the counting chamber. The four reactions tested in these experiments are



Since no radioactivity appeared in any of the butene isomers, the last reaction could not have occurred to any measurable extent. The first three reactions, however, could have occurred, and schematically

TABLE 4

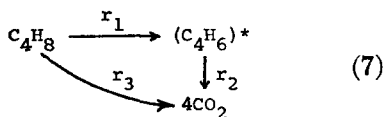
Isotope Effects during OXD and Isomerization of *trans*-2-Butene- d_0 , d_6 in O_2 over MgFe_2O_4

Reaction temperature ($^\circ\text{C}$)	1,3-Butadiene		1-Butene		<i>cis</i> -2-Butene	
	IE ^a	At. Exch. ^b	IE	At. Exch.	IE	At. Exch.
300	3.9	0	2.4	0.02	1.6	0.01
350	2.9	0	2.3	0.02	—	—
400	2.6	0	1.8	0.03	1.3	0.01

^a IE calculated from Eq. (2).

^b At. Exch. refers to the number of H or D atoms exchanged intermolecularly per molecule during the OXD or isomerization reactions.

they can be condensed into the network



where the various r 's represent the intensive reaction rates (independent of any kinetic assumptions) for each pathway. If the starting mixture contains n -butene and a trace of labeled butadiene, the specific activities of the butadiene and CO_2 ($a_{C_4H_6}$ and a_{CO_2}) will change as the reaction proceeds and can be used to determine the relative reaction rates at each point during the reaction. The specific activity of the butadiene will decrease monotonically with time, but the specific activity of the CO_2 will go through a maximum if neither r_2 nor r_3 is zero; this is exactly what was observed in Fig. 3. It has been shown (13) that the maximum in a_{CO_2} is related to the reaction rates at that point by the equation

$$r_2/(r_2 + r_3) = 4a_{CO_2}/a_{C_4H_6}. \quad (8)$$

The data shown in Fig. 3 give a ratio of $r_2/r_3 = 1.5$. Thus, the CO_2 is formed both from the butene reactant and from the product butadiene. After about 50% con-

version of the butene, the two reactions r_2 and r_3 are occurring at about the same rates. If both reactions were first order in hydrocarbon partial pressures (although this assumption may not be strictly valid) and of the same order in O_2 concentration, the constant for butadiene oxidation would be about double that for butene oxidation at this temperature since the partial pressures of the hydrocarbons are about 30 and 50 Torr, respectively, after this reaction time (see Fig. 1).

OXD in a Microcatalytic Reactor with No Gaseous Oxygen

During OXD the extracted hydrogen atoms combine with oxygen to form water. To test whether the oxygen comes from the oxide lattice or directly from the gas phase O_2 , pulses of butene were passed over a catalyst sample in a microcatalytic reactor using helium as the carrier gas. Formation of butadiene would indicate participation of the lattice (or adsorbed) oxygen. The 0.5 g of catalyst was thermostated at $350^\circ C$, and each pulse contained 1.16×10^{19} molecules of *trans*-2-butene. Each series of experiments was conducted with a fresh catalyst sample that had been treated for 1 hr at $520^\circ C$ in 760 Torr of flowing O_2 and then evacuated for different lengths of time at $520^\circ C$ before being exposed to the flowing He stream.

The results are shown in Fig. 4 where the ordinate indicates number of molecules of products that were recovered from each pulse. The open symbols describe data obtained after $520^\circ C$ evacuation for 30 min; the filled symbols give the butadiene formed after a $520^\circ C$ evacuation for 7 hr. In no case was CO_2 observed in the products. The evacuation time was the only difference between the two runs. Since no gaseous O_2 was present, the OXD had to involve adsorbed and/or lattice oxygen. During the 10 pulses after the 30-min evacuation, a total of about 2.7×10^{19} molecules of butadiene was formed.

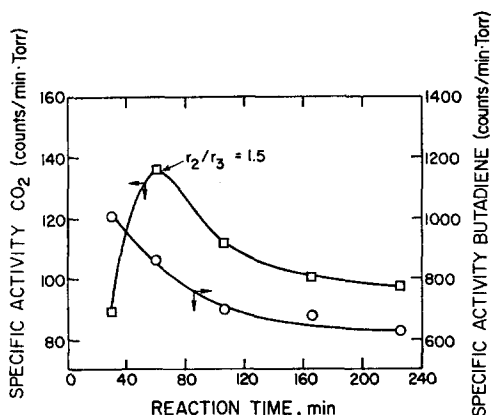


Fig. 3. Specific activity of CO_2 and butadiene during OXD of *trans*-2-butene (containing a trace of $[^{14}C]$ butadiene) over 0.25 g of $MgFe_2O_4$ at $350^\circ C$.

Assuming an oxide surface with each oxide ion occupying 10 \AA^2 , the surface could accommodate about 3.5×10^{19} oxide ions. Thus, well over half a monolayer of oxygen atoms could have been removed from the surface as the catalyst was reduced by the butene, and the activity decreased with each successive pulse as oxygen was depleted. However, the activity did not fall absolutely to zero, but instead continued at a low value for many more pulses than are shown in the figure. This may indicate that a slow bulk diffusion of oxide ions kept the surface partially supplied with active oxygen species. The more stringent evacuation used in the second run probably accounts for the lower activity since it presumably removed more of the active surface oxygen ions.

Relative to OXD, the *n*-butene isomerization reaction was much faster in the microcatalytic reactor where O_2 was absent than it was in the recirculation reactors where O_2 was present.

DISCUSSION

While the batch recirculation reactor was not ideally suited for determinations of reaction orders, the qualitative findings that the OXD reaction was zero order in O_2 and first order in butene concentration agree with some literature data on similar catalysts. Rennard *et al.* (3) have shown that OXD is zero order in oxygen over ferrites, but they also found it was zero order in olefin. However, their olefin partial pressures were greater than those used in these experiments, and this may account for the difference in the two findings. Over Bi/Mo catalysts the OXD reaction was reported by Schuit and co-workers (14, 15) and by Zimin *et al.* (16) to be first order in butene concentration. Sterrett and McIlvried (12) used a nine-parameter Langmuir-Hinshelwood rate equation to fit their data over a zinc-chromium ferrite catalyst.

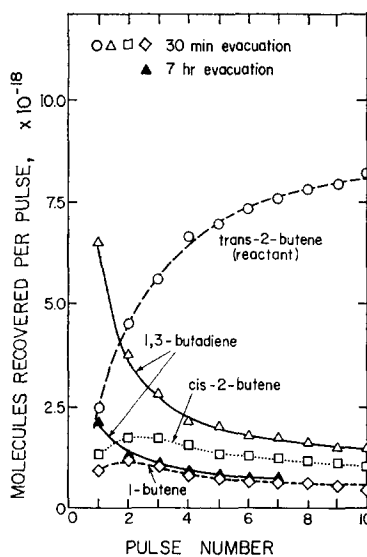


FIG. 4. Products formed during passage of successive pulses of *trans*-2-butene (1.16×10^{19} molecules/pulse) over 0.5 g of MgFe_2O_4 in a microcatalytic reactor at 350°C .

The zero-order oxygen dependence observed is also supported by the electrical conductivity measurements of Cares and Hightower (6) on cobalt ferrite. As long as there was even a small partial pressure of O_2 , the conductivity was low. When the O_2 completely disappeared, the surface became rapidly reduced by the hydrocarbon, and the conductivity increased markedly. The fact that no CO_2 was formed in the absence of gaseous O_2 implies that total combustion depends to some degree on O_2 concentration, at least at low O_2 pressures. However, with large excess of O_2 (see Table 1) the selectivity appeared to be independent of O_2 , which means that total combustion as well as OXD must be zero order in O_2 under these conditions. Additional work in more appropriate flow reactors will be necessary to define completely the kinetics, including the effects of reaction products on the rates.

The mechanism proposed by Rennard and Kehl (3) and by Massoth and Scarpello (2) for OXD on ferrites and Cr-

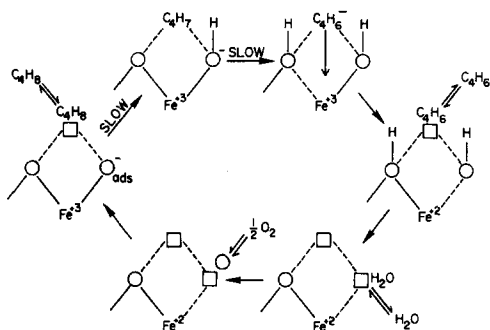


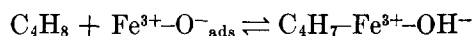
FIG. 5. Modified Rennard-Massoth mechanism for OXD over MgFe_2O_4 .

substituted ferrites can be modified somewhat to explain most of our observations. In Fig. 5 the butene adsorption site is postulated to be an anion vacancy (\square). Oxygen is regarded as adsorbed onto another anion vacancy in the form of a radical ion O^- , although no direct evidence for the existence of O^- was reported by Rennard (3) or Massoth (2). To support this postulate they cite a discussion by Rideal (17) and the fact that if lattice O^{2-} replaces O^- in the mechanism, an unreasonable two-step reduction in iron valence must occur. Hydrogen abstraction is regarded as occurring in two steps. The first is homolytic and produces a C_4H_7 allyl fragment π -bonded to the Fe^{3+} ion and an OH^- group. The second is heterolytic, H^+ attaching to the lattice O^{2-} and leaving a C_4H_6^- - Fe^{3+} complex. This complex dissociates with reduction of the Fe^{3+} to Fe^{2+} and desorption of butadiene. The hydroxyl groups combine to give water and regenerate the lattice O^{2-} and the exposed active center, Fe^{2+} , associated with two anion vacancies. Reoxidation of Fe^{2+} to Fe^{3+} occurs when gas-phase oxygen is rapidly adsorbed as O^- , thus completing the cycle.

This mechanism by itself does not necessarily demand any particular kinetics. Whether the reaction orders are zero or first or inverse depends on the relative strengths of adsorption and the rate-

limiting steps. Adsorption of O_2 must be rapid enough to maintain the surface essentially covered with the O^- species to explain the zero-order dependence on O_2 . Unless the partial pressure of olefin is high, the surface is probably sparsely covered with adsorbed butene if the reaction is linear in butene concentration. It would not be surprising to see inhibition by product butadiene at high diolefin partial pressure, but this has not been carefully investigated by us. Others (12) have found such inhibition over similar catalysts.

The observation that *n*-butene isomerization occurs more rapidly in the absence of gaseous O_2 than with O_2 present agrees with the results Rennard and Kehl (3) obtained over ZnCrFeO_4 . Since their catalyst prerduced with H_2 gave the same isomer yield as one pretreated with O_2 , they concluded that isomerization by reversal of the butene adsorption step



could be excluded since O^-_{ads} (and probably also Fe^{3+}) would be at very low concentrations on the reduced surface. Isomerization must then occur by butene adsorption on a reduced (Fe^{2+}) site even in the presence of gas-phase oxygen. At such a site only the first homolytic hydrogen abstraction may occur if the iron valence is not to be reduced below Fe^{2+} . Readdition of hydrogen then completes the isomerization.

The deuterium distribution data provide additional insight into the mechanism. The rather large isotope effects (over 2 at 400°C) approach the maximum one would expect if C-H rupture completely dominates the rate-limiting step. Similarly, C-H cleavage is strongly involved in the isomerization reactions as well, even though neither double-bond migration nor *cis-trans* rotation results in exchange of H and D atoms between molecules. If an H atom is separated from the hydrocarbon

skeleton during isomerization, the same atom must be returned to the molecule upon completing of the reaction. Absence of intermediate deuterated products in Table 3 implies that both the adsorbed H/D species and the adsorbed hydrocarbon skeleton are immobile on the surface at these reaction temperatures. This is consistent with the proposed mechanism which requires both H atoms to be strongly bonded as hydroxyl groups within the same active center. It also requires each allyl fragment to be associated with only one iron atom. Direct evidence for the $\text{C}_4\text{H}_7\text{-Fe}^{3+}$ or C_4H_7^- complexes has not been presented for this catalyst, although there is considerable evidence for allyl fragments being π -bonded to other catalysts (2, 3, 14, 15, 18-21).

The ^{14}C experiments have established that CO_2 is formed directly from both butene and product butadiene and that these two steps have similar rates when the reactant partial pressures are comparable. Carbon dioxide formation was significantly increased when the catalyst was reduced. On the other hand, neither CO_2 nor CO was formed in the absence of gas-phase oxygen. Based on the same reasoning as in the case of isomerization, the majority of butene molecules oxidized to CO_2 appear to be those adsorbed on Fe^{2+} sites where OXD is not possible. Since butadiene on either type of site may only desorb or react to CO/ CO_2 , a similar conclusion about it cannot be drawn. Evidently, adsorbed butene and butadiene are oxidized to CO_2 by reaction with gas-phase oxygen or adsorbed oxygen originating in the gas phase and not by reaction with lattice oxygen. The fact that CO_2 formation was observed to be zero order in O_2 at high partial pressures strongly supports the adsorbed oxygen source as opposed to the gas-phase oxygen source.

An essential difference in behavior between MgFe_2O_4 and the Cr-substituted

ferrites resides in the carbon dioxide formation steps. On the Cr-substituted ferrites a carbonaceous deposit was formed in the absence of gas-phase oxygen, while no such formation was observed with the MgFe_2O_4 . This deposit reacted with water in a water-gas-shift reaction to form a small amount of CO_2 even in the absence of gas-phase oxygen (3). No bulk reduction of Rennard and Kehl's catalyst occurred. Clearly, a similar process does not take place on MgFe_2O_4 since no CO_2 is formed without gas-phase oxygen. This points out the considerable resistance to catalyst bulk reduction conferred by Cr substitution.

Another paper will discuss the solid state changes that occurred during OXD over the MgFe_2O_4 .

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