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Catalytic Properties of Iron Oxide. III. Oxidative Dehydrogenation of Butenes over Iron Oxide Catalysts

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Oxidative dehydrogenation of butenes was investigated by use of a flow reactor over three iron oxide catalysts having different structures, *i.e.*, α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4, which were prepared *in situ* by controlled reduction and reoxidation with a pulse method. Under the working conditions of catalytic oxidation, the structures of α- and γ-Fe_2O_3 remained unchanged, while Fe_3O_4 was oxidized to γ-Fe_2O_3, the oxidation state of iron being Fe(III) in all of three iron oxide catalyst. These results are consistent with the kinetics that the reaction was of zeroth order in the partial pressure of oxygen and of nearly first order in the butene partial pressure. γ-Fe_2O_3, as well as γ-Fe_2O_3 formed from Fe_3O_4 under the catalytic conditions, was very active and selective for the reaction, as expected from the results obtained previously with a pulse reactor. It was concluded from the following facts that the oxygen species responsible for this reaction is lattice oxygen of γ-Fe_2O_3 and that the reaction proceeds by the redox cycles of γ-Fe_2O_3 $\rightleftharpoons \gamma$-$Fe_2O_{3-x}$. i) Reactivity of γ-iron oxide surface in the stoichiometric oxidation of butenes to butadiene did not change, when the surface oxygen was stepwisely removed by CO-pulses from γ-Fe_2O_3 to γ-$Fe_2O_{2.8}$. ii) Formation of butadiene from a butene pulse was little affected by whether butenes were pulsed with oxygen or not.

Iron oxide is widely used in oxidation reasctions a single or mixed oxides. However, as for allylic oxidation of olefin, it is not a selective catalyst.[2)] Recently, we found by use of a pulse method that metastable γ-Fe_2O_3(maghemite) was very active and selective in oxidative dehydrogenation of butenes.[3)] Reactivity and oxygen mobility of γ-Fe_2O_3 were already investigated in detail in relation to the oxidation of carbon monoxide.[1)]

In the present study, we attempted to confirm the relationship between the structure and oxidation state of iron oxide and the catalytic activity for oxidative dehydrogenation. It was of prime interest whether or not the high activity and selectivity of γ-Fe_2O_3 observed by a pulse method can be reproduced in a flow reactor. Kinetic studies, structure determination of iron oxide under working conditions, and comparison of catalytic and stoichiometric oxidations were also carried out, in order to clarify the reaction mechanism and the nature of the active oxygen species.

Experimental

Apparatus and Procedure. Apparatus for the reaction was a combination of a pulse reactor and a flow reactor. The pulse reactor was the same that described previously,[3)] in which carrier gas (He) was deoxygenated by a molecular-sieve trap kept at liquid nitrogen temperature. After the structure and oxidation state of iron oxide was controlled by its reduction and oxidation with the pulse method described previously,[3)] the system was changed to a flow system by the operation of valves, and reaction gas mixtures (butene, oxygen, and helium) were introduced to pass over the catalysts. The reaction system was carefully designed, so that the catalyst was never exposed to any trace of oxygen during the valve operation. For example, a 6-way valve was covered by a metal jacket in which a stream of dry helium was continuously passed, to avoid oxygen diffusion from air into the flow of the feed gas. After 1 h of the flow experiment (usually reaction became almost stationary within 1 h), the system was changed again to the pulse system to examine the oxidation state and the structure of catalysts. Ordinary pulse-experiments were also carried out in some cases.

Reagents and Catalysts. α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4 were the same as described in Part II.[1)] $MgSO_4$–SiO_2 (abbreviated as Mg–S) and CaO were also the same as used before.[4,5)] Butenes (Takachiho Shoji, >99.9%) and pentenes (Tokyo Kasei, >99%) were obtained commercially and used without further purification.

Results and Discussion

Comparison of α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4 in Oxidative Dehydrogenation of 1-Butene (Flow Method). Reaction of 1-butene over iron oxides having different initial structures and oxidation states, which were prepared *in situ* as described in Experimental section was measured by the flow method at 300 °C. Typical results are given in Table 1. Reaction became nearly stationary within 1 h, the conversion becoming 1/2—2/3 of the initial value within this period. Deactivation was small when butene pressure was low and oxygen pressure was high. This deactivation was probably due to carbon deposit, since the initial activity was restored by burning off of the carbon deposit by oxygen pulses at 300 °C. The selectivity to butadiene was almost constant during the flow experiments.

After the flow experiments, the system was changed again to the pulse system by the procedure described in the Experimental section, carefully avoiding the contamination of the catalysts. Then the oxidation states of the catalysts were determined from the amounts of oxygen uptake by the catalysts from O_2-pulses. Although the structures of iron oxides were not determined by X-ray diffraction analysis, they were easily estimated from the oxidation state, color, and magnetic properties. These results are also given in Table 1. The oxidation states and structures of α-Fe_2O_3 and γ-Fe_2O_3 did not change during the flow experiments, when oxygen was present more than 0.5%. On the other hand, Fe_3O_4 was oxidized to γ-Fe_2O_3.

Table 1 clearly shows, in spite of the presence of deactivation, that the catalytic activity and selectivity

Table 1. Oxidative dehydrogenation of 1-butene over iron oxide catalysts by a flow method at 300 °C

Starting iron oxide	Feed gas (% in He)		Stationary conversion	Selectivity to butadiene	Structure after run
	O_2	1-Butene	%	%	
α-Fe_2O_3	5.1	6.5	3	38	α-Fe_2O_3
γ-Fe_2O_3	5.4	5.5	12	89	γ-Fe_2O_3
γ-Fe_2O_3	0	4.8	0	—	mainly Fe_3O_4
Fe_3O_4	7.6	7.7	17	91	γ-Fe_2O_3

Total flow rate: 30 cm^3 min^{-1}, amount of catalyst: 150 mg.

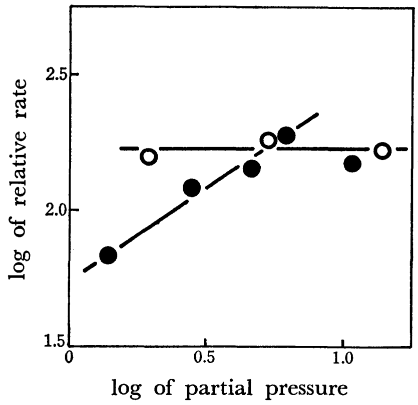

Fig. 1. Dependence of the rate on the partial pressure of 1-butene or oxygen.

Partial pressures are expressed by % in feed gas (1 atm). Reaction temperature: 300 °C, W/F: 5.0× 10^{-2} g min cm^{-3}, ○: dependency on O_2 (butene: 4.5%), ●: dependency on butene (O_2: 4.5%).

were much higher with γ-Fe_2O_3 than with α-Fe_2O_3. Fe_3O_4 was little active at first, but it soon became comparable with γ-Fe_2O_3. This is natural, since Fe_3O_4 was oxidized to γ-Fe_2O_3 during the run. These results are in complete agreement with the results obtained by use of a pulse method.[3] Thus, it was confirmed also with a flow method that iron(III) oxide exhibits quite different behavior in allylic oxidation of olefin depending on its structure, γ-Fe_2O_3 (maghemite) being very active and selective.

Sazonova *et al.*[6] also studied the structural change of iron oxide during the oxidative dehydrogenation, and reported that iron oxide was in the states of α-Fe_2O_3 and Fe_3O_4 at high and low pressures of oxygen, respectively. However, the iron oxide they assigned to Fe_3O_4 could be γ-Fe_2O_3 in view of the present study. The X-ray powder diffraction patterns of Fe_3O_4 and γ-Fe_2O_3 are very close with each other. The selectivity they reported was not very high, probably because of the higher reaction temperature (365 °C).

Kinetics of Oxidative Dehydrogenation of 1-Butene over γ-Fe_2O_3 (Flow Method). Reaction mechanism was examined by a kinetic study. Figure 1 shows the dependency of the rate on the partial pressures of oxygen and 1-butene. As obvious from the figure, the reaction is of zeroth order with respect to oxygen. Selectivity of butadiene formation was nearly unchanged in this range of oxygen pressure. As for the rate dependency on the butene partial pressure, the rate data deviate from the straight line at high pressure. This was caused by significant deactivation of catalyst at this pressure region. At lower pressure-region, the reaction order was 0.7th. If the deactivation were properly taken into account, the reaction order would become closer to first order.

If the catalytic oxidation proceeds by a reduction-oxidation cycles of catalyst (redox mechanism), the result that kinetics was zeroth order in oxygen and first order in 1-butene means that the oxidation step of catalyst is much more rapid than the reduction step, and, therefore, the catalyst should be in a high oxidation state under the working conditions. This is in accord with the oxidation state actually found (Table 1). Furthermore, it was observed in the case of pulse experiments that the rate of reduction of γ-Fe_2O_3 by butene was slower than that of oxidation of γ-Fe_2O_{3-x} by oxygen. The reduction step was also slower than the oxidation step in the case of the oxidation of carbon monoxide over γ-Fe_2O_3.[1]

Comparison of the Rates of Catalytic and Stoichiometric Oxidation of 1-Butene (Pulse Method). In the redox mechanism, in which the reduction of catalyst is the slow step, the rate of stoichiometric oxidation of substrate by catalyst (oxidation of 1-butene by γ-Fe_2O_3 in the present system) is expected close to the rate of catalytic oxidation (1-butene+O_2 over γ-Fe_2O_3). This statement is valid when the oxidation states of the catalyst are the same in the stoichiometric and catalytic processes. Therefore, it is necessary that the rate of the former process is correctly measured for γ-Fe_2O_{3-x} having the same oxidation state as in the catalytic oxidation.

We measured the rate of the stoichiometric process by the reaction of a very small amount (usually 0.2 cm^3) of 1-butene pulsed over γ-Fe_2O_3 (50 mg), and measured the rate of catalytic process by a small pulse of a mixture of 1-butene and oxygen (usually, 1.0 cm^3 of 1 : 4 mixture). Under the working conditions, x of γ-Fe_2O_{3-x} was close to zero as described above, and the rate of butadiene formation in the stoichiometric oxidation was nearly independent of x in the range of x from 0 to 0.2 (*cf.* Fig. 3), so that the comparison by the present method is meaningful. We already reported the two rates were close enough to support the redox mechanism.[3] In the present study, the comparison was made in a little more accurate way.

Typical results are shown in Fig. 2, where % conversions to butadiene of 1-butene pulsed sequentially (with or without oxygen) are given, together with the extents of isomerization to 2-butenes. The trends seen in Fig. 2 were sufficiently reproducible. In runs

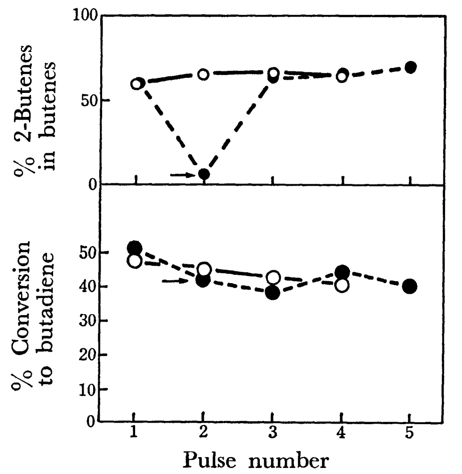

Fig. 2. Reactivity of 1-butene pulse with and without oxygen over γ-Fe_2O_3.
——: Run 1, ----: Run 2
Size of butene pulses was 0.2 cm^3. Data indicated by arrows are for the pulse of 1-butene (0.2 cm^3) pulsed with O_2 (0.8 cm^3).

1 and 2, the second pulses were 1-butene with oxygen and without oxygen, respectively, and all the other pulses contained only 1-butene. Conversion to butadiene decreased slightly by repeated pulses, due to carbon deposit. Results in Fig. 2 clearly show that the rates of two processes (stoichiometric and catalytic) were very close with each other (see the second pulse), supporting the redox mechanism.

The dependency on reaction temperature of butadiene formation in the stoichiometric process was small, apparent activation energies obtained from the conversions of first pulses being 15 kJ mol^{-1} (200—300 °C) and 25 kJ mol^{-1} (270—320 °C) for γ- and α-Fe_2O_3, respectively.

When the reaction temperature was raised to 350 °C, the rate of catalytic oxidation became significantly higher than the stoichiometric oxidation and the formation of carbon dioxide increased. At higher temperatures a mechanism which involves gaseous or adsorbed oxygen and favors complete oxidation is probably operative besides the redox mechanism.

As for the isomerization, two facts are noted: (i) the catalytic activity was much enhanced by the decrease in the oxidation state, butene composition from the second and subsequent pulses (without O_2) being in equilibrium, and (ii) the presence of gaseous oxygen greatly suppressed the isomerization rate. These two phenomena are probably both related to the number of iron sites exposed on the surface, which the reduction of catalyst may increase and (physical) adsorption of oxygen may decrease.

Reactivity of γ-Fe_2O_3 with 1-Butene as a Function of the Extent of Pre-reduction. Reaction of 1-butene pulse in the stoichiometric oxidation by iron oxide was measured over γ-Fe_2O_3, which was pre-reduced to various extents *in situ* by pulses of carbon monoxide. Reduction by CO-pulses minimized contamination of iron oxide during the reduction procedure. Figure 3 shows % conversions of 1-butene to butadiene plotted as a function of the extent of pre-reduction expressed by x of Fe_2O_{3-x}. The conversion remained unchanged in the range of x from 0 to 0.2 (Fe_2O_3 to $Fe_2O_{2.8}$). This is in contrast to the gradual decay of reactivity observed when γ-Fe_2O_3 was pre-reduced by butene itself (see Fig. 2). The decay in the latter case is, therefore, likely due to oxidation or polymerization products from butadiene. Further pre-reduction decreased the reactivity and finally to null at Fe_3O_4. Isomerization increased rapidly upon the pre-reduction as was before.

Reduction of Fe_2O_3 to $Fe_2O_{2.8}$ corresponds to the removal of several layers of oxygen from the surface of Fe_2O_3 (Fe ion going into inner bulk[1,8]). Therefore, the constant reactivity observed in the region between Fe_2O_3 and $Fe_2O_{2.8}$ was not the reactivity of adsorbed oxygen but that of lattice oxygen, since, if the adsorbed oxygen were responsible, the reactivity should have decreased much more rapidly when the oxygen was removed from the surface.

Reactivity and quantity of adsorbed oxygen on α-Fe_2O_3 were studied recently by Iwamoto *et al.* by means of thermal desorption.[7] They found several different adsorbed species, but the total oxygen atoms adsorbed was only about 2% of the surface layer (1.5×10^{19} O-atom m^{-2}).[1] Oxygen adsorbed reversibly on γ-Fe_2O_3 was about 20% of the surface layer at 12 kPa and 300 °C, as determined by a static measurement. But this was reversibly desorbed and not present when 1-butene was pulsed. Therefore, the amount of adsorbed oxygen present in the pulse experiments was probably much smaller than that utilized in butadiene formation from a butene pulse (without O_2). Then, also from this consideration, we can say that the contribution of adsorbed oxygen must be small in the stoichiometric pulse experiments. Actually, the % conversion to butadiene little changed when the pulse size was increased from 0.1 to 0.4 cm^3, indicating that the effect of small quantity of adsorbed oxygen is very low.

Oxygen Responsible for Selective Oxidation. Figure 2 demonstrated that the catalytic oxidation and the stoichiometric oxidation are governed by the same oxygen species, and the results in Fig. 3 indicate that the oxygen species responsible for the stoichiometric oxidation is lattice oxygen. If these two results are combined, it may be concluded that the oxygen species responsible for the catalytic oxidation of butenes over γ-Fe_2O_3 is the lattice oxygen. Possible reasons why γ-Fe_2O_3 was highly active and selective have been discussed previously.[1,3] It may be remarked that γ-Fe_2O_3 has an inverse spinel structure with cation deficiency and that reduction-oxidation between γ-Fe_2O_3 and Fe_3O_4 proceeds readily by the diffusion of Fe ion.[1,3,8] Spinels containing iron (ferrites) are already known as good catalysts for oxidative dehydrogenation of butenes.[9]

Here, the following may be worthy to remark as for the meaning of "lattice oxygen." (i) "Lattice oxygen" in the bulk cannot participate directly in the oxidation reaction. Of course, oxygen must be on the surface when it reacts with a substrate. (ii) "Lattice oxygen" on the surface is never in the same

Table 2. Relative reactivities of olefins measured by a pulse method

Catalyst, reaction temp, and reaction.	C=C-C-C	$\mathrm{C{=}C{-}\overset{\overset{C}{\vert}}{C}{-}C}$	$\mathrm{C{=}\overset{\overset{C}{\vert}}{C}{-}C{-}C}$	$\mathrm{C{-}\overset{\overset{C}{\vert}}{C}{=}C{-}C}$
α-Fe_2O_3, 270 °C				
oxid[a]	1.0	1.3	0.9	0.7
isom[b]	1.0	0.4	25	3.1
γ-Fe_2O_3, 180 °C				
oxid[a]	1.0	1.3	—	—
isom[b]	1.0	<0.1	—	—
$Fe_2O_{2.9}$,[c] 120 °C				
isom[b]	1.0	0.5	3.2	2.1
CaO, 100 °C				
isom[b]	1.0	1.0	2—3	—
Mg-S, 100 °C				
isom[b]	1.0	1.2	$>10^2$	—

a) Oxidative dehydrogenation to form diene. b) Double bond isomerization. c) α-Fe_2O_3 was reduced by CO pulses.

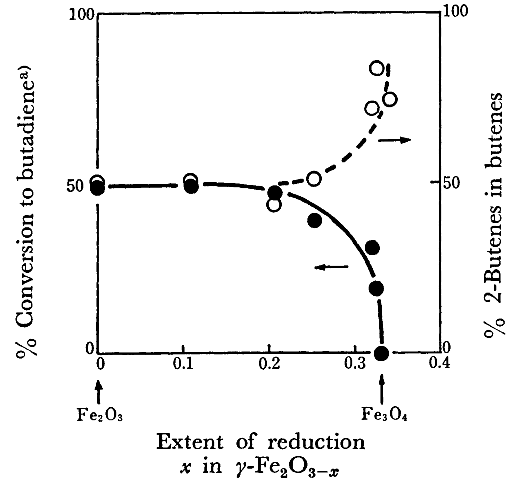

Fig. 3. Reactivity of 1-butene with γ-Fe_2O_{3-x} as a function of the extent of pre-reduction.
Reaction temperature: 200 °C, γ-Fe_2O_{3-x}: 50 mg, pulse size: 0.2 cm^3, pre-reduction: by CO-pulses (1 cm^3 each) at 300 °C.
a) No CO or CO_2 was formed.

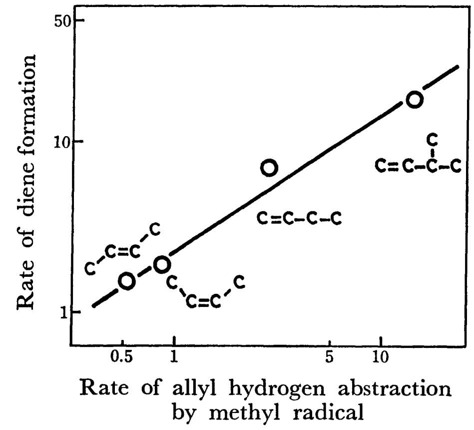

Fig. 4. Relative reactivity of olefins over γ-Fe_2O_3 (pulse method) plotted against the rate of allyl hydrogen abstraction by methyl radical.

electronic state as in the bulk. In some cases, surface "lattice oxygen" might be better described as O^- than as O^{2-}. Even in the bulk, it is not correct to regard oxide ion as having double negative charge, since electron is more or less delocalized to cation. Thus, it is not easy to determine in a general way whether the oxygen on the surface is lattice or adsorbed oxygen and whether the oxygen species responsible for catalytic oxidation is lattice or adsorbed oxygen. Sometimes, differentiation of lattice oxygen from adsorbed oxygen may not be meaningful. However, we may be able to state that the oxygen responsible for the catalytic oxidation is "lattice oxygen," when the rates of stoichiometric and catalytic processes agree and the oxygen used in the former process is not adsorbed oxygen from gas phase, as discussed in the preceding paragraph based on the results in Figs. 2 and 3.

Relative Reactivities of Olefins (δ_R-effect).[10)] Effects of substituents on the reactivity provide useful information on the nature of reaction intermediate. In Fig. 4, reactivities of several olefins measured by the pulse method over α-Fe_2O_3 at 270 °C are plotted against the rate of hydrogen abstraction at allyl position at 65 °C, following Voge and Adams.[11)] The data were obtained from the first pulses over freshly prepared iron oxides. According to the discussion of Voge and Adams,[11)] the linear plot in Fig. 4 indicates that the formation of allylic intermediate is rate-determining. Relative reactivity normalized to one hydrogen atom at allylic positions was calculated from the reactivities of six olefins to be primary : secondary : tertiary = 1 : 4 : 12. However, the very rapid isomerization often observed over iron oxides is not consistent with the idea that the formation of allylic species is also the rate-determining step of isomerization.

We speculate on the basis of the discussion described below that the oxidation proceeds *via* an allyl radical (or cation) and the isomerization *via* an allyl anion.[12)] Allylic species is likely the intermediate of oxidation because of the results in Fig. 4 and because it seems difficult that butadiene is formed *via* an intermediate other than allylic species. Evidence which suggests a different intermediate for isomerization is also obtained from the δ_R-effects summarized in Table 2. Results obtained for typical solid acid (Mg–S) and base (CaO) are also given in this table. Since two reactions (oxidation and isomerization) proceeded over iron oxide simultaneously and could be competitive, the δ_R-effects observed might have been obscured to some extent. However, the following qualitative discussion may be made.

It is remarkable in Table 2 that in the case of iron oxides the methyl substitution at 3-position (3-methyl-1-butene) increased the rate of oxidation but decreased the isomerization. Suppressive effect of the 3-methyl group on isomerization was also observed over $Fe_2O_{2.9}$ at 120 °C, where the competitive oxidation was negligible. Therefore, the opposite behavior of oxidation and isomerization upon the methyl substitution is meaningful and suggests that two reactions proceed *via* different intermediates. Alkyl cations are not likely the intermediate for isomerization, because, if the alkyl cation were the intermediate, 2-methyl-1-butene should have been far the more reactive as in the case of Mg–S, due to the stability of tertiary cation.

The reactivity patterns of isomerization of iron oxides were more like that of CaO than that of Mg–S, so that allyl anions are presumably the intermediates as in the case of CaO.5) The fact that the *cis*/*trans* ratio of 2-butene from the isomerization of 1-butene was about 1.5 at 150—200 °C is not in conflict with the allyl anion intermediate. If one assumes allyl radicals (or cations) for oxidation and allyl anions for isomerization, the opposite effects of 3-methyl group on oxidation and isomerization can reasonably be explained, since a methyl group destabilizes the anion but stabilizes the cation or radical.13,14) Co-existence of two allylic intermediates, anionic and covalent, has been proposed for the isomerization of butene over chromia.15) Change in the selectivity from acrolein to benzene in the allylic oxidation of propene over several oxide catalysts was also explained by the change in the charge of allylic intermediate.2a)

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