

Reasons for the Different Selectivities in the Selective Oxidation of Butene on α - and γ -Fe₂O₃

Selectivity in catalytic reactions over transition metal oxides has been shown recently to depend on the bulk crystallographic form of the oxide. For example, in the oxidation of butene, α - and γ -Fe₂O₃ differ significantly in the selectivity for butadiene (1, 2). In the oxidation of methanol, the orthorhombic and rhombohedral forms of MoO₃ also differ greatly in the selectivity for formaldehyde (3). In the case of Fe₂O₃, Misono *et al.* first reported that in a pulse reaction study, the butadiene selectivity is much higher for γ - than for α -Fe₂O₃ (2). This difference was later demonstrated for steady state reactions as well (1). At 300°C, for example, γ -Fe₂O₃ was over 90% selective, while α -Fe₂O₃ was about 50% selective. While this difference is now well documented (1, 2, 4), it has yet to be explained. We have recently shown that on α -Fe₂O₃, the adsorbed butadiene and/or its adsorbed precursor (allylic) intermediate is very sensitive to degradation by gas-phase oxygen (5). The reactivity is so high that a small pulse of oxygen at -78°C can almost totally oxidize the adsorbed butadiene and its precursor to combustion products. This extreme sensitivity to degradation by gas-phase oxygen is perhaps the reason for the low selectivity on α -Fe₂O₃. If so, adsorbed butadiene or its precursor should be less sensitive to degradation by gas-phase oxygen on γ -Fe₂O₃. Here we report the results of such an investigation.

γ -Fe₂O₃ was prepared from α -Fe₂O₃ which was prepared by precipitation from a ferric nitrate solution with ammonium hydroxide as described before (6, 7). Its BET area was 14 m²/g. Two different preparations gave similar results. Conversion to γ -

Fe₂O₃ was achieved by first reducing α -Fe₂O₃ to Fe₃O₄ at 300°C in a CO/CO₂ (1/99, v/v) stream that was purified by a glass beads column at 350°C, which removed gas-phase iron carbonyl impurities. Reoxidation of Fe₃O₄ by oxygen at 300°C yielded γ -Fe₂O₃. The conversion was confirmed by X-ray diffraction.

After cooling the γ -Fe₂O₃ in O₂ to room temperature and purging with He, adsorption of *cis*-2-butene was achieved by introducing a pulse of 5×10^{18} molecules of the hydrocarbon in a stream of purified helium, into the reactor at -78°C. After equilibration, the gas-phase butene was purged out and thermal desorption followed. The reactor system and the experimental procedure were identical to those described before (5). It has been established that the adsorption-desorption experiments were conducted under conditions that were free of diffusional effect, and that one reaction product was formed per active site. Essentially identical results were obtained if 1-butene was used instead of *cis*-2-butene.

On warming up the γ -Fe₂O₃ with adsorbed *cis*-2-butene in a stepwise fashion, unreacted *cis*-2-butene and other butene isomers began to desorb at about -20°C. Their desorption was complete by about 25°C. Butadiene began to evolve at about 0°C and was totally desorbed by about 70°C. Evolution of CO₂ began at about 200°C. Figure 1 shows the fraction of butadiene and CO₂ precursors left on the surface after desorption at each temperature. The total amount of butadiene produced was 1.5×10^{17} molecules/m², and of CO₂/4 was about 1.7×10^{17} molecules/m². These correspond to the densities of sites that pro-

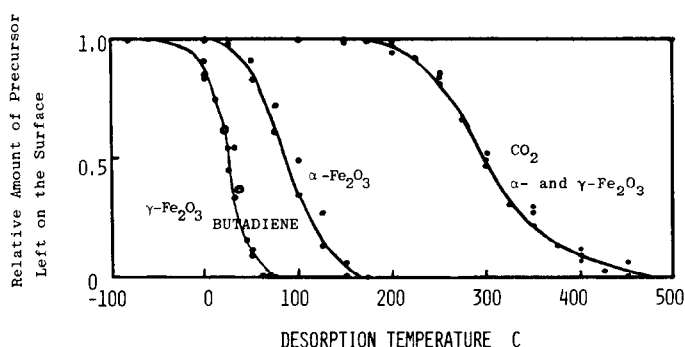


FIG. 1. The fraction of butadiene and CO_2 precursors left adsorbed on the catalyst surfaces as a function of desorption temperature in a butene adsorption experiment. Filled points are for standard adsorption-desorption experiments, open points are for those in which the desorption process was interrupted for passage of an oxygen pulse over the catalyst at the indicated temperatures.

duce these products on a fresh $\gamma\text{-Fe}_2\text{O}_3$ surface.

After the first experiment, the catalyst was converted to $\alpha\text{-Fe}_2\text{O}_3$ by heating in O_2 at 450°C , and then reconverted back to γ . It was found that the amount of butadiene produced decreased randomly with each conversion from almost no decrease to 30–40% decrease. The desorption profile of this butadiene product remained unchanged. The BET area decreased gradually by less than 5% for each conversion. The amount of CO_2 was essentially unchanged (within 10%). The decrease in butadiene production could be eliminated if the catalyst was heated to 300°C only during desorption instead of 450°C , and then reoxidized in O_2 at 300°C for 2 h for the next experiment.

A small and varying amount of CO_2 was also desorbed below 200°C . Its amount varied from 0.03 to 0.3×10^{17} molecules/ m^2 , and it was present in blank runs without adsorbed butene. It was from adsorption from the residual CO_2 during the CO/CO_2 reduction of the catalyst, and could be greatly eliminated if the catalyst was heated briefly to 300°C before adsorption experiments.

The desorption profile for $\alpha\text{-Fe}_2\text{O}_3$ is also shown in Fig. 1. While CO_2 evolution was the same, butadiene evolution was at a higher temperature than $\gamma\text{-Fe}_2\text{O}_3$.

If butadiene was used instead of *cis*-2-butene in an identical adsorption-desorption experiment, the desorption profile as shown in Fig. 2 was obtained. Desorption from multilayer adsorption took place below about 0°C . Above 0°C the profile was essentially the same as the butadiene profile in butene experiments. CO_2 was also produced above 200°C .

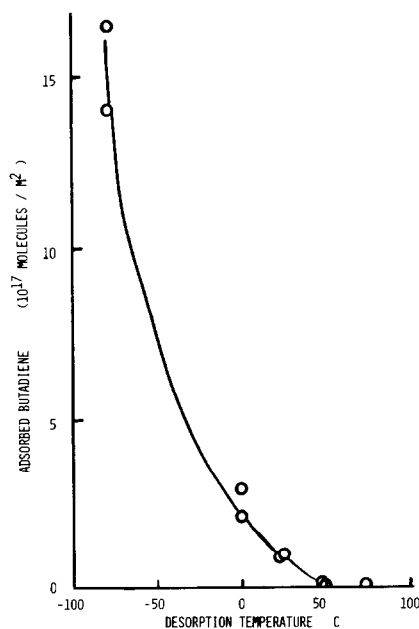


FIG. 2. The amount of butadiene left adsorbed on the $\gamma\text{-Fe}_2\text{O}_3$ surface as a function of desorption temperature in a butadiene adsorption experiment. CO_2 production is not shown.

These results suggest that in the production of butadiene from butene on $\gamma\text{-Fe}_2\text{O}_3$, desorption of the product is the rate-limiting step. This is also true for $\alpha\text{-Fe}_2\text{O}_3$ (5). The shift to lower temperature for butadiene evolution on γ - than on $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 1) points to the fact that the activation energy for the overall process of butadiene production in which the butadiene desorption is rate limiting, is lower on γ - than on $\alpha\text{-Fe}_2\text{O}_3$. Since the activation energy for CO_2 production is the same, this will contribute to a higher butadiene production rate relative to CO_2 on $\gamma\text{-Fe}_2\text{O}_3$, and a higher selectivity.

The sensitivity of adsorbed butadiene precursor on $\gamma\text{-Fe}_2\text{O}_3$ to gas-phase oxygen was also investigated. After the adsorption of *cis*-2-butene and desorption to 23 or 45°C, a pulse of oxygen (30 times the amount of adsorbed butadiene precursor) was passed over the catalyst at room temperature. Then desorption was resumed. Results of two such experiments are shown in Fig. 1. Similar results were obtained in some preliminary experiments. As shown in the figure, the amount of butadiene produced was the same as without the oxygen pulse. Thus the precursor is not susceptible to degradation by gas-phase oxygen. In comparison, if the butadiene precursor on $\alpha\text{-Fe}_2\text{O}_3$ had been heated to 75°C when butadiene began to desorb, an O_2 pulse (10 times smaller than the one used for $\gamma\text{-Fe}_2\text{O}_3$) at as low as -78°C significantly degraded the subsequent desorption of butadiene, as was reported earlier (5) and confirmed in this study. Thus the butadiene precursor is much less sensitive to oxygen attack on $\gamma\text{-Fe}_2\text{O}_3$ than $\alpha\text{-Fe}_2\text{O}_3$. Since the nature of adsorbed butadiene and the π -allyl precursor are likely similar on the two iron oxides, this difference is probably due to the better ability of $\alpha\text{-Fe}_2\text{O}_3$ to activate oxygen, than $\gamma\text{-Fe}_2\text{O}_3$.

We should mention, however, that if adsorbed butene on $\alpha\text{-Fe}_2\text{O}_3$ had only experienced a temperature of 25°C, an O_2 pulse did not cause significant reduction (less

TABLE I
Pulse Reactions of Butene at 300°C^a

Catalyst	Reactant	Carrier	Oxidation products (10 ¹⁷ molecules)	
			Butadiene	CO ₂ /4
$\alpha\text{-Fe}_2\text{O}_3$ (40 mg)	<i>cis</i> -2-Butene	He	4.36	0.38
		O ₂	1.60	8.83
$\gamma\text{-Fe}_2\text{O}_3$ (16 mg)	1-Butene	He	16.1	1.32
		O ₂	12.4	5.11

^a Butene pulse size was 2.6×10^{18} molecules. Products were collected for 10 min for $\alpha\text{-Fe}_2\text{O}_3$, and 30 min for $\gamma\text{-Fe}_2\text{O}_3$ after the pulse.

than 10%) in subsequent butadiene production. This was interpreted as an indication that on the selective oxidation sites of $\alpha\text{-Fe}_2\text{O}_3$, only the adsorbed allylic intermediate and/or butadiene was sensitive to oxygen attack, and not adsorbed butene. The above-mentioned differences to O_2 attack between α - and $\gamma\text{-Fe}_2\text{O}_3$ may be due to the temperature experienced by the adsorbed precursor. However, we believe that it is more likely a difference in the ability of the catalyst to activate gas-phase oxygen that degrades butadiene precursors. This belief is further supported by results of other experiments described below.

When the *cis*-2-butene oxidation reaction was studied at 300°C in a pulse reaction experiment using $\alpha\text{-Fe}_2\text{O}_3$, the ratio of butadiene to carbon dioxide produced was very dependent on whether He or O_2 was used as a carrier gas. Table I shows the typical results (5). In contrast, when $\gamma\text{-Fe}_2\text{O}_3$ was used as the catalyst under otherwise identical conditions, the ratio was much less dependent on whether He or O_2 was used as a carrier. Since steady state reactions can be carried out at 300°C on both iron oxide, this difference is a direct indication of the different sensitivities of the butadiene precursors to oxygen attack.

In fact, one would expect that this difference should be manifested also in steady state reactions as the dependence of the selectivity on the oxygen partial pressure. Because of the sensitivity to oxygen degradation, the selectivity for butadiene on

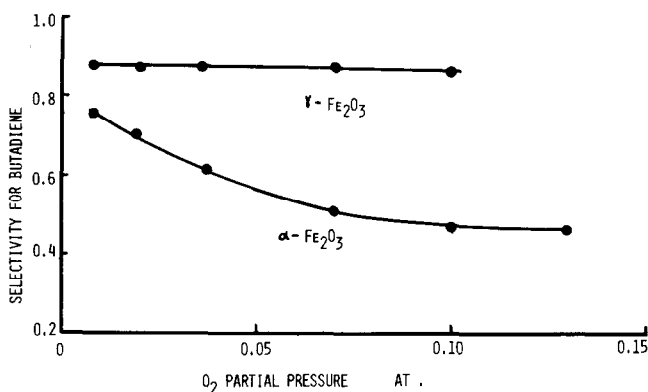


FIG 3. The selectivity for butadiene in steady state 1-butene oxidation as a function of oxygen partial pressure. Other conditions: total flow rate, 300 ml/min; 300°C; about 30 mg of catalyst; 1-butene pressure = O₂ pressure.

α -Fe₂O₃ is expected to decrease with increasing oxygen pressure. On γ -Fe₂O₃, such dependence is expected to be much weaker. These expectations have been confirmed experimentally. Figure 3 shows the results of these experiments carried out under low conversion (<3%) conditions. Indeed, over the range of oxygen pressure studied, the selectivity was unchanged on γ -Fe₂O₃, but decreased with increasing oxygen pressure on α -Fe₂O₃.

We have therefore identified two phenomenological reasons for the much higher selectivity for butadiene on γ - than on α -Fe₂O₃ in the oxidation of butene. While the activation energy for CO₂ production is the same, that for butadiene production is substantially lower on γ - than on α -Fe₂O₃. This results in a higher butadiene production rate, relative to CO₂, on γ -Fe₂O₃. The lower activation energy for butadiene production on γ -Fe₂O₃ also results in a shorter surface residence time of the butadiene molecule and its precursor, which reduces the probability of being degraded by oxygen, and results in a higher selectivity. In addition, the adsorbed butadiene precursor on γ -Fe₂O₃ is not sensitive to degradation by gas-phase oxygen, but is very sensitive on α -Fe₂O₃. This difference is attributed to the ability of α -Fe₂O₃, but not γ -Fe₂O₃, to activate oxygen.

When different ferrites are compared with respect to these properties, some interesting trends emerge. Referring to the summary shown in Table 2, the butadiene desorption temperatures are about the same for α -Fe₂O₃ and ZnFe₂O₄ (5, 6, 8) but lower for γ -Fe₂O₃. The Fe³⁺ in the former two catalysts are in octahedral sites, while those in γ -Fe₂O₃ are distributed in tetrahedral and octahedral sites. It could be that surface-exposed tetrahedral Fe³⁺ ions bind hydrocarbons less strongly than octahedral Fe³⁺ ions, and is the active site in γ -Fe₂O₃ for butadiene production. On the other hand, the exposed octahedral Fe³⁺ ions are

TABLE 2

Comparison of Different Ferrite Catalysts in Butene Oxidation

Oxide	Crystal structure	C ₄ H ₆ Desorption temperature ^a (°C)	Sensitivity to O ₂ pulse	C ₄ H ₆ Formed 1st/2nd pulse ^b
α -Fe ₂ O ₃	Corundum	88	Yes	4.3
FeCrO ₃	Corundum	—	—	4.4
γ -Fe ₂ O ₃	Spinel	28	No	1.7 ^c
ZnFe ₂ O ₄	Spinel	~88 ^d	—	1.6

^a Temperature at the midpoint of the butadiene evolution curve in the thermal desorption of butene, as in Fig. 1.

^b Ratios of the amount of butadiene formed in experiments where pulses of butene were passed over the catalyst at 200°C in a stream of He.

^c Ratio of the first to the tenth pulse; from Ref. (2).

^d From Ref. (8).

the active sites on α -Fe₂O₃ and ZnFe₂O₄. Since the binding of hydrocarbons involve the properties of the surface ion only, the effect of the bulk crystal structure is only indirect. However, the decrease in butadiene production with pulse number in a pulse reaction experiment at 200°C can be directly correlated with the bulk structure. This indicates that the amount of butadiene produced in subsequent pulses depends on the rate of regeneration of the surface sites consumed in the previous pulse. Such regeneration involves reoxidation of the site by diffusion of lattice oxygen from the bulk to the surface, its rate depends on the crystal structure. Steady state studies at 300°C with a 1/1 butene-to-oxygen feed show that the selectivity for butadiene at low conversion is about the same on α -Fe₂O₃ (9) and ZnFe₂O₄ (10), and higher on γ -Fe₂O₃. Thus under these conditions, the steady state selectivity is likely primarily determined by the surface conditions and less by bulk diffusivity of lattice oxygen.

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