

Oxygen on Iron Oxide: Effect on the Selective Oxidation of Butane

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The effect of preadsorbed and gas phase oxygen on the selective oxidation of butene to butadiene on α -iron oxide was investigated using adsorption-desorption and pulse reaction technique. It was found that irreversibly adsorbed oxygen did not affect the butene oxidation reaction. However, the presence of gas phase oxygen significantly reduced the production of butadiene and increased the production of carbon dioxide. This decrease in butadiene production was due to the high reactivity of adsorbed butadiene precursors toward weakly adsorbed oxygen. However, these butadiene precursors were not reactive toward nitrous oxide. Therefore, under steady-state conditions, the rate of production of butadiene is determined by the competition between the desorption of butadiene and the degradation of the precursors by oxygen.

INTRODUCTION

Oxygen is known to adsorb on oxide surfaces in atomic and molecular forms that carry different charges (1). These different oxygen species show different effects in catalytic reactions, especially selective oxidation reactions. For example, in the oxidation of isobutene to acetone and methacrolein, isobutene was shown to adsorb on an O^- species on nickel oxide (2). In the oxidation of ethylene to ethylene oxide on silver, the difference in reactivity of atomic and molecular oxygen is still under intensive investigation (3-5). It has been generally assumed that weakly adsorbed oxygen tends to promote combustion reactions, while strongly adsorbed oxygen either tends to promote selective oxidation or is inactive. In this report, the results of our investigation on the reaction between gas phase and adsorbed oxygen and butene in the oxidative dehydrogenation reaction on α -iron oxide are presented.

Among simple binary oxides, iron oxide is one of the most selective catalysts for the oxidative dehydrogenation of butene (6, 7). It has been shown that the two primary ox-

idation products, butadiene and carbon dioxide, are produced on two independent sites (8). These two sites must differ either in their atomic nature or in their atomic environments. It is possible that they differ in the nature of adsorbed oxygen at or near the site. Indeed, the amounts of adsorbed oxygen and adsorbed butene were found to be comparable (9). Furthermore, the participation of an atomic O^- species in this reaction on ferrite catalysts has been postulated (10).

Over the range from room temperature to 450°C, there are three types of adsorbed oxygen on α -iron oxide. The three types differ in their temperature of adsorption and desorption (9, 11, 12). The low-temperature (α) form adsorbs and desorbs below 200°C, the medium-temperature (β) form between 200- and 350°C, and the high-temperature (γ) form over 350°C. Based on temperature-programmed desorption results, the α form is believed to be a molecular species (12). On the other hand, the β form is believed to be an atomic species because its desorption follows a second-order kinetics (9). Therefore, by selectively adsorbing one of these forms of oxygen each time, their effect on the reaction of butene can be investigated.

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EXPERIMENTAL

α -Iron oxide was prepared as before by precipitation with ammonium hydroxide from a ferric nitrate solution (8, 9). Its BET area was 17 m²/g. Experiments were conducted in a quartz u-tube reactor in the system described previously (8). In all the experiments, about 40 mg of catalyst was used that formed a bed of less than 2 mm thick. The helium stream (Linde high purity grade) was purified with a silica gel trap at -196°C, and the oxygen stream (Linde hydrocarbon-free grade) was purified with a silica gel trap at -78°C.

Standard pretreatment of the catalyst was to heat it in oxygen (40 ml min⁻¹) at 400°C for 0.5 h, and 450°C for 10 min. Then the catalyst was purged with helium (40 ml min⁻¹) for 2 h at 300°C, and 0.5 h at 450°C. Afterward it was cooled in helium to -78°C for *cis*-2-butene adsorption if preadsorption of oxygen was not needed. If adsorption of oxygen at 450°C was desired before butene adsorption, the catalyst was exposed to the oxygen stream at this temperature after the pretreatment. For oxygen adsorption at 500°C, the pretreatment temperatures were also raised from 450 to 500°C. The temperature was then decreased at 10°C/min to a lower value at which the catalyst was purged with helium for 2 h. It was lowered to either 430 or 450 or 500°C if only γ oxygen was desired, to 240°C if both β and γ oxygen was desired, and to -78°C if α , β , and γ oxygen were desired. Afterward the temperature was further lowered to -78°C for *cis*-2-butene adsorption.

The standard procedure for butene adsorption-desorption was to introduce a pulse of 5×10^{18} molecules of *cis*-2-butene into the reactor of about 35 ml. After allowing the butene pulse to equilibrate for 0.5 h with the catalyst, the reactor was purged with helium for 1 h. Thermal desorption was then performed by heating the catalyst at 15°C/min to 210°C to desorb all hydrocarbon products, and then to 430°C to desorb CO₂ and water. By holding the temperature

at 430°C for 15 min and sometimes by also passing a small pulse of oxygen at 430°C, quantitative desorption of all products (98 to 100%) was achieved. All desorbed products were first collected in a Chromosorb trap at -196°C for later gas chromatographic analysis as described previously (8, 9).

In some experiments, there were variations from this standard procedure. In cases when thermal desorption was performed using oxygen carrier instead of helium, the desorbed products were collected in the Chromosorb trap at -160°C provided by an isopentane slush bath to avoid condensation of oxygen. Control experiments showed that -160°C was low enough for quantitative trapping of carbon dioxide and all hydrocarbons of interest. Other variations will be described when appropriate.

Pulse reaction of *cis*-2-butene was conducted on catalysts pretreated and preadsorbed with various species of oxygen in the same manner as those for butene adsorption-desorption experiments. After oxygen adsorption and purging, the catalyst was brought to the desired temperature. Butene pulses each of 2.5×10^{18} molecules were introduced either in a helium or an oxygen carrier. All the products evolved within 10 min of the pulse were collected in the Chromosorb trap for analysis as described above. Then the catalyst was heated to thermally desorb all the species that remained on the catalyst. These were also collected and analyzed.

In some butene adsorption-desorption experiments, thermal desorption was interrupted so as to investigate the reactivity of the adsorbed species with oxygen. Thus thermal desorption was first carried out from -78°C to a specified temperature. The temperature was then further adjusted to another value at which a pulse of either oxygen or N₂O was passed over the catalyst. After passage of the pulse, thermal desorption was continued and the desorbed products analyzed.

In some other experiments, butadiene

was used instead of *cis*-2-butene in the adsorption-desorption experiments. The procedure used was otherwise identical. The catalyst was found to deactivate slightly after prolonged use (15 or more runs under standard conditions) without change in selectivity. The deactivation could be due to loss of surface area but no attempt was made to determine it. Prolonged heating at high temperature ($>450^{\circ}\text{C}$) facilitated deactivation. All the data reported here were obtained before the catalyst showed significant deactivation ($<15\%$ of the initial value), and had been repeated using different charges of catalyst. In most cases, only the typical data rather than all of the data are shown in the tables.

The reactor without catalyst was found not to adsorb oxygen or cause detectable reaction of butene or butadiene in the adsorption-desorption and the pulse reaction experiments. It did not decompose N_2O under the conditions studied either.

RESULTS AND DISCUSSION

The most sensitive determination of the effect of preadsorbed oxygen on the oxidation of butene will be one in which each active site undergoes one reaction with butene. The adsorption-desorption procedure employed here was similar to the one that has been shown to achieve the condition of one reaction per site (8, 13). The only difference was that *cis*-2-butene was adsorbed

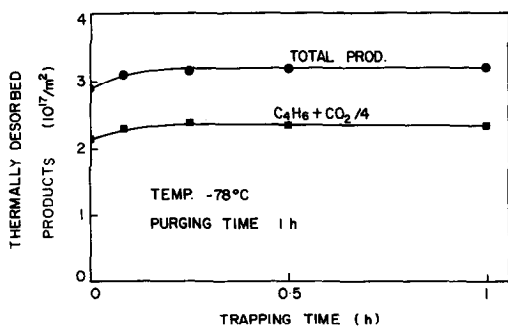


FIG. 1. The amounts of thermally desorbed oxidation products versus trapping time of *cis*-2-butene. Standard pretreatment of about 40 mg of catalyst, 1 h purging, adsorption (trapping), and purging at -78°C .

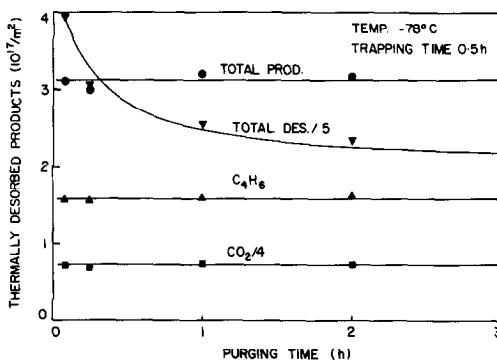


FIG. 2. The amounts of thermally desorbed products versus purging time at -78°C . Standard pretreatment of about 40 mg of catalyst, 0.5 h trapping of *cis*-2-butene at -78°C . Data for total products included 1-butene, *t*-2-butene, butadiene and $\text{CO}_2/4$; data for total desorption included *c*-2-butene as well.

at -78°C instead of room temperature. For this matter, control experiments were performed to ensure that the modification did not invalidate the conditions of (i) full equilibration of active sites with butene, (ii) no readsorption of desorbed products, and (iii) each site adsorbs only one butene.

The first control experiment was to investigate the effect of the exposure time of the catalyst to butene (trapping time) on the thermally desorbed oxidation products. The results are shown in Fig. 1 which indicated that beyond a trapping time of 20 min, the amounts of thermally desorbed oxidation products remained constant. This indicated that beyond this time, every active site had been equilibrated with butene, and there was no multiple reaction at each site. It should be noted that the oxidation products were only evolved during thermal desorption and not during purging at -78°C .

The second control experiment was to investigate the purging time after butene adsorption. The results are shown in Fig. 2. The amounts of thermally desorbed oxidation products were independent of purging time. This indicated that the gas phase butene was adequately removed before thermal desorption such that there was no multiple reaction at each site, and that the helium purging gas was adequately purified

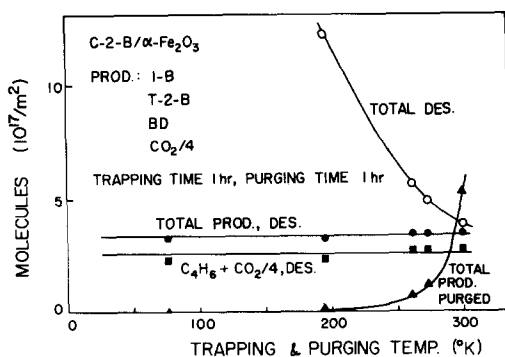


Fig. 3. The amounts of thermally desorbed products versus temperature of adsorption and purging. Standard pretreatment of about 40 mg of catalyst, 1 h trapping, and 1 h purging. Data for total products and for total desorption were the same as those in Fig. 2.

that it did not contain impurities that could degrade adsorbed butene. From these two experiments, the standard condition of 0.5 h trapping and 1 h purging was selected.

The last control experiment was to investigate the adsorption temperature. The results of the investigation over the range from -196 to 25°C are shown in Fig. 3. The amounts of thermally desorbed oxidation products were independent of temperature.

This further substantiated the conclusion that the active sites had been equilibrated with butene. It also indicated that the adsorption of butene on the oxidation sites was not activated. These results, together with those reported earlier on the effect of purging flow rate and of temperature programming rate during thermal desorption (8, 13) strongly indicated the validity of the one to one stoichiometry between active site density and the amount of thermally desorbed oxidation products.

This adsorption-desorption technique was then used to investigate the reaction of butene on catalysts containing different preadsorbed oxygen species. Different preadsorbed oxygen species were introduced using different oxygen exposure temperatures as described in the experimental section. The results are shown in Table 1. The amounts of oxidation products were found to be independent of the presence of preadsorbed oxygen. In fact, even the thermally desorbed isomers were not affected by the preadsorbed oxygen. It should be noted that these results could only be obtained using a properly purified oxygen stream. If

TABLE 1

Effect of Preadsorbed Oxygen on the Oxidation of *cis*-2-Butene in Adsorption-Desorption Experiments^a

Adsorbed oxygen species	Adsorption temperature ^b (°C)	Thermally desorbed products (10^{17} molecules/m ²)					B.D.
		1-Butene	<i>t</i> -2-Butene	<i>c</i> -2-Butene	Butadiene	CO ₂ /4	B.D. + CO ₂ /4
$\alpha + \beta + \gamma$	450, -78	0.22	0.65	9.0	2.16	1.21	0.64
	450, -78	0.22	0.68	10.7	2.14	1.20	0.64
	450, -78	0.32	0.67	8.5	2.04	1.16	0.64
	500, -78	0.24	0.94	7.9	2.28	1.39	0.62
$\beta + \gamma$	450, 240	0.26	0.69	8.7	1.92	0.95	0.67
	500, 240	0.22	0.94	7.7	2.10	1.14	0.65
γ	450, 430	0.22	0.79	8.8	2.11	0.97	0.69
	450, 430	0.23	0.78	8.6	2.02	0.97	0.68
	450, 450	0.25	0.94	8.6	2.25	1.10	0.67
	450, 450	0.21	0.85	10.0	2.13	0.95	0.69
	450, 450	0.23	0.90	8.5	2.25	1.11	0.67
	500, 500	0.21	1.13	6.5	2.35	1.18	0.67

^a About 40 mg of catalyst that corresponded to a surface area of 0.7 m^2 ; standard adsorption and desorption procedures.

^b The catalyst was exposed to oxygen at the first temperature, while in oxygen the temperature was lowered to the second temperature at which the reactor was purged with helium.

TABLE 2

Effect of Oxygen Partial Pressure on the Thermal Desorption Products of *cis*-2-Butene^a

P_{O_2} (atm)	Product distribution (10^{17} molecules/m ²)				
	1-Butene	<i>t</i> -2-Butene	<i>c</i> -2-Butene	Butadiene	CO ₂ /4
$\sim 1.5 \times 10^{-7}$	0.21	0.85	10.0	2.13	0.95
	0.25	0.94	8.6	2.25	1.10
$\sim 5 \times 10^{-7}$	0.22	0.78	10.4	1.99	0.98
1	0.04	0.09	6.8	0.05	5.43

^a About 40 mg of catalyst that corresponded to 0.7 m²; standard pretreatment and adsorption procedure was used.

the oxygen stream was insufficiently purified, a decrease in the amount of oxidation products was observed.

There are two possible explanations for the results in Table 1. It is possible that although oxygen and butene adsorb on the same active site, the butene oxidation reactivity of the active site is not affected by the presence of adsorbed oxygen. This requires that the adsorbed oxygen does not physically block the site, and does not affect the chemical nature of the site. Another possibility, which we feel is more plausible, is that oxygen and butene adsorb on different surface sites. The preadsorbed oxygen adsorbs on slightly reduced surface iron ions because of the high electron affinity of oxygen, and butene adsorbs on oxidized surface iron ions because of the high electron density of butene.

While preadsorbed oxygen showed no effects, the presence of gas phase oxygen was found to change the product selectivity. This effect was investigated by performing the thermal desorption in a carrier of three different oxygen partial pressures. Because of impurities in the helium supply and air-leak in the apparatus, the helium carrier purified by the silica gel trap at -196°C contained about 1.5×10^{-7} atm (1 atm = 101×10^3 Pa) of oxygen. If the trap temperature was at -160°C , the partial pressure of oxygen became 5×10^{-7} atm. Thermal desorption was then performed using helium carriers purified by these two methods and a pure oxygen carrier. The results are shown

in Table 2. Within experimental uncertainties, the desorbed products were the same using the two helium carriers. This indicated that small variations in oxygen partial pressure at these low values are not important. However, desorption in an oxygen carrier resulted in almost total combustion of hydrocarbon. By monitoring the temperature region in which the thermal desorption products appeared, it was found that in both He and O₂ carrier, butadiene desorbed below 210°C , and carbon dioxide between 210 and 430°C . Because readsorption of desorbed product was negligible under our conditions as determined above, this result indicated that the reaction of the adsorbed hydrocarbon is sensitive to the presence of gas phase oxygen.

The trends observed in Tables 1 and 2 for the adsorption-desorption experiments were also observed in pulse reaction experiments. Table 3 summarizes results of these pulse experiments. It shows that although preadsorbed oxygen did not affect the product distribution, using oxygen instead of helium as the carrier greatly increased the combustion reaction with substantial decrease in the isomers and butadiene production. Although readsorption of products was shown not to occur in the adsorption-desorption experiments, it could occur in these pulse reaction experiments. However, with the very small amount of catalyst used, the extent of readsorption should be small. Therefore, we can conclude that while preadsorbed oxygen shows no ef-

TABLE 3
Pulse Reaction of *cis*-2-Butene on α -Fe₂O₃^a

Reaction temperature (°C)	Carrier gas	Surface oxygen species	Pulse reaction Product distribution (10 ¹⁷ molecules)				Thermally desorbed products ^e (10 ¹⁷ molecules)	
			1-Butene	<i>t</i> -2-Butene	Butadiene	CO ₂ /4	Butadiene	CO ₂ /4
100	He	(γ) ^b	1.30	2.61	0.69	0	1.20	0.56
	He	(γ) ^b	1.41	3.07	0.77	0	1.17	0.66
	He	$\alpha + \beta + \gamma$ ^d	1.46	2.49	0.73	0	1.03	0.83
	O ₂	$\alpha + (\gamma)$ ^c	0.15	0.17	0.15	0.06	0	3.68
	O ₂	$\alpha + \beta + \gamma$ ^d	0.12	0.13	0.12	0.04	0	3.07
200	He	(γ) ^b	2.31	5.37	4.87	0	0	1.00
	He	$\alpha + \beta + \gamma$ ^d	2.35	5.12	4.66	0	0	1.00
	O ₂	$\alpha + \beta$ ^c	0.46	0.39	0.61	1.09	0	2.77
	O ₂	$\alpha + \beta + \gamma$ ^d	0.50	0.44	0.67	1.00	0	2.88
300	He	(γ) ^b	2.49	2.95	4.36	0.38	0	1.06
	O ₂	$\beta + \gamma$ ^d	0.47	0.43	1.60	0.83	0	0

^a About 40 mg of catalyst for a surface area of 0.7 m²; standard pretreatment of the catalyst; *cis*-2-butene pulse size 2.6×10^{18} molecules.

^b After standard pretreatment at 450°C, the catalyst was cooled in He to the reaction temperature at which butene pulses were introduced.

^c After standard pretreatment at 450°C, the catalyst was cooled in He to the reaction temperature. The carrier was then switched to oxygen before butene pulses were introduced.

^d After standard pretreatment at 450°C, the catalyst was cooled in O₂ to the reaction temperature. For those experiments using O₂ carrier, butene pulses were then introduced. For those using He carrier, the oxygen stream was switched to He, purged for 2 h before introduction of butene pulses.

^e After the entire *cis*-2-butene pulsed passed through the reactor, the catalyst was heated to 430°C in helium. These columns showed the amounts of thermally desorbed species.

fects, a high partial pressure of oxygen oxidizes rapidly the surface hydrocarbon species to combustion products.

The production of butadiene from butene involves at least three surface intermediates: adsorbed butene, π -allyl, and butadiene. One or more of these may be particularly vulnerable to attack by gas phase oxygen. The following series of experiments were performed to investigate this. First, the amounts of the various product precursors on the surface were investigated as a function of the desorption temperature. The results are shown in Fig. 4. In these experiments, after standard pretreatment of the catalyst and adsorption of *cis*-2-butene at -78°C, the catalyst was warmed up stepwise to the indicated temperatures for 0.5 h each. The desorbed products for each

interval were collected and analyzed. From these data, the cumulative amount for each product can be calculated. The difference between the total cumulative amount and the amount desorbed up to any temperature then corresponded to the amount of the precursors left on the surface, which are the values plotted in Fig. 4. Over this temperature range, the amount of CO₂ precursor was constant and was not shown. As seen from the figure, if the catalyst was at 25°C, most of the precursors for butene isomers and all of that for butadiene remained adsorbed. At 75°C, none of the isomer precursors was left, while most of the butadiene precursors still remained adsorbed.

The reactivity with gas phase oxygen of these adsorbed precursors was then investigated as follows. A catalyst with adsorbed

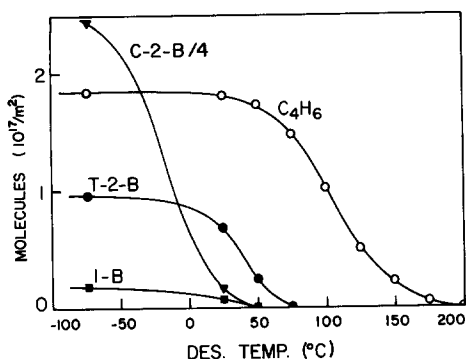


FIG. 4. The amounts of various product precursors adsorbed on the catalyst as a function of desorption temperature. Each precursor is labeled by the final product desorbed. Standard pretreatment of about 40 mg of catalyst, adsorption was achieved by 0.5 h trapping, 1 h purging at -78°C , desorption was by stepwise increase to the indicated temperatures. The amount of each precursor was assumed to be the same as the total cumulative amount of desorbed product minus the amount desorbed up to the indicated temperature.

cis-2-butene was warmed up in helium to either -78 , 25 , or 75°C (referred to as desorption temperature). Afterward the temperature was adjusted to the pulsing temperature at which a pulse of O_2 was passed over the catalyst. The number of O_2 molecules in the pulse was about three times the number of adsorbed butadiene precursor. After the O_2 pulse totally left the reactor, thermal desorption was carried out and the amounts of these thermally desorbed products are shown in Table 4. These data showed that the reactivity of adsorbed butene depends strongly on the desorption temperature, but only weakly on the pulsing temperature. For a desorption temperature of -78°C , the oxygen pulse did not change the thermal desorption products. For a desorption at 25°C , the oxygen pulse resulted in some degradation of butene isomers and a slight degradation of butadiene. For a desorption at 75°C , the oxygen pulse greatly degraded butadiene to carbon dioxide. Although the oxygen pulse size was small, it was sufficient to initiate the combustion of butadiene precursor. This is because a similar result was obtained if the

butadiene precursor was trapped for 0.5 h in a much larger pulse of oxygen (50×10^{17} molecules).

This series of experiment with oxygen pulses was also examined with adsorbed butadiene. The procedure used was identical to that with *cis*-2-butene except that butadiene was used. Figure 5 shows the amount of butadiene left on the surface after purging at the indicated desorption temperature. These values were determined by subsequent thermal desorption. Again the precursor for carbon dioxide was constant over this temperature range and is not shown. The reactivity with gas phase oxygen of the adsorbed butadiene was also investigated after desorption to either -78 , 25 , or 75°C . The results are shown in Table 5. The amount of butadiene left on the surface after -78°C adsorption was much larger than that at higher temperatures. This indicated multilayer adsorption at -78°C . The adsorbed butadiene at this temperature was inactive to gaseous oxygen. For the desorption at 25 and 75°C , O_2 pulses degraded the adsorbed butadiene even at a pulsing temperature of -78°C . This observation was similar to that observed for the butadiene precursor shown in Table 4.

Taking data from Tables 4 and 5 together, it can be concluded that the oxidative dehy-

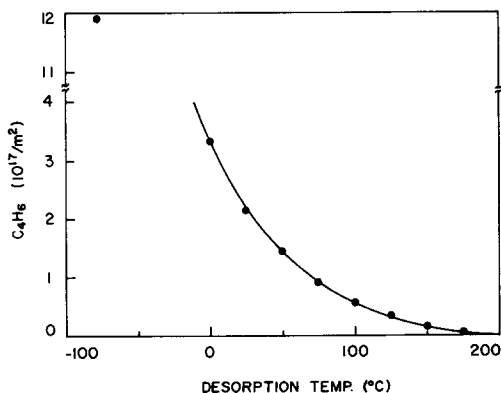


FIG. 5. The amounts of adsorbed butadiene as a function of desorption temperature. Experimental conditions were identical to those of Fig. 4.

TABLE 4
Reaction of Butadiene Precursors with Gas Phase Oxygen and N₂O on Iron Oxide^a

Catalyst desorption temperature (°C)	Gas pulse	Pulsing temperature (°C)	Pulse size (10 ¹⁷ molecules)	Thermal desorption products (10 ¹⁷ molecules/m ²)						Total C ₄
				1-Butene	<i>t</i> -2-Butene	<i>c</i> -2-Butene	Butadiene	CO ₂ /4		
-78	O ₂	None	None	0.23	0.90	9.0	2.21	1.05	13.4	
		-78	4.2	0.20	0.91	9.8	1.97	1.01	13.9	
25	O ₂	None	None	0.07	0.68	0.64	1.81	1.13	4.33	
		-78	4.2	0.05	0.33	0.46	1.78	1.57	4.19	
75	O ₂	25	4.2	0.03	0.29	0.38	1.53	1.88	4.11	
		None	None	0	0.02	0	1.47	1.13	2.62	
-78	-	-78	4.2	0	0	0	0.41	2.07	2.48	
		-78	50 ^b	0	0	0	0.30	2.08	2.38	
75	N ₂ O	75	4.2	0	0	0	0.27	2.31	2.58	
		None	None	0	0.02	0	1.47	1.13	2.62	
-78	-	-78	4.2	0	0	0	1.33	1.37	2.70	
		-78	50 ^b	0	0	0	1.40	1.36	2.76	

^a About 40 mg of catalyst for a surface area of 0.7 m²; standard pretreatment and adsorption of *cis*-2-butene.

^b These pulses were trapped in the reactor at -78°C for 0.5 h. The reactor was then purged, and thermal desorption followed.

TABLE 5
Reaction of Adsorbed Butadiene with Oxygen Pulses^a

Catalyst desorption temperature (°C)	Pulsing temperature (°C)	O ₂ pulse size (10 ¹⁷ molecules)	Thermal desorption product distribution (10 ¹⁷ molecules/m ²)		
			Butadiene	CO ₂ /4	Total C ₄
-78	None	None	11.9	2.96	13.0
	-78	4.2	12.0	2.91	12.6
25	None	None	2.18	2.39	4.57
	-78	4.2	1.40	2.68	4.08
75	-78	50	1.47	2.74	4.21
	None	None	0.97	2.39	3.36
	-78	4.2	0.36	2.71	3.07
	75	4.2	0.23	3.06	3.29

^a About 40 mg of catalyst for a surface area of 0.7 m²; standard pretreatment and adsorption of butadiene.

drogenation of butene to butadiene proceeds as follows. Butene first adsorbs onto the selective oxidation site without molecular transformation at low temperature. This adsorbed butene is inactive toward gas phase oxygen. Conversion of butene to π -allyl and then to butadiene takes place between 40 and 70°C. The adsorbed butadiene on this site is reactive toward gas phase oxygen. The π -allyl may also be reactive but we have no direct evidence to support it.

It should be mentioned that in the experiments reported in Tables 4 and 5, the number of oxygen molecules in the oxygen pulses were too small for the total combustion of the C₄ hydrocarbons. In fact only about one oxygen molecule in the oxygen pulse was consumed for every adsorbed butadiene precursor, whereas eight oxygen molecules were required for total combustion of butene. Thus the eventual combustion to CO₂ on thermal desorption had to be

TABLE 6
Reaction of Butadiene Precursor on a Partially Reduced Iron Oxide with Gas Phase Oxygen^a

Sequence of experiment ^b	Thermal desorption procedure	Thermally desorbed products (10 ¹⁷ molecules/m ²)				
		1-Butene	<i>t</i> -2-Butene	<i>c</i> -2-Butene	Butadiene	CO ₂ /4
1	Std ^c	0.21	0.75	8.6	1.79	0.91
2	Std	0.34	1.14	9.1	1.79	0.39
3	Std	0.36	1.24	8.9	1.19	0.20
4	75-78°C O ₂ ^d	0.30	1.09	10.9	0.13	1.68
5	Std	0.37	1.31	9.3	1.30	0.20

^a About 40 mg of catalyst for a surface area of 0.7 m²; standard pretreatment and adsorption of the catalyst before the first experiment.

^b Experiments were conducted in the indicated order. The catalyst was not exposed to oxygen between experiments.

^c A standard procedure involved adsorption of *cis*-2-butene and purging at -78°C, and then thermal desorption to 430°C.

^d In this experiment, after adsorption and purging of *cis*-2-butene at -78°C the catalyst was warmed to 75°C for 0.5 h, cooled to -78°C when a pulse of 4.2 × 10¹⁷ molecules of O₂ passed over the catalyst. This was followed by thermal desorption.

accomplished with participation of lattice oxygen. However, the participation of lattice oxygen was required equally in experiments with and without admission of the oxygen pulse. Therefore, the difference in the ratio of butadiene to CO_2 reported in these two tables for the different experiments reflected the reactivity of the butadiene precursor with gas phase oxygen and not the effect of lattice oxygen.

It should also be emphasized that the term gas phase oxygen is used loosely to include both gas phase and weakly adsorbed oxygen molecules. It does not imply a straight Rideal-Eley mechanism.

Degradation of the butadiene precursors by another oxidant N_2O was also studied in experiments similar to those using O_2 pulses. In these experiments, the catalyst was pretreated under the standard conditions. After adsorption of *cis*-2-butene at -78°C , the catalyst was warmed to 75°C . If the catalyst was cooled back to -78°C at which a pulse of N_2O of 4.2×10^{17} molecules was passed over the catalyst, subsequent thermal desorption resulted in products identical to those without the N_2O pulse (Table 4). That is, at -78°C , N_2O did not degrade the butadiene precursors. However, if the N_2O pulse was administered at 75°C , the amount of subsequent thermally desorbed CO_2 increased but only by half as much as the increase using O_2 pulse. This increase in CO_2 production can be attributed to the decomposition of N_2O into N_2 and O_2 , and the O_2 then caused degradation of butadiene precursors.

In order to test whether or not the lack of observable degradation in butadiene production by N_2O at -78°C was due to the fact that N_2O was not activated at this temperature, the following experiment was performed. On a catalyst with adsorbed *cis*-2-butene after 75°C desorption, the degree of decomposition of the N_2O pulse on passing over the catalyst at -78°C was monitored by analyzing the composition of the exiting pulse. With 50×10^{-7} molecules of N_2O in the pulse, 3.8×10^{16} N_2 molecules but no

O_2 molecules (except the background of about 0.1×10^{16} molecules) were collected. Thus 3.8×10^{16} O atoms must have stayed on the surface. If each O atom resulted in the degradation of one butadiene precursor, the decrease in butadiene yield would be detectable. However, if every two O atoms combined to form an O_2 species which then reacted with the butadiene precursors, the decrease in butadiene yield became comparable to the experimental uncertainty, and more experiments had to be performed to reduce the standard deviation before a conclusion can be drawn. It should be mentioned that at -78°C , about 3×10^{17} molecules of N_2O were adsorbed on the catalyst that can be desorbed below 75°C with some decomposition.

The difference in reactivity of the butadiene precursors toward O_2 and N_2O is interesting. N_2O is known to be active in selective oxidation (14). It is also known that on molybdenum oxide (14) and cobalt-magnesium-oxide (15), N_2O decomposes at room temperature to form O^- adsorbed species which is very active in the oxidative dehydrogenation of ethane. Our results suggested that the degradation of butadiene precursors on iron oxide requires an O_2 and not an O^- species. This implies that the degradation proceeds via a peroxide intermediate.

The reactivity of the butadiene precursor toward gas phase oxygen on a slightly reduced catalyst surface was also investigated. Table 6 shows the typical data for one such sequence of experiments. Reduction of the catalyst was achieved by thermal desorption of butene in a helium carrier because the production of carbon dioxide, water, and butadiene must be accompanied by reduction of the surface. Therefore, by repeatedly performing thermal desorption of butene without reoxidizing the catalyst in between desorptions, the catalyst can be increasingly reduced. In the sequence of experiment shown in Table 6, the catalyst after the standard pretreatment was subjected to three consecutive thermal desorp-

tion cycles without exposure to oxygen. The production of CO₂ and butadiene gradually decreased, indicating reduction of the catalyst. After the third cycle, the catalyst was exposed to butene, warmed up to 75°C, and then cooled to -78°C when a pulse of oxygen was passed over the catalyst. Subsequent thermal desorption showed that, similar to data in Table 4, severe degradation of butadiene precursor occurred. A fifth thermal desorption cycle following that reproduced the data of the third cycle. Thus the behavior of the butadiene precursor was the same on an oxidized and a reduced surface.

CONCLUSIONS

Based on the results presented, the following conclusions can be drawn.

(1) Preadsorbed oxygen on iron oxide does not affect the adsorption of butene or the oxidation of butene to butadiene and carbon dioxide. Since oxygen adsorption is usually accompanied by electron transfer from the solid, the adsorption probably occurs on slightly reduced surface iron ions. Then butene probably adsorbs on oxidized surface iron ions.

(2) The precursors to butadiene is very reactive to gas phase oxygen. The degradation of the precursors probably occurs via its reaction with weakly adsorbed oxygen which is present in a significant amount only in the presence of gaseous oxygen. The precursors, however, reacts much less rapidly with N₂O. This may suggest that the degradation proceeds via a peroxide intermediate. The reaction of butadiene precursors with oxygen has very low activation energy, and proceeds rapidly even at -78°C.

(3) Together with the results of the earlier investigations (8, 13), it can be concluded that there are two types of oxidation sites on iron oxide. The first type, the combustion site, produces only carbon dioxide and water. The second type, the selective oxidation site, produces either butadiene or carbon dioxide in two competing pathways.

Butene adsorbs on this site is transformed at 40-70°C to adsorbed π -allyl and adsorbed butadiene. The rate of transformation increases with temperature. However, these adsorbed butadiene precursors can also react with weakly adsorbed oxygen and undergo degradation. The rate of this latter process depends only very weakly on temperature, but on the oxygen partial pressure. Therefore, as shown in Table 3, the degree of degradation in butadiene production from this site decreases with increasing temperature for the same oxygen partial pressure, but increases with increasing oxygen pressure.

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