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The Catalytic Oxidation of 1-Butene over Bismuth Molybdate

V. The Kinetics of the Oxidation: B. Experiments with Continuous Flow and Recirculation; Reduction and Reoxidation of Bi–Mo

PH. A. BATIST, H. J. PRETTE, AND G. C. A. SCHUIT

From the Department of Inorganic Chemistry, Technological University, Eindhoven, The Netherlands

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The kinetics of the oxidation of 1-butene over the $Bi_2O_3 \cdot MoO_3$ (koechlinite) catalyst were investigated in continuous flow experiments and in experiments with recirculation of the feed. The reaction was strongly inhibited by the product butadiene especially at lower temperatures and is zero-order in the oxygen pressure. The order of the butene partial pressure could not be determined because of the predominance of the inhibition by the product. The initial rate of reduction of the catalyst by 1-butene is approximately equal to that of the catalytic reaction: it is also strongly inhibited by butadiene and the rate appears to be determined by the combined influences of inhibition and progressive oxygen depletion. Contrary to reduction by hydrogen, that follows the usual parabolic law, it does not progress further than Mo^{5+} and Bi^{3+}. Reoxidation of catalyst once reduced is fast and not inhibited by butadiene. Therefore, the diene inhibition has to be viewed as a competition between butene and butadiene for the same oxidized site. It is concluded that the absence of diene inhibition in pulse experiments is caused by the diene adsorption being slow in comparison to the residence time in pulse technics. By combining the data the conclusion can be drawn that the curved log k vs. $1/T$ relation observed is caused by the interference of the diene inhibition. The diene-inhibited reaction has an activation energy of 36 kcal mole^{-1}, the noninhibited reaction, of 11 kcal mole^{-1}.

INTRODUCTION

In the present paper we are concerned with kinetics of the oxidation over the $Bi_2O_3 \cdot 2MoO_3$ catalyst, low-temperature koechlinite. A preceding paper (*1*), described this catalyst as somewhat unusual in its kinetic behavior. We shall report on the oxidation of 1-butene, carried out either in continuous flow or under recirculation conditions in order to obtain more detailed information about the kinetic expression.

In the continuous flow 1-butene is oxidized in a single passage with artificial air, a mixture of 80% helium and 20% oxygen, and the conditions are characterized by a steady state situation at the catalyst surface. In the recirculation experiments (a closed system), 1-butene and oxygen, diluted with helium, and the products repeatedly pass the catalyst. Now the composition of the supply changes proportionally to the reaction and there is no steady state. The reason, why the various forms of studying the oxidation reaction were chosen, is that they represent situations in which the ratios of hydrocarbon to active sites (or of hydrocarbon to lattice oxygen in the catalyst) differ considerably. For the technics used they are increasing in the sequence: Pulse reaction < Continuous flow, and Recirculation. Moreover, they represent situations in which adsorption–desorption reactions attain equilibrium. In the pulse experiments the inhibition by products may be considered as negligible, because there is simply not enough produced to cover all the sites. In the flow experiments inhibition may be of predominant influence. Recirculation particularly is suited to demonstrate inhibition kinetics in the case that the products are more strongly adsorbed on the catalyst than the corresponding reactants. Continuous flow experiments are not particularly suitable for the detection of reduction–reoxidation mechanism, because the catalyst, in the absence of gaseous oxygen, rapidly loses its oxidizing capacity. Recirculation experiments, carried out with 1-butene in the absence of gaseous oxygen, are more instructive in this connection, and are particularly suitable where it is intended to deplete the catalyst as function of time with the aim to demonstrate to which extent the bulk oxygen is able to react. The catalyst once reduced can also be reoxidized with oxygen during recirculation and the possibility is created to compare the speed of reduction and that of reoxidation of the catalyst. If, therefore, a certain model such as the reduction–reoxidation mechanism is discussed, we shall have to show that it is in agreement with the results obtained in the various types of experimental setups, with the additional demand that the kinetics of the reaction arise from one and the same kinetic expression modified in accordance with the experimental situation.

Experimental Procedures

A. *Continuous Flow*

Different weights of catalyst (particle size 0.20–0.40 mm) were used in a quartz-glass microreactor with a bore of 10 mm. Constant feeds of 1-butene (20 ml min^{-1}) and of artificial air (100 ml min^{-1}), regulated by Tri-Flat tubes, were brought into contact with the catalyst at different

TABLE 1
Scheme of Calculations

Temp. (°C)	O_2	CO_2	1-Butene	*trans*	*cis*	Diene	Steam	Y^a	$Y_0 - Y$
Recorded signals									
—	67	—	129	—	—	—	—	—	—
343	60	1.8	108	1.4	2.0	15.4	—	—	—
355	55.5	2.7	92	2.4	3.6	27.6	—	—	—
367	50	4.0	70.8	6.2	5.6	44.8	—	—	—
379	44	5.8	46.4	7.2	8.8	62.4	—	—	—
391	40	6.6	30.0	9.4	9.8	75.4	—	—	—
414	32	10.4	11.2	11.2	9.6	90.4	—	—	—
Corrected signals									
—	134	—	129	—	—	—	—	—	—
343	120	3.2	108	1.4	2.0	15.9	19.1	—	—
355	111	4.9	92	2.4	3.6	28.4	33.3	—	—
367	100	7.2	70.8	6.2	5.6	46.1	53.3	—	—
379	88	10.4	46.4	7.2	8.8	64.2	74.6	—	—
391	80	11.9	30.0	9.4	9.8	77.6	89.5	—	—
414	64	18.7	11.2	11.2	9.6	93.1	111.8	—	—
Gas composition (%)									
—	51.0	—	49.0	—	—	—	—	49.0	—
343	44.6	1.2	40.0	0.5	0.7	5.9	7.1	41.3	7.7
355	40.3	1.7	33.4	0.9	1.3	10.3	12.0	35.6	13.4
367	34.6	2.5	24.5	2.1	1.9	15.9	18.4	28.5	20.5
379	29.8	3.5	15.5	2.4	2.9	21.4	24.9	20.3	28.7
391	26.0	3.9	9.7	3.0	3.2	25.2	29.0	16.0	33.0
414	20.0	5.9	3.5	3.5	3.0	29.1	35.0	10.0	39.0

[a] Y = total butenes.

temperatures, in order to obtain information about the butene conversion as function of reaction temperature. For determination of order dependencies a constant weight of catalyst at a constant temperature was brought into contact with feeds varying in composition. Via a switch cock, samples of exit gas were pulsed to a 8-m column with He carrier gas, filled with 30% by weight of 2.4 dimethylsulfolane on chromosorb (30–50 mesh) to separate the gas components. The advantage of oxidation with artificial air instead of normal air is that now pure oxygen (not mixed with N_2) can also be detected. The amount of steam produced during oxidation is easily calculated by summation of the amounts of CO_2 and butadiene. Table 1 illustrates the method of calculation, when 1-butene and artificial air (19.6 and 100 ml min^{-1}, respectively) are fed to 800 mg of catalyst at different temperatures. For comparison of the gas components in unity of volume, the recorded signals have to be corrected by multiplication with the appropriate factors, i.e., CO_2, $1.8\times$; O_2, $2.0\times$; diene $1.03\times$; after which the data in the form of corrected signals can be obtained, then the steam values are inserted in Table 1 and apart from small amounts of undetectable compounds the list of gaseous components is complete. If the total amount is considered as 100%, then the composition of the gas can be expressed in percent. The conversion is defined as the

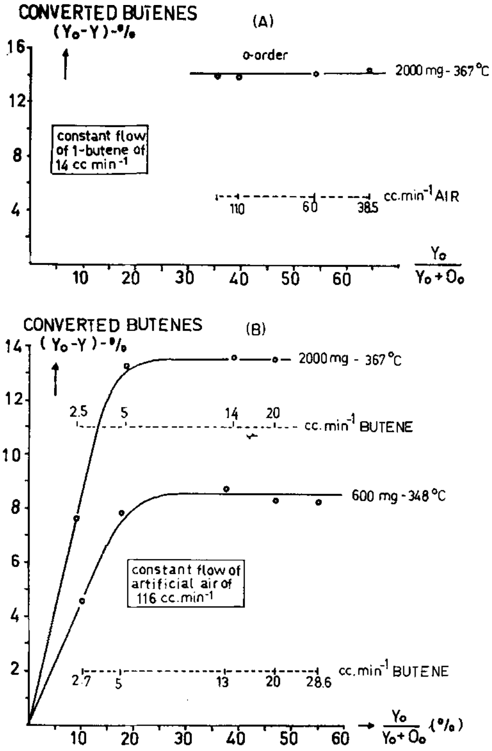

FIG. 1. Reaction kinetics: (A) the dependency on oxygen pressure; (B) the dependency on butene pressure.

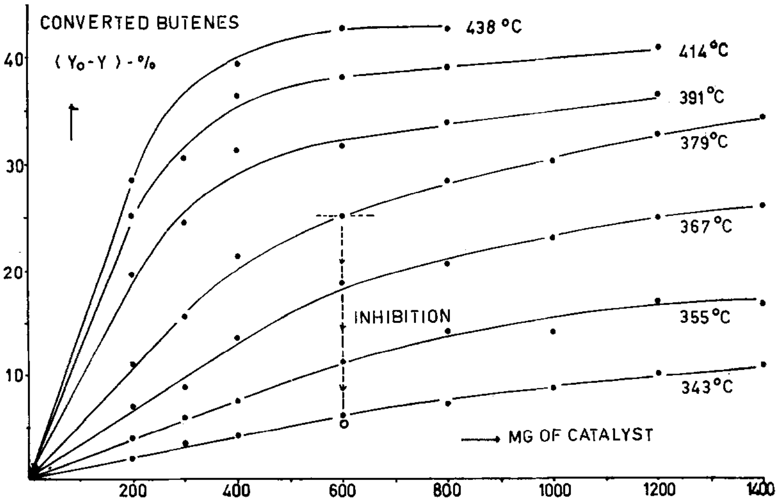

FIG. 2. Butene conversions as a function of the amount of catalyst at various temperatures: constant feeds of 20 ml min^{-1} of 1-butene and 100 ml min^{-1} of artificial air.

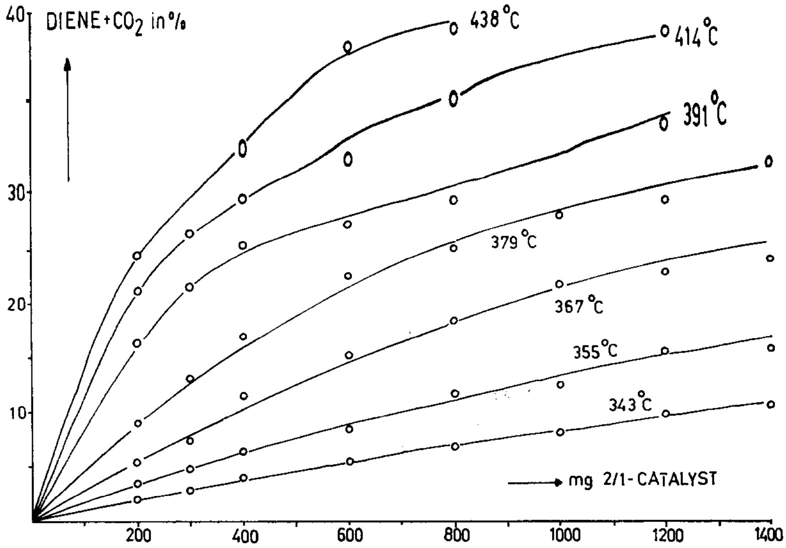

FIG. 3. Formation of oxidation products as a function of the amount of catalyst at various temperatures.

difference of butene concentration before and after reaction.

B. Recirculation

The apparatus consisted of the following accessories: a quartz-glass microreactor filled with 500 mg of catalyst (particle size 0.20–0.40 mm), a furnace, a trap filled with 5 ml of water, a magnetic pump with a gas speed of 350 ml min^{-1}, a flow rater, pressure meters, gas bulbs of 58 and 43 ml, 10 storage valves of 1.5 ml each and a switch cock connected with the column of a gas chromatograph for leak control and for analysis. The total volume of the apparatus was 280 ml. Before starting the oxidation, the apparatus was tested to be free from air leakage for a long period of pumping with He. Mixtures of oxygen and 1-butene, diluted with He, were pumped over the catalyst at various temperatures. At different times, gas samples were drawn from the circulation apparatus and storaged in some of the valves. After termination of the experiments the tube, containing the 10 valves, was unscrewed and connected to the column of the gas chromatograph, after which the samples were analyzed successively.

The water vapor produced during the

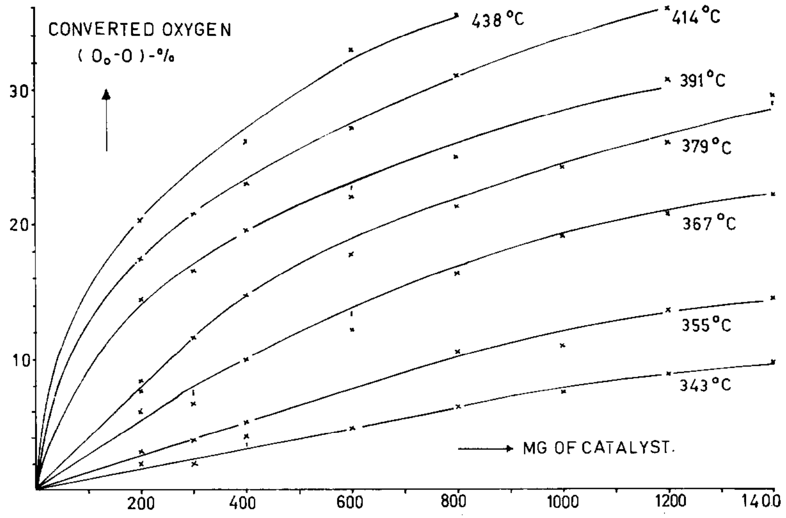

FIG. 4. Oxygen conversions as a function of the amount of catalyst at various temperatures.

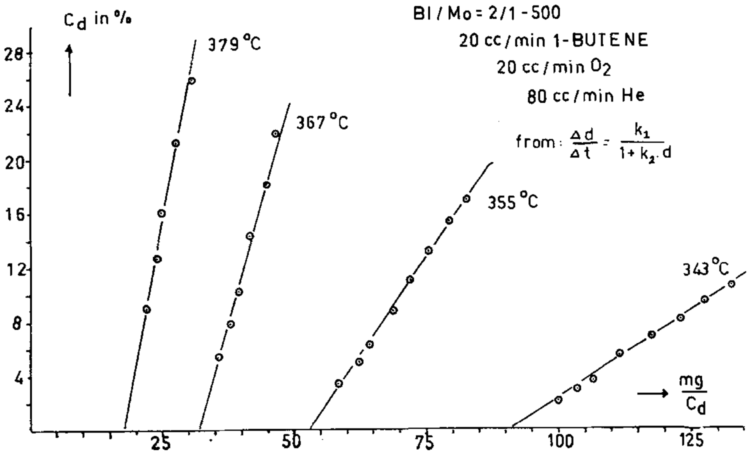

FIG. 5. Continuous flow data at temperatures below 390°C plotted according to Eq. (2).

oxidation is condensed in the trap while the reactants and products, with a constant grade of humidity, are pumped back to the catalyst. The reaction, therefore, is conditioned by a constant water vapor pressure and no information can be obtained with regard to the influence of water on the rate.

The reduction and reoxidation experiments were also carried out in the recirculation apparatus. The reduction of the catalyst with 1-butene in the absence of gaseous oxygen occurred in the range of temperatures between 320 and 467°C. The reoxidation of the catalyst proceeded at lower temperatures and n-butane, which is not oxidizable in our experiments, was used as a reference in measuring the oxygen concentrations.

RESULTS

Continuous Flow Experiments

The experiments were started with an investigation concerning the partial pressure dependencies. In Fig. 1B, the dependency of the butene conversion on the butene partial pressure is represented. With a constant flow of artificial air and varying flows of 1-butene over 600 mg of

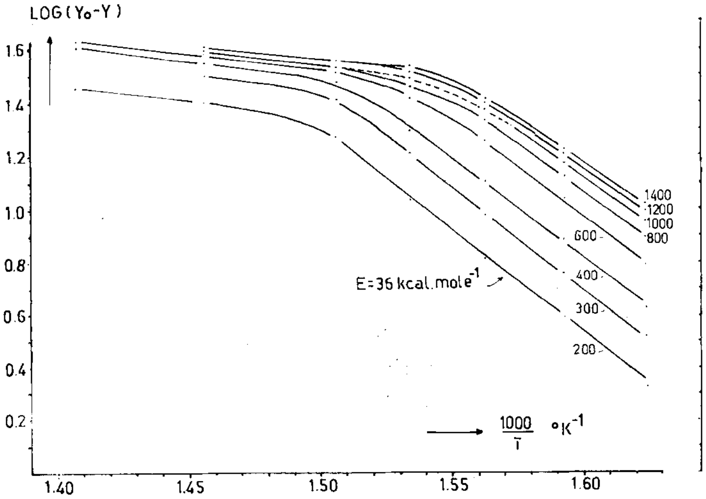

FIG. 6. Arrhenius plot for all continuous flow data, including the high-temperature data, treated according to zero-order kinetics on butene and zero-order kinetics on oxygen.

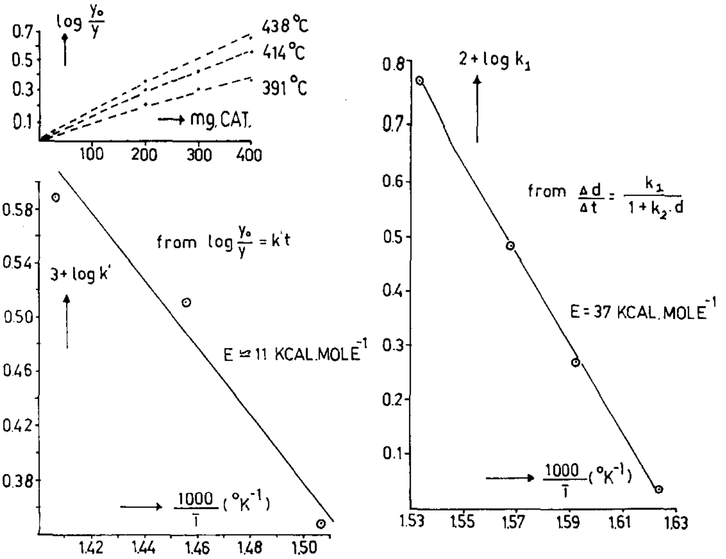

FIG. 7. Arrhenius plots for the data at low temperatures (right side) and for the data at high temperatures (left side).

catalyst at 348°C, the butene conversion reached a constant level at butene inputs surpassing 5 ml min^{-1}, which pointed to a zero-order dependency of butene in this range. Only with butene flows smaller than 5 ml min^{-1} the reaction appeared to be first order in butene. Because of this striking change of order, we repeated this experiment in another microreactor with a bore of 13 mm with more catalyst and at 367°C. Again the same phenomena are observed (see the center of Fig. 1). In Fig. 1A, the dependency on the oxygen partial pressure is represented. With a constant input of 1-butene and varying inputs of artificial air over 2000 mg of catalyst at 367°C the conversion of butenes was constant, which pointed to a zero-order dependency on the oxygen partial pressure. The range of oxygen partial pressures is somewhat restricted: on one side by the danger of explosion when high oxygen concentrations are used, on the other side by an incipient reduction of the catalyst with too low feeds of artificial air. In Fig. 2 the conversion of butenes is represented, for constant feeds of 19.6 ml min^{-1} of 1-butene and 100 ml min^{-1} of artificial air, brought into contact with different weights of catalyst at various reaction temperatures. The formation of oxidation products is represented in Fig. 3 and the corresponding conversions of oxygen in Fig. 4. Figure 2 shows that with higher amounts of catalyst, the conversions do not increase linearly with the amount of catalyst; they curve sharply, which we assumed as being caused by butadiene inhibition. This assumption was tested on its validity with an experiment at 379°C with 600 mg of catalyst in

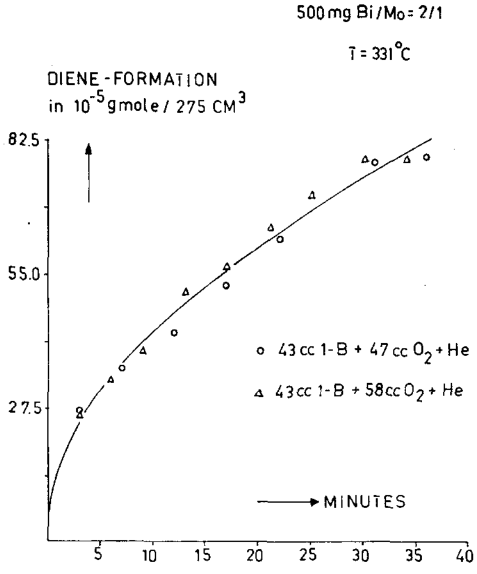

FIG. 8. Circulation experiments: determination of the dependency on oxygen pressure.

which feeds of 1-butene and artificial air (19.6 and 100 ml min^{-1}, respectively) were supplied with 17.6 ml min^{-1} of butadiene. The marked point in Fig. 2 shows the conversion of butene to be strongly decreased when butadiene was admixed to the feeds of reactants. It was necessary to represent the curved lines in Fig. 3 and at temperatures below 391°C by the following formula:

$$-\frac{\Delta c}{\Delta t} = \frac{\Delta d}{\Delta t} = \frac{k_1}{1 + k_2 \cdot d} \tag{1}$$

in which c represents the butene concentration and d the diene concentration. After integration one obtains:

$$d = 2k_1t/k_2d - 2/k_2, \tag{2}$$

and it is shown in Fig. 5 that for the whole range of weights of catalyst and below 391°C, straight lines are indeed obtained, allowing the calculation of k_1 and k_2. They are summarized in Table 2. It can be derived from Eq. (1) that in the initial stage of the conversion, i.e., at low diene contents one obtains:

$$\frac{\Delta d}{\Delta t} = k_1, \tag{3}$$

which represents a zero-order reaction. Indeed the slopes of the conversion–catalyst weight curves between 200 and 500 mg are

TABLE 2
RATE CONSTANTS AT DIFFERENT TEMPERATURES

Temp. (°C)	k_1 ($\times10^{-2}$; %/mg)	k_2 ($\times10^{-2}$) (%)$^{-1}$	k_1 (initial slopes) ($\times10^{-2}$)
343	1.0909	8.465	1.0092
355	1.8668	6.428	1.9069
367	3.0550	3.823	3.1877
379	5.8750	6.237	5.3207

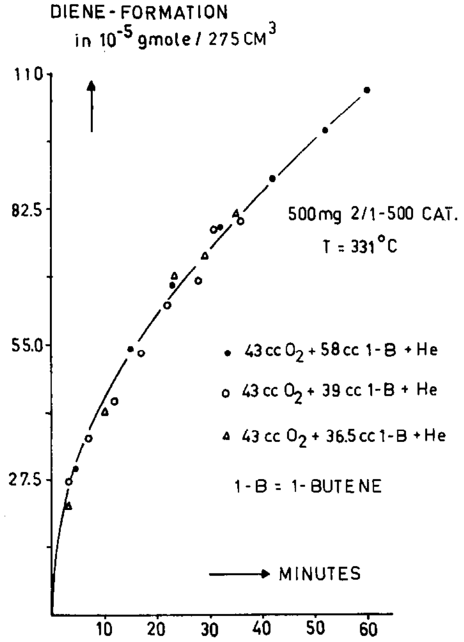

FIG. 9. Circulation experiments: determination of the dependency on the butene pressure.

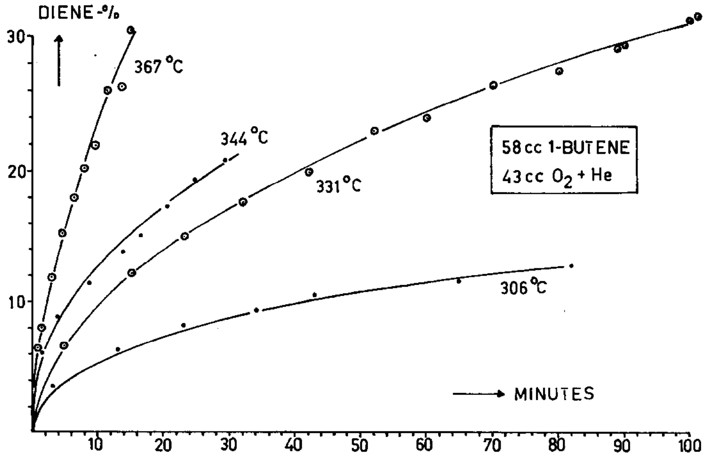

FIG. 10. Butadiene formation as a function of time at various temperatures on 500 mg of Bi/Mo = 2/1 catalyst.

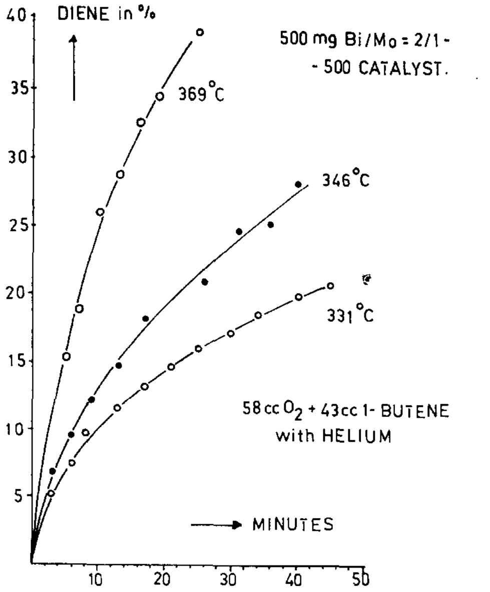

FIG. 11. Butadiene formation as a function of time at various temperatures on 500 mg of catalyst.

fairly straight in accordance with the integrated formula:

$$d = k_1 \cdot t \qquad (4)$$

Data for k_1 obtained in this way are compared with those for the total lines and are seen to be in satisfactory agreement herewith. From these k_1-values we calculated the activation energy of 37 kcal mole^{-1}, as shown in Fig. 7 on the right side.

When the whole range of experimental data of Fig. 2, including those at the higher temperatures, were treated according to zero-order kinetics in 1-butene and in oxygen, then going from low to high reaction temperatures the earlier reported (*1*) change of activation energy was observed again (see the right side of Fig. 6). Furthermore, Eqs. (1)–(4) do not fit the data obtained at temperatures above 391°C. However, the data in Fig. 2 at the temperatures higher than 391°C seem to fit first-order kinetics in butene and zero-order kinetics in oxygen:

$$-\Delta c/\Delta t = k' \cdot c, \qquad (5)$$

the expression earlier reported by Adams *et al.* (*2*).

The data in Fig. 2, belonging to the temperature range 391–438°C, treated according to this assumption are represented in Fig. 7 (the top print on the left side). The activation energy calculated, also represented in Fig. 7 (on the left side) proved low, 11 kcal mole^{-1}, hence in full agreement with the results of the pulse experiments.

Recirculation Experiments

All experiments were carried out in a He atmosphere with 500 mg of catalyst, not replaced during the various oxidations, in order to maintain the profile of flow

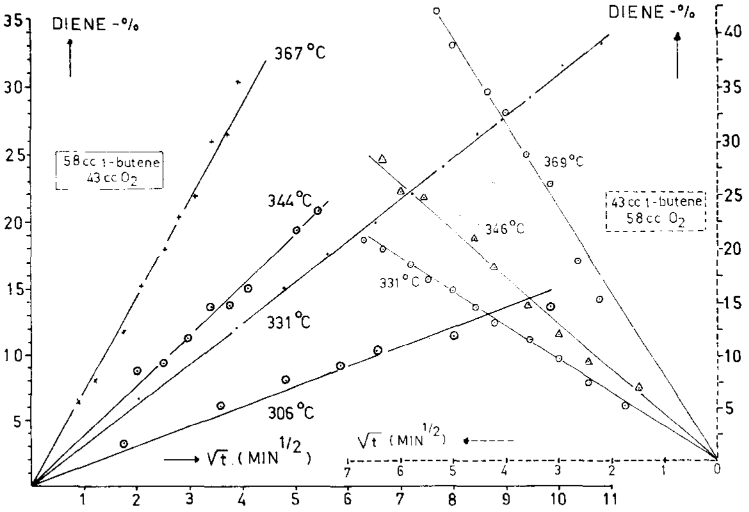

FIG. 12. Data of recirculations plotted according to Eq. (7).

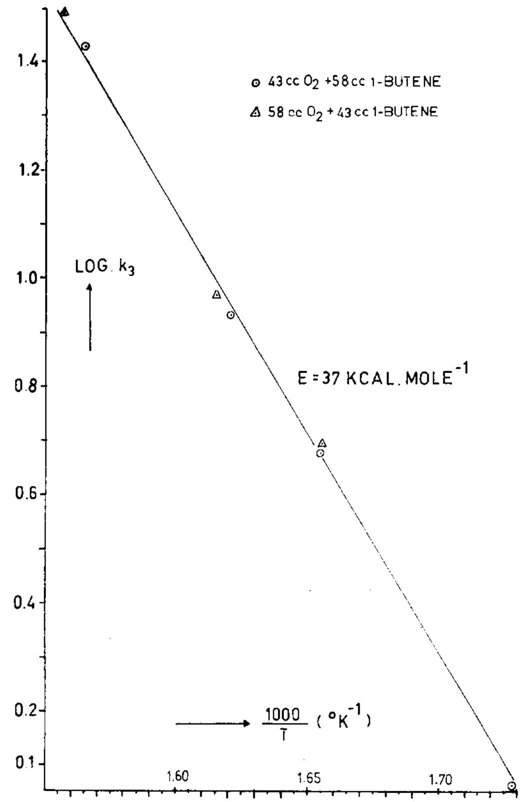

FIG. 13. Arrhenius plot for the data of recirculation experiments.

through the bed constant. The activity of the catalyst remained stable during all our operations, presumably because after each run the catalyst was reactivated by pumping air over it at 367°C. Also here the kinetics were investigated. In Fig. 8 we represent the results of the oxidation of 43 ml of 1-butene with different amounts of oxygen (47 and 58 ml) by plotting the diene formation against the reaction time. The data for both runs, carried out at 331°C, fit the same line, from which we conclude that different amounts of oxygen do not affect the diene production, provided that sufficient oxygen is present to prevent reduction of catalyst. It is hence confirmed that the reaction is zero order in oxygen. In Fig. 9 experiments are represented in which a constant amount of oxygen (43 ml) is used with varying amounts of 1-butene and again the diene production as function of time appears not affected by

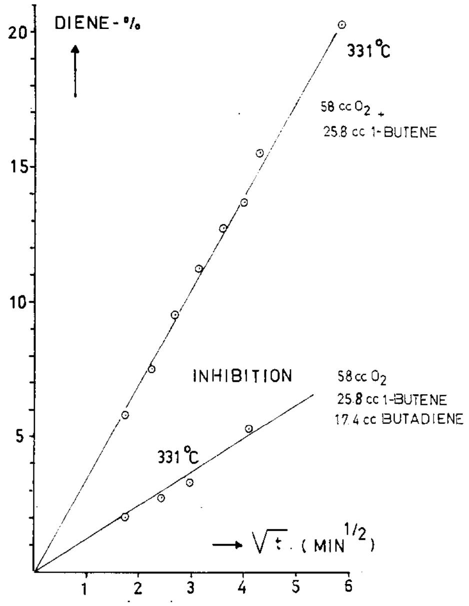

FIG. 14. Decrease of speed of reaction when diene is admixed to butene and oxygen.

the amount of 1-butene used, in other words the reaction seems to be 0-order with respect to 1-butene. In Fig. 10 a series of experiments are represented in which 43 ml of oxygen and 58 ml of 1-butene are recirculated over the catalyst at 4 different temperatures. Similar experiments are carried out with 43 ml of 1-butene and 58 ml

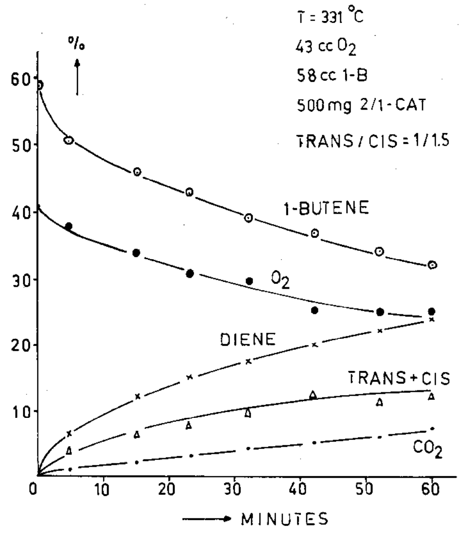

FIG. 15. Product distribution at 331°C as a function of time.

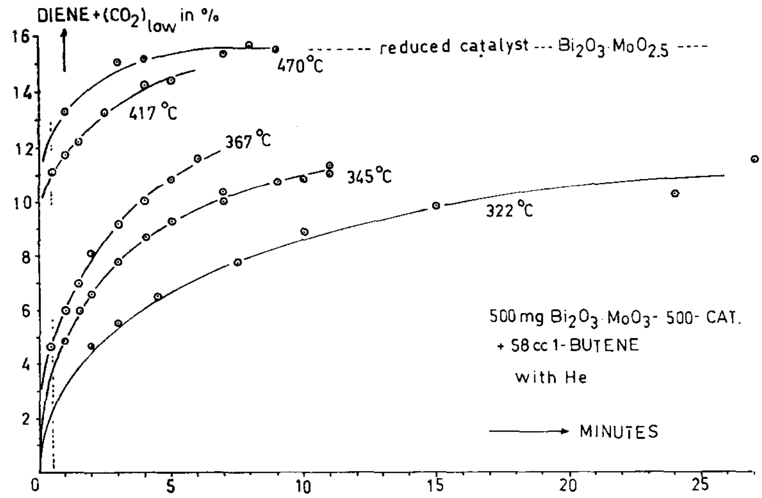

FIG. 16. Formation of oxidation products during reduction of 500 mg of catalyst at various temperatures.

of oxygen at 3 different temperatures and the results are given in Fig. 11.

The data were adapted to a kinetic expression in which the inhibition by butadiene was considered to be predominant:

$$\Delta d/\Delta t = k_3/d. \qquad (6)$$

After integration:

$$d = (2k_3)^{1/2} \cdot (t)^{1/2}. \qquad (7)$$

All experimental data fit the integrated equation (see Fig. 12) and from the slopes of the lines the rate constants (k_3) are calculated. They are given in Table 3.

For both series of experiments, the Arrhenius plot is represented in Fig. 13 and the value of the activation energy of 37 kcal mole^{-1} is found to be the same as derived in the continuous flow experiments in the low range of temperatures. From Eq. (7), one has to expect that when diene is admixed previously to 1-butene and oxygen the rate will be strongly affected. This is confirmed experimentally and the results are represented in Fig. 14. Finally in Fig. 15 the product distribution is represented when 58 ml of 1-butene and 43 ml of oxygen were recirculated over the catalyst at 331°C.

Reduction and Reoxidation Experiments

The results of the reduction of 500 mg of catalyst with 58 ml of 1-butene at different temperatures, carried out in the recirculation apparatus in helium atmosphere and in the absence of gaseous oxygen, are represented in Fig. 16, where the diene formation is plotted against the reduction time. As shown, the reaction, carried out at for instance 470°C, is terminated when 15.5% butadiene is produced. This corresponds to an amount of removed bulk oxygen according to the following reaction:

$$Bi_2O_3 \cdot MoO_3 \rightarrow Bi_2O_3 \cdot MoO_{2.5} + 0.5\ O_{at}.$$

TABLE 3
RATE CONSTANTS AT DIFFERENT TEMPERATURES

Temp. (°C)	$k_3[(\%)^2\ min^{-1}]$	Temp. (°C)	$k_3[(\%)^2\ min^{-1}]$
With 58 ml of 1-butene + 43 ml of O_2		With 58 ml of O_2 + 43 ml of 1-butene	
306	1.155	331	4.961
331	4.743	346	9.245
344	8.50	369	30.968
367	26.94		

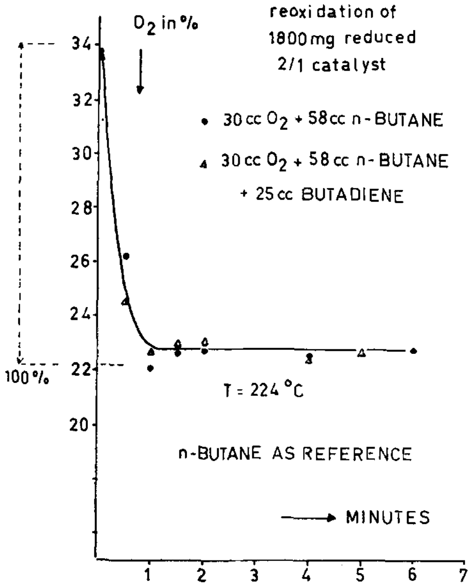

FIG. 17. Reoxidation of reduced catalyst at 224°C in the presence and in the absence of butadiene.

As much oxygen is removed as corresponds with the transformation of Mo^{6+} into Mo^{5+}. The reduction at 470°C proceeds very fast and the initial steps are hard to measure. In the lower range of temperatures (322–367°C) the speed of reduction is decreased, and it is shown in Fig. 16 that less oxygen is removed from the bulk. We will pay attention to some general aspects: (i) The X-ray diagram of the reduced material (of a blue black color) was similar to that of the nonreduced yellow catalyst. All reflections were present although sometimes with a small decrease in the intensities. Apparently, the position of the metal atoms is not affected by reduction, obviously a favorable property for a stable catalyst. (ii) Reoxidation of the reduced Bi/Mo-2/1 catalyst with gaseous oxygen proceeded so fast that we were forced to carry out the reaction at much lower temperature in order to measure the rate. The results of reoxidation of 1800 mg of reduced material at 224°C are represented in Fig. 17 and it is seen that even at this temperature the catalyst is reoxidized for 95% within 1 min, producing a green colored substance. To reach the 100% level of reoxidation (a yellow catalyst) higher reaction temperatures were required. Only for the reoxidation of the last 5% the slow oxygen diffusion phenomena became evident.

It is also shown in Fig. 17 that when the experiment is repeated with a mixture of gaseous oxygen and butadiene the fast rate of reoxidation is not inhibited by the presence of butadiene: in other words, there is no strong interaction between butadiene and the reduced site. Generally, one may conclude that the rate of reoxidation of a reduced site is faster than the rate of formation of a reduced site. Among

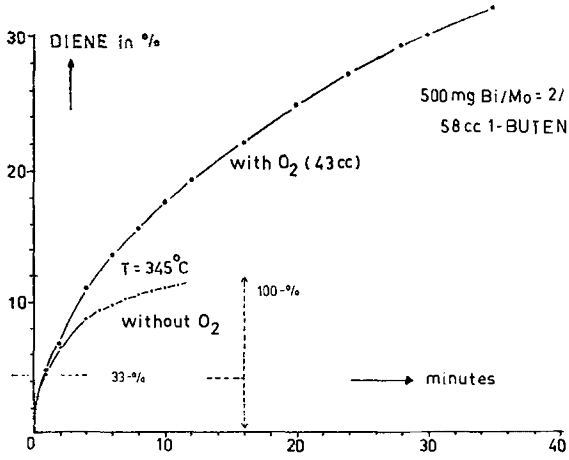

FIG. 18. Butadiene formation at 345°C as a function of time in the presence and in the absence of gaseous oxygen.

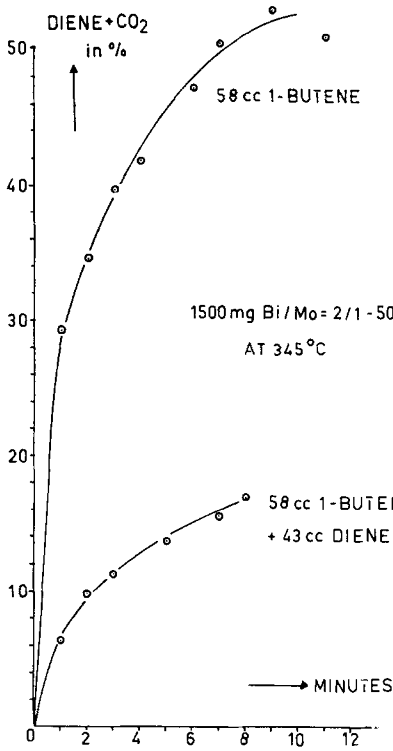

FIG. 19. Decrease in speed of reduction by the presence of butadiene.

other things this accounts for the zero-order dependency of oxygen of the catalyzed reaction. (iii) Consequent to the reduction–reoxidation mechanism, mentioned here, one has to expect that under recirculation conditions the initial speed of the reduction must be equal to that of the butene oxidation with gaseous oxygen. This was confirmed by comparing experiments at 344 and 345°C in which 500 mg of catalyst reacted with 58 ml of 1-butene, either in the presence of 43 ml of oxygen or in the absence of this gas: both represented in Fig. 18; as shown, within 2 min the diene formations in both experiments were equal, the curves coincide initially. (iv) Since we know that the butene oxidation is strongly inhibited by butadiene, this appears to prove that the surface reaction leading to the reduction must also be inhibited by butadiene. In fact, as is shown in Fig. 19, representing experiments in which 1500 mg of catalyst is reduced either by 58 ml of 1-butene at 345°C or by a mixture of 58 ml of 1-butene and 43 ml of butadiene, the presence of butadiene suppresses the rate of reduction. (v) The results of reduction of 326 mg of catalyst with a mixture of 20% H_2 + 80% N_2, carried out with a Stanton Thermo Balance at 2 different temperatures, are represented in Fig. 20. As shown, the reductions with hydrogen are slow and far more oxygen is removed from the bulk than in the reduction experiments with 1-butene (see Fig. 16). The amount of 33 mg of oxygen, finally re-

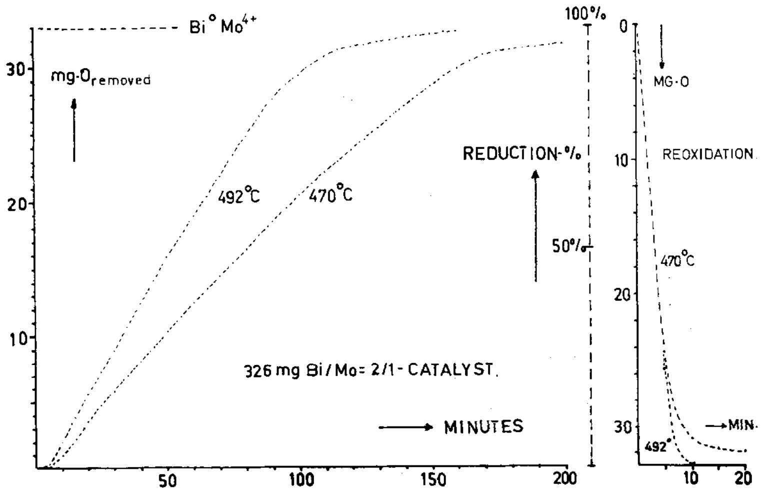

FIG. 20. Reduction of catalyst with hydrogen as a function of time at two temperatures: reoxidation of reduced material with air as a function of time.

moved, might correspond to following reduction of catalyst:

$$Bi_2O_3 \cdot MoO_3 \rightarrow Bi_2^0 + MoO_2 + 4\ O_{at}.$$

Figure 20 also shows that when the catalyst once reduced is reoxidized with air at the same temperatures, the speeds of reoxidation are considerably faster than those of the reduction. Within 10–20 min the catalyst reduced is completely reoxidized and the original yellow color is obtained again.

Discussion

Let us summarize first the main experimental results: (i) The reaction is strongly inhibited by butadiene, particularly at low temperatures. (ii) Oxygen repletion is very fast in accordance with zero-order dependency on the oxygen partial pressure, provided enough oxygen is present to prevent pronounced reduction of the catalyst. (iii) Information of the dependency on the butene pressure is somewhat inconclusive because of the predominance of diene inhibition. There seems to be a certain amount of evidence that the order changes from one to zero in the temperature range of 440–320°C. (iv) Butadiene inhibition occurs on oxidized sites and not on reduced sites, because reoxidation with oxygen of reduced catalyst is not inhibited by diene, while catalyst reduction by butene is inhibited by butadiene.

The rate of the reaction can be derived from one represented according to a Langmuir-Hinselwood type of expression:

$$\text{rate} = k \frac{k_1 \cdot p_b}{1 + k_1 \cdot p_b + k_2 \cdot p_d}, \qquad (8)$$

when it is assumed that $k_2 \cdot p_d > k_1 \cdot p_b > 1$; the first-order term $k_1 \cdot p_b$ in the nominator probably escapes detection when inhibition is predominant. It now becomes informative to compare the results of the present experiments with those of the pulse experiments reported earlier (*4*). There we had found hardly any inhibition and a first-order dependency on the butene pressure. The question remains how to reconcile these findings. We can do so by assuming the adsorption of butadiene, that is strongly, to be relatively slow, hence a high activation energy of adsorption in combination with a high heat of adsorption. In the pulse experiments the rate of butadiene adsorption is too slow to interfere with the reaction in the short residence times (1 second), characteristic for pulse situations. Hence, Eq. (8) degenerates into:

$$\text{rate} = k \frac{k_1 \cdot p_b}{1 + k_1 \cdot p_b}$$

$$\text{or into rate} = k \cdot k_1 \cdot p_b. \qquad (9)$$

In the continuous flow and in recirculation experiments, where the catalyst is exposed to gas mixtures for longer time (2000 sec in recirculations), inhibition becomes fully operative. Experimental evidence, derived from experiments by Matsuura in our laboratory, will be reported in the near future to prove this assumption. Although the pulse experiments are misleading at first sight, they produced valuable information if handled correctly. The low activation energies obtained in the pulse experiments even at low temperatures might be connected with the adsorption–desorption equilibriums of butene. The high activation energies in the continuous flows and in recirculations at low temperatures have to be considered as connected with adsorption–desorption of butadiene. The suggestion, earlier given by us (*1*), that a low oxygen diffusion as the rate determining step should be considered as the origin of appearance of high activation energies now is proved to be not in agreement with the present results. Let us now discuss the results of our reduction experiments. In one of our previous reports (*3*), concerned with the reduction of a Bi/Mo = 48/52 catalyst, we introduced a diffusion model to arrive at a correct interpretation of the kinetics of reduction. There were 2 parameters introduced in this model, viz., the rate constant (α) of the surface reaction, supposed to be first order in butene, and the diffusion coefficient (D) characterizing the slow transport of oxygen through the bulk to surface and considered as the rate-determining step. The diffusion was assumed to be independent on the amount of oxygen present in the bulk and the kinetics of reduction was described by a simple equation:

$$\text{Percent of reduction} = -A + B \cdot t^{1/2} \quad (10)$$

in which $A = S \cdot \rho \cdot D/\alpha$ and $B = 2 \cdot \pi^{-1/2} \cdot S \cdot \rho \cdot D^{1/2}$.

In this model inhibition is not taken into account and it is therefore not surprising that the inhibited reductions of the Bi/Mo = 2/1 catalyst (see Fig. 16) do not fit Eq. (10). To describe the kinetics of the reduction with butadiene inhibition more than the 2 parameters mentioned are needed. So far we have not succeeded in formulating a mathematical expression for this problem that embodies the decrease of rate due to the simultaneous action of progressing depletion and surface poisoning. Another interesting aspect is given by the observation that butene reduction leads to $Mo^{5+} \cdot Bi^{3+}$ while reduction with hydrogen at higher temperatures produces $Mo^{4+} \cdot Bi^{0}$. In our former experiments on a differently prepared Bi/Mo = 48/52 catalyst butene and hydrogen both produced $Mo^{4+} \cdot Bi^{0}$ with similar diffusion coefficients. As far as we can ascertain at this moment, the reduction phenomena with hydrogen on both catalysts are comparable, where they differ in the reduction with butene. Although no numerical value of the diffusion constant could be determined here, there is no doubt that in the preliminary stages of the reaction the diffusion coefficient is considerably greater, perhaps even comparable to that of the reoxidation process. This appears to indicate that there are two different diffusion paths for the O^{2-} ion, in agreement with the model given earlier. What at any rate is clear is that the method of catalyst preparation is of considerable importance for the way in which the catalyst acts. Further information on this point appears necessary before one can venture into a definite model for the oxidation reaction in general.

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