# Study on Olefin Oxidation by Periodic-Pulse Technique

II. Oxidative Dehydrogenation of 1-Butene Using Various Oxide Catalysts

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The oxidative dehydrogenation of 1-butene proceeds with a higher selectivity than does the oxidation of propylene. Butadiene and 2-butenes are shown to be produced by the reactions between gaseous 1-butene and surface oxygen. Carbon oxides are formed between the adsorbed residue and oxygen from the gas phase in the Bi–Mo oxide catalyst. Some of the active sites over the Bi–Mo and Bi–W oxide catalysts seem to be inhibited by the poisoning of the adsorbed residue at a higher partial pressure of 1-butene. The rate of isomerization in the continuous-flow technique is smaller or greater than that in the periodic-pulse technique for reducible catalysts like Sn–P and Bi–W oxides, or for oxidizable ones like Sn–Sb and Sb–Mo oxides, respectively. An intermediate trend is notable in Bi–Mo oxide and MoO_3. It follows that the catalysts used in this experiment can be placed in this order with regard to the reducibilities of the catalyst;

$$Bi\text{–}W \quad Sn\text{–}P \quad MoO_3 \quad Bi\text{–}Mo \quad Sn\text{–}Sb \quad Sb\text{–}Mo$$
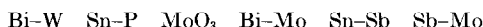
where the more to the left the catalyst lies, the more easily it can be reduced. This is supported by the partial pressure dependence in the periodic-pulse technique and by the variation in the rate of isomerization with the pulse number in the one-shot pulse technique. The results in the oxidative dehydrogenation of 1-butene were similar to those in the oxidation of propylene reported previously. It seems that isomerization takes place via the allyl intermediate.

INTRODUCTION

The previous paper (*1*) dealt with propylene oxidation by the periodic-pulse technique. It has been shown that this technique is useful for indicating the catalyst property related to the so-called reducibility. The findings from separative analysis and from electrical-conductivity measurements led to the following conclusions. Over easily reducible catalysts, combustion took place by means of a reaction between the irreversibly adsorbed residue and oxygen from the gas phase. On the other hand, over a catalyst free from the adsorbed residue, the reaction proceeded between surface oxygen and propylene from the gas phase. These reactions could be explained in terms of the surface oxidation states. Furthermore, it seemed reasonable that the reaction took place according to the reduction–reoxidation mechanism, irrespective of the reaction technique.

In this paper, the technique is applied to the oxidative dehydrogenation of 1-butene. The present results are compared with those of propylene oxidation previously reported. It has been reported that oxidative dehydrogenation proceeds via π-allyl intermediate, as in the oxidation of propylene. With this in view, a consistence may be supposed between the butadiene and acrolein formations. Moreover, the isomerization must be remarkable, because it proceeds without any consumption of ad-

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sorbed species, such as oxygen and hydrocarbon.

EXPERIMENTAL METHODS

The reaction apparatus and the catalyst are the same as those in the oxidation of propylene; they were shown in the previous paper (1), together with the definition of the variables of the periodic-pulse technique.

A gas chromatograph with a capacity for thermal-conductivity detection was used for the analysis of the gases in the intermediate-cell method (2). Samples were injected into 5-m $\beta\beta'$-ODPN and 7-m γ-butyrolactone columns to separate carbon dioxide, 1-butene, trans- and cis-2-butenes, and butadiene; then they were passed into a 1.5-m molecular sieve 13X column to separate oxygen, nitrogen and carbon monoxide. $\beta\beta'$-ODPN and γ-butyrolactone and the molecular sieve were connected in a line before and after the thermal conductivity cell, respectively, and gas analysis was performed by only one shot.

Experiments were carried out with 0.8 g of the catalyst and with 2.72 g of the fused alumina as a diluent at 386°C. The total flow rate was 60 ml/min, and the standard partial pressures of butene and oxygen were 0.25 and 0.21 atm, respectively, in the periodic-pulse technique.

In order to draw a clear distinction between the usual pulse technique and the periodic-pulse technique, we will call the former the "one-shot pulse technique." In the one-shot pulse technique, helium, deoxygenated with a reduced copper–chromite catalyst in an electric furnace, was used as the carrier gas. Experiments were carried out with 0.5-g portions of the catalyst at 386°C, using 1 ml of 1-butene.

RESULTS

Separative Analysis

As in the case of propylene oxidation, the reaction steps were determined by means of separative analysis. When O–R (30,30), over 95% of the butadiene and isomers (i.e., cis- and trans-2-butenes) were

detected at the R-pulse using the Bi–Mo* catalyst. Since the experimental error is estimated at about 5%, this result shows that butadiene and 2-butenes are formed at the R-pulse. Accordingly, oxidative dehydrogenation and isomerization may be said to take place between gaseous butene and surface oxygen. This way of determination was not applied to acrolein formation, however, because of the difficulty caused by the liquid product.

Over the Bi–Mo catalyst, about 80% of the carbon dioxide was found to be formed at the O-pulse, as in the propylene oxidation, but over the other catalyst it was difficult to determine the production step of carbon oxides with accuracy because of its small yield compared with those of butadiene and 2-butenes.

Partial Pressure Dependence

Figures 1, 2, and 3 show the influence of the partial pressure of 1-butene on the rates of diene and isomer formations. The rates in relation to the diene and the isomers
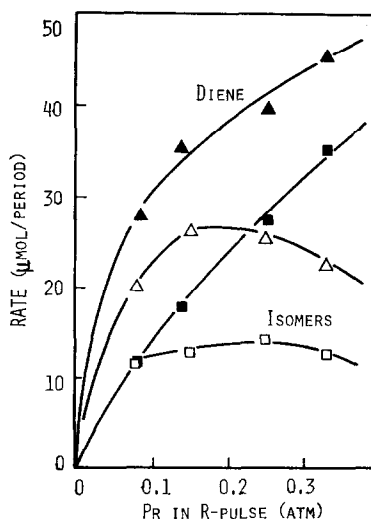

FIG. 1. Dependence of the rate of formation on P_R in the R-pulse over the Bi–Mo(1/1) catalyst: ($\triangle\square$), O–R(15,15), i.e., $t_O = t_R = 15$ sec, 386°C; ($\blacktriangle\blacksquare$), O–R(15,15), 414°C.

* The metal oxide catalysts used in this study are represented in this way, while the atomic ratio is shown in Table 1.
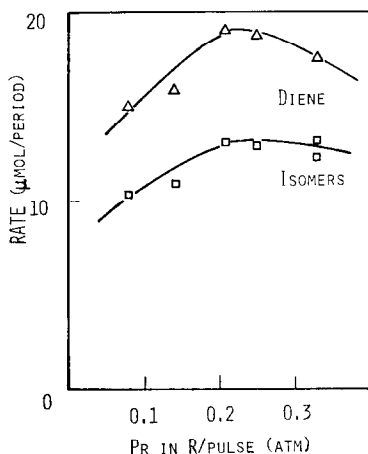
FIG. 2. Dependence of the rate of formation on P_R in the R-pulse over the Bi–W catalyst at O–R(15,15) and 386°C.

were found to have their maximum values with respect to the 1-butene pressure at O–R(15,15) and 386°C over the Bi–Mo and Bi–W catalyst, as is shown in Figs. 1 and 2, respectively. The maximum values in the diene and isomer formations disappeared at 414°C over the Bi–Mo catalyst. The partial pressure dependence of the diene and isomer formations is profoundly influenced by the reaction temperature, unlike as in the propylene oxidation.

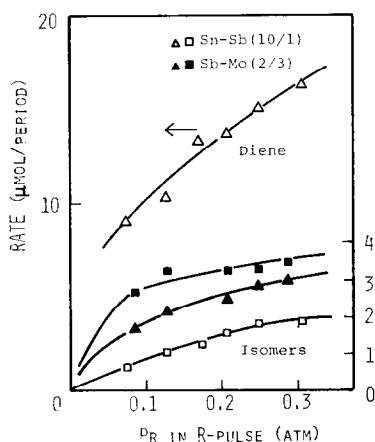In the oxidation of propylene over the Bi–Mo catalyst, the appearance of the

FIG. 3. Dependence of the rate of formation on P_R in the R-pulse at O–R(15,15) and 386°C.

maximum value in the acrolein formation with respect to the propylene pressure was attributed to the irreversible adsorption of hydrocarbon at the R-pulse. Also, in this paper, on the basis of similar phenomena, the maximum values in the diene and isomer formations can be explained. However, there is a marked difference between them, as described below. The decrease in the rate of formation was fully compensated for by the abrupt increase of carbon oxides in the propylene oxidation, while it was not compensated for by any other reactions in the butene oxidation. Consequently, it seems that the sites accommodating the irreversibly adsorbed residue are reproducible by the oxidation of the catalyst under the present experimental conditions, while some of the active sites become inactive as a result of poisoning at the higher partial pressure in the butene oxidation. Such a difference may originate in the reactivity of the adsorbed residue. It is considered that the adsorbed residue is more reactive in the case of propylene than in that of 1-butene. This is supported by the lower selectivity in the propylene oxidation. One possible explanation for the dependence on the partial pressure over the Bi–Mo and Bi–W catalysts is as follows: the diene and the isomer are formed by the action of surface oxygen, and a part of the hydrocarbon is adsorbed irreversibly on the catalyst surface with a low concentration of surface oxygen. At a higher partial pressure of 1-butene, the active sites may become inactive as a result of poisoning by the irreversibly adsorbed residue.

Over the Sn–Sb and Sb–Mo catalysts, the rates increased in monotonous proportion to the reactant pressure. As is clear from the interpretation of the maximum yield, this result suggests that the reactions over the Sn–Sb and Sb–Mo catalysts proceed in a small amount of the irreversibly adsorbed residue. This will be discussed later, together with other findings.

Figure 4 shows the influence of the partial pressure of oxygen on the rates of the diene and isomer formations. It may be observed that both of the rates increase in
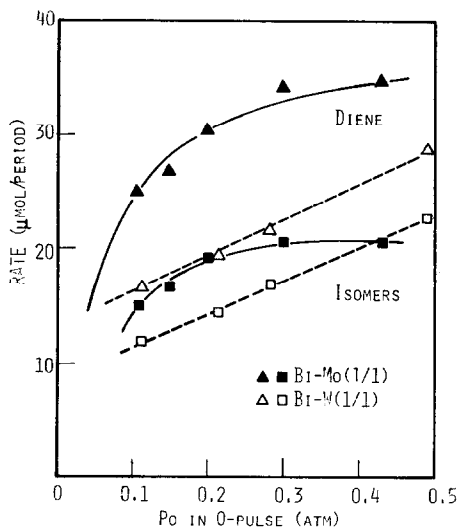
FIG. 4. Dependence of the rate of formation on P_O in the O-pulse at O–R(15,15) and 386°C.

proportion to the oxygen pressure. When oxygen was absent at the O-pulse, neither isomerization nor oxidative dehydrogenation proceeded over the Bi–Mo catalyst.

One-Shot Pulse Technique

The results obtained by the one-shot pulse technique using the Bi–Mo, Sb–Mo, Bi–W, and Sn–P catalysts are shown in Figs. 5 and 6.

Pure 1-butene was repeatedly injected without the reoxidation of the catalyst, and so the catalyst became reduced. In the Bi–Mo catalyst, the diene and isomer yields decreased as the pulse number increased. In the Sb–Mo catalyst, the diene yield was nearly constant, while the isomer yield decreased with the increase in the pulse number. These results show that isomerization as well as oxidative dehydrogenation decreased with the reduction of the catalyst. On the contrary, it was found in the Sn–P and Bi–W catalysts that the isomer yield increased near the pulse number of 1–4, and that the reaction proceeded under the conditions of a low mass balance.

Catalysts gave different results in the same manner as in the partial pressure dependence described above. It seems that the low mass balance over the Bi–W catalyst accords well with the high amount of the adsorbed residue, surmised in the previous section.

One-shot pulse technique can give information about the reaction on a fresh catalyst which holds the higher oxidation state. It is, therefore, found as described above that the reaction can take place on the fresh catalyst when oxygen is not contained in the gas composition, unlike as in the periodic-pulse technique.
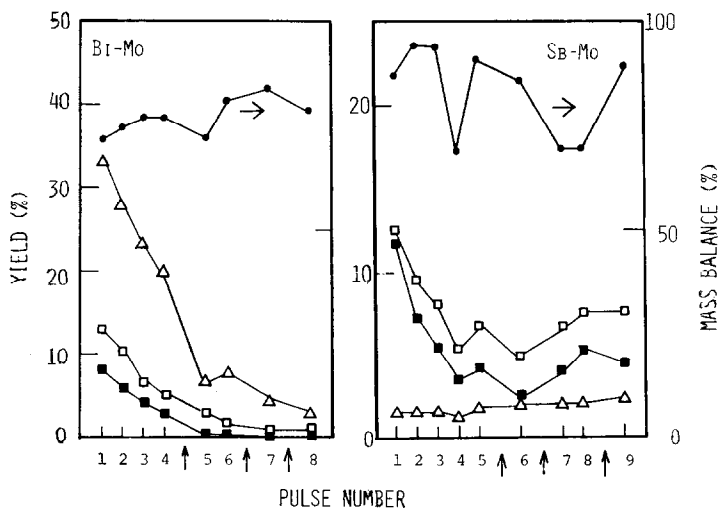

FIG. 5. The variation in the catalyst activity with repeated injections in the one-shot pulse technique: (△) butadiene; (□) cis-2-butene; (■) trans-2-butene; (●) carbon mass balance; (↑) 10-ml injection of 1-butene.

Fig. 6. The variation in the catalyst activity with repeated injections in the one-shot pulse technique: ($\triangle$) butadiene; ($\square$) cis-2-butene; ($\blacksquare$) trans-2-butene; ($\bullet$) carbon mass balance; ($\uparrow$) 10-ml injection of 1-butene.
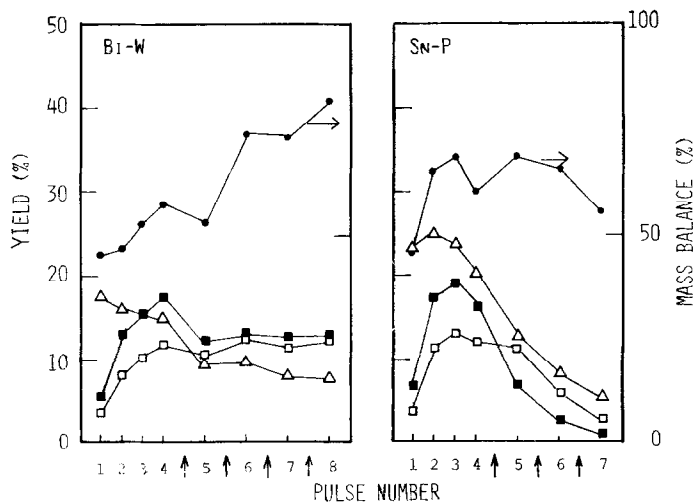
Period Dependence

The dependences of the rates on the period were examined for all the catalysts. It was found, as in the case of the propylene oxidation, that the periodic-pulse reaction coincided with the continuous-flow reaction at the normalized pressure by the extrapolation of the period to 0 sec. Table 1 shows the results obtained by both techniques. Some typical results on the isomerization over the Sb–Mo, Bi–Mo, and Bi–W catalysts are shown in Fig. 7. As the period was shortened, the rates of isomerization increased and decreased over the Sb–Mo and Bi–W catalysts, respectively. Over the Bi–Mo catalyst, the rate had its minimum value at the period of 30 sec. Moreover, it was found that these variations in the isomerization were not compensated for by any other reactions, such as oxidative dehydrogenation or combustion. Thus, there is a clear difference between the catalysts in the period dependence of the isomerization.

From the results of the period dependence observed in the isomerization, the catalysts may be placed in the following sequence;

Bi–W   Sn–P   MoO₃   Bi–Mo   Sn–Sb   Sb–Mo

where the sequences of (MoO₃, Bi–Mo) and

(Sn–Sb, Sb–Mo) are not so rigid as to be interchangable. The amount of isomers in the continuous-flow technique is smaller than that in the periodic-pulse technique in the Bi–W and Sn–P catalysts, although the former is greater than the latter in the Sn–Sb and Sb–Mo catalysts. A tendency

TABLE 1

COMPARISON BETWEEN THE PERIODIC-PULSE
AND CONTINUOUS-FLOW REACTIONS

Catalyst	Technique	Butadiene	2-Butenes
		(mmoles/hr g-cat)	
Bi–Mo(1/1)	p[a]	3.73	2.19
	f[b]	5.28	4.98
Bi–W(1/1)	p	3.09	2.26
	f	2.51	1.16
Sb–Mo(2/3)	p	0.514	1.49
	f	0.594	4.20
Sn–Sb(10/1)	p	2.19	0.280
	f	3.50	0.395
Sn–Sb(4/1)	p	2.31	0.241
	f	3.66	0.346
Sn–P(10/1)	p	1.88	7.96
	f	1.85	4.85
MoO₃	p	0.376	3.15
	f	0.480	2.69

[a] Periodic-pulse technique under the following condition: O–R(15,15); P_R, 0.25 atm; P_O, 0.21 atm.

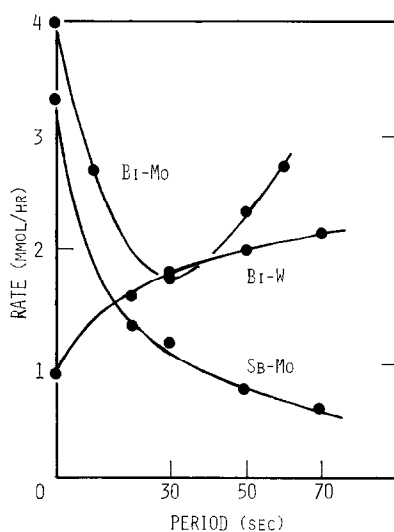[b] Continuous-flow technique at the normalized pressure.

FIG. 7. Dependence of the rate of isomerization on the period using various catalysts. The rates when period is 0 sec show the continuous-flow technique at the normalized pressure.

intermediate between them is found in the Bi–Mo and MoO_3 catalysts. As mentioned above, the catalysts represented different trends in the partial-pressure dependence and in the one-shot pulse technique as result of their properties. These results support such a sequence arranged on the basis of the period dependence.

The rates of oxidative dehydrogenation in the continuous-flow reaction were greater than, or nearly equal to those in the periodic-pulse reaction over all the catalysts except Bi–W. When this finding is compared with that on acrolein described in previous paper, the inclinations in the period dependences for all the catalysts are found to be roughly consistent, with a few marked exceptions, in the Bi–W and Sb–Mo catalysts.

DISCUSSION

In the previous paper (1), the catalysts were characterized by the periodic-pulse technique and by electrical conductivity measurements. Various phenomena in the combustion reaction of propylene were explained on the basis of the difference in the surface oxidation states. All the phe-

nomena could be attributed to the reducibilities of the catalysts. The catalysts may be divided into those of a reduced surface, like Sn–P, Bi–W, and Bi–Mo, and those of an oxidized one, like Sn–Sb and Sb–Mo.

Therefore, the fact observed here about isomerization accords well with that in Part I in view of the catalyst sequence. For example, the sequence of the catalysts based on the electrical conductivity measurements is found to be similar to that shown in this paper:

Sn–P   Bi–W   Bi–Mo MoO_3 Sb–Mo   Sn–Sb
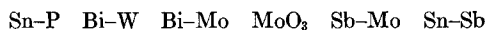
where the more on the left side the catalyst lies, the more easily it can be reduced. The clear consistency in the catalytic behavior taken from oxidations of propylene and 1-butene suggests that the findings of the present study can be interpreted from a point of view similar to that in the previous paper.

As is shown in Fig. 4, the greater amount of isomers is formed in the higher surface-oxidation state. Moreover, the isomerization may be inhibited by the poisoning of the active sites by the irreversibly adsorbed residue over the reducible catalysts, as may be speculated on the basis of the results of the partial pressure dependence. These facts suggest that the variation in the rate of isomerization corresponds to that of the numbers of active sites available for it. It may, therefore, be considered that the lengthening of the period increases or decreases the number of active sites over the Bi–W or Sb–Mo catalysts. Such a variation in the concentration of the active sites can possibly be explained as in the following description.

In the periodic-pulse technique, the oxidation in the O-pulse and the reduction in the R-pulse proceed separately, without competition, at the same time. Both the reactions influence the surface oxidation state of the catalyst in a different manner from those in the continuous-flow reaction, in which they take place at the same time. In the periodic-pulse technique, the slower reaction proceeds without the disturbance of the faster one; this results in the em-

phasis of the slower one when they are integrated through a period. In other words, the total reaction is deformed in enlarging the slower reaction in the periodic-pulse technique. Such an enlarging becomes great as the period is lengthened. This may be the basic reason for the dependence on the period of the surface oxidation states available for isomerization.

The results in Fig. 7 can be explained in the following way. It was found that the reaction over the Bi–W catalyst proceeded in the lower surface-oxidation states, as described above. From this fact, it may be considered that the rate of the adsorption of butene exceeds that of combustion over the Bi–W catalyst. In the long period, the slower reaction, i.e., the reoxidation due to combustion, is enlarged; this brings about the increase in the number of active sites available for isomerization. As for the Sb–Mo catalyst, the contrary explanation can be made. The condition of the Bi–Mo catalyst is dependent on the period, and its property lies in a situation intermediate between the two catalysts described above.

The surface-oxidation state which influences the isomerization seems to vary before it reaches the steady state. This idea is supported by the results obtained by the one-shot pulse technique in the nonsteady state. In the previous paper, it was shown that the period dependence exhibits a variation in the rate with time-on-stream in the pulse in which the reaction takes place. This principle cannot, however, be applied to isomerization, because it proceeds under a constant surface-oxidation state without the consumption of any adsorbed species, such as oxygen and hydrocarbon.

On the other hand, the period dependence of butadiene is found to be similar to that of acrolein except in the cases of the Bi–W and Sb–Mo catalysts. The similarities seem to be reasonable enough, because oxidative dehydrogenation as well as oxygen addition can be thought to proceed via the same intermediate. The exceptional behavior of the Bi–W catalyst is difficult to explain.

It is remarkable that isomerization is markedly influenced by the oxidation states of the catalysts and that the difference of the period dependence in the isomerization is useful for the ordination of the catalysts in indicating the surface conditions. The findings concerning isomerization indicate about the reaction mechanism that its reaction proceeds via the same intermediate as the oxidative dehydrogenation. This consideration is supported by the studies of Batist, Lippens and Schuit (3) and Matsuura and Schuit (4). Malyan, Bakshi and Gelbstein (5) indicated that isomerization took place via the carbonium ion, because the addition of water to the gas phase resulted in an increase in the isomers. The fact presented above, however, can not be explained by the carbonium-ion mechanism.

On the other hand, Leftin and Herman (6) reported that the isomerization of 1-butene on the silica–alumina catalyst was initiated by the abstraction of hydrogen on Lewis-type acidic sites. In comparison with the π-allyl mechanism presented above, it is considered that these reaction mechanisms for the isomerization have the common feature that all the active sites act as electron-acceptors, although they can be distinguished by the participation of surface oxygen. Uchida et al. (7) reported recently that the oxidative dehydrogenation of naphthenic hydrocarbons occurs on an activated alumina catalyst, which is known as a typical solid-acid catalyst. These studies using an alumina catalyst seem to suggest the similarity of the active sites available for oxidation and acid-catalyzed reactions. The difference and similarity between the acid site and the active oxidizing site need to be established more precisely.

As was mentioned in the previous paper, the heightening of the selectivity in the oxidation reaction is probable upon a decrease in the adsorbed residue connected with the combustion. Most catalysts for industrial use contain an n-type semiconductor, like molybdenum, tin, and vanadium oxides, which can easily be reduced under the present experimental conditions. More attention, therefore, should be paid to the irreversibly adsorbed material rather than to the active oxygen.

The irreversibly adsorbed material may be decreased by changing the quality of the active sites contributing to the irreversible adsorption into those of the isomerization. This change in the active site is probable in view of the fact that the rate of isomerization is sensitive to influence from the coverage of the adsorbed residue. It has been reported that the addition of a polar material to the gaseous component increased the selectivity. Adzhamov et al. (8) indicated the inhibition effect of ammonium on the entire oxidation using a bismuth molybdate catalyst. Some investigators (9, 10) have reported that the addition of water vapor suppressed the deep oxidation and increased the process selectivity. It is considered that these basic materials, such as ammonium and water, are adsorbed tightly on the catalyst surface, and that they decrease the irreversibly adsorbed material, thus leading to a combustion reaction.

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