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Study on Olefin Oxidation by Periodic-Pulse Technique

I. Propylene Oxidation into Acrolein Using Various Oxide Catalysts

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By the periodic-pulse technique, distinguished from the conventional continuous-flow reaction by the alternate feeding of oxygen and hydrocarbon, the oxidation of propylene was investigated over various oxide catalysts. It is shown that the reaction takes place according to the same mechanism, i.e., the reoxidation–reduction mechanism, irrespective of the reaction technique. We attempted to characterize various oxide catalysts by the periodic-pulse technique and by electrical-conductivity measurements. The speculations regarding surface oxidation states on the basis of a separative analysis of the combustion reaction and the electrical conductivity during the reaction are consistent. Combustion is found to take place at the oxygen-regeneration pulse (O-pulse) over the Sn–P, Bi–W, and Bi–Mo oxide catalysts, which are severely reduced, while at the propylene-reaction pulse (R-pulse) over the Sn–Sb and Sb–Mo oxide catalysts, the catalysts maintain higher oxidation states. The catalysts can also be classified into three groups on the basis of the period dependence;

(a) Bi–Mo, B–iW (b) Sn–Sb, Sb–Mo
(c) MoO_3, Sn–P

The catalysts are divided into Group (b) and Groups (a) and (c) on the basis of the results of the combustion reaction; these results are correlated with the characterization of the separative analysis and electrical-conductivity measurements. On the basis of these findings, some discussions are made of the catalyst properties controlling their surface oxidation states. Furthermore, the roles of bismuth and antimony are speculated on.

INTRODUCTION

Acrolein synthesis by the oxidation of propylene has been investigated as one of the most basic reactions in a mild oxidation. The studies have been carried out mainly over bismuth molybdate catalysts, which are industrially important. Adams and Jennings (*1*) offered a mechanism in which the oxidation of propylene into acrolein proceeds via a π-allyl intermediate using the isotopic technique. Their proposal seems to be accepted in the literature. Batist, Lippens and Schuit (*2*) proposed that olefinic hydrocarbon can be combined with the anion vacancy which belongs to the molybdenum atom.

It is necessary to solve the puzzle concerning the high selectivity of the bismuth molybdate catalyst. Sachtler and de Boer (*3*) have proposed a reducibility parameter in order to interpret the activities and selectivities of mixed oxide catalysts. However, it is clear that the explanation based on the reducibility is insufficient at least, as far as the present results are concerned. In order to determine the factor that determines selectivity in the oxidation reaction, it may be necessary to consider the formation of by-products as well as the main reaction.

The present authors have already developed the periodic-pulse technique, reported the experimental results, and compared the continuous-flow and one-shot pulse techniques* using the example of the oxidative dehydrogenation of ethylbenzene into styrene (*4*). In the periodic-pulse technique, oxygen and hydrocarbon are fed into the reactor alternately and separately; the reactions proceed under the surface condition of having a certain width between the lower and higher oxidation states. The results of the periodic-pulse technique were approximate to those of the continuous-flow technique rather than to those of the one-shot pulse technique, in which a reactor is inserted between the sample inlet and the separate column of the gas chromatograph. In addition, it is remarkable that the reaction proceeds under a nonsteady state, i.e., a periodic variation in the surface oxidation state.

Taking advantage of the characteristics of the periodic-pulse technique described above, it can be expected that new information can be obtained about the oxidation reaction. The catalysts are characterized as to the surface oxidation state by means of this technique, used in connection with the electrical-conductivity measurements.

EXPERIMENTAL METHODS

Terms

Figure 1 shows a periodic-pulse technique diagram, in which some variables are defined as follows;

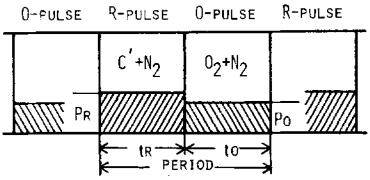

FIG. 1. Time diagram of the periodic-pulse technique.

O-pulse—a pulse consisting of oxygen and nitrogen;

R-pulse—a pulse consisting of hydrocarbon and nitrogen;

N-pulse—a pulse consisting of only nitrogen;

Pulse width (t)—a feed time of each pulse (sec);

Period—the total sum of each pulse width, i.e., ($t_O + t_R$) (sec)

Partial pressure—described in each pulse; for example, P_O in the O-pulse means the partial pressure of oxygen in the O-pulse.

Normalized pressure—a partial pressure in the continuous-flow technique, which is defined as follows: normalized pressure of oxygen (or olefin) =

$$[t_O/(t_O + t_R)]\, P_O \;\{\text{or } [t_R/(t_O + t_R)]\, P_R\}$$

Experimental Procedure

The reactions were carried out using the experimental apparatus shown in Fig. 2. Each reactant mixture was fed into a reactor, via one of the three-way solenoid valves, which were connected with a electric circuit constructed with timers and relays. The stream was connected with the reactor side when the electric current was operating against the solenoid valve, and with the purge side in other cases. The pressure of the gas stream was regulated by water pressure on the purge side in order to make it flow steadily. The current was dried with silica gel for oxygen, nitrogen and air, and with calcium chloride for

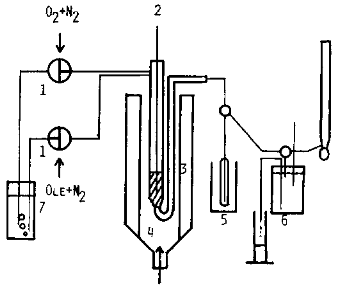

FIG. 2. Reaction apparatus for the periodic-pulse technique: (1) three-way solenoid valve; (2) thermocouple; (3) electric furnace (sand bath); (4) reactor; (5) liquid trap; (6) gas-sampling vessel; (7) pressure regulator.

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* In order to draw a clear distinction between the usual technique and the periodic one, we will call the former the one-shot pulse technique.

propylene, and it was controlled with a capillary flow meter. Because of the cyclic change in the gaseous composition, the gaseous products were collected in a gas-sampling vessel for several periods (about 200 ml). Liquid products were trapped in ice- and dry ice–acetone-cooled tubes. Analysis was carried out by gas chromatography under the following conditions; a 20-cm silica gel column at 60°C for CO_2 and propylene, a 1.5-m molecular sieve 13X column at room temperature for O_2, N_2, and CO, and a 2-m $\beta\beta'$-ODPN column at 60°C for acrolein. The silica gel and molecular sieve are connected in a line before and after the thermal conductivity cell respectively (*5*). The hydrogen used as a carrier gas was allowed to flow into the silica gel column to separate carbon dioxide, propylene, and other substances, and then it was allowed to flow into the molecular sieve column to separate oxygen, nitrogen, and carbon monoxide. Gas analysis was performed by only one shot.

The reaction has been carried out at 386°C with a 6.56-g catalyst unless otherwise described. The amounts of carbon oxide formed represent one-third of them.

Catalysts

The following eight oxide catalysts were used in this experiment: Bi–Mo(1/1)*, Bi–Mo(1/1)/SiO_2, Bi–W(1/1), MoO_3, Sb–Mo(2/3), Sn–Sb(10/1), Sn–Sb(4/1), and Sn–P(10/1). They were prepared in the following way.

An unsupported Bi–Mo catalyst was prepared by the method described by Adams *et al.* (*6*). A supported Bi–Mo catalyst was prepared from a bismuth-molybdate precipitation and ethyl orthosilicate. The mixture, with a little nitric acid added, was hydrolyzed with a vibration mixer. The supported silica gel was 30 wt %. The Bi–W catalyst was prepared by coprecipitation from nitric bismuth nitrate and tungstic acid solutions. The MoO_3 catalyst was prepared from the precipitate of an ammonium molybdate solution with nitric acid. The Sb–Mo catalyst was prepared by mixing ammonium molybdate, antimony trioxide, and a little water, after which the mixture was dried at 110°C. The powder obtained was formed into a pellet under pressure. The Sn–Sb and Sn–P catalysts were prepared from the tin hydroxide gel by adding antimony and orthophosphoric acid, respectively. Tin hydroxide gel was prepared by adding more ammonium hydroxide than equivalent to a tin chloride solution in order to precipitate it and by then washing with water until the pH equaled 7.

The calcination of the Bi–Mo, Bi–Mo/SiO_2, Bi–W, Sb–Mo and MoO_3 catalysts was done at 450°C for 3 hr; that of the Sn–P catalyst, at 500°C for 2 hr; and that of the Sn–Sb catalyst, at 1000°C for 4 hr. The particle size was 28–48 mesh except the Sb–Mo catalyst (20–48 mesh). The surface areas of these catalysts were measured by the BET method; they are summarized in Table 1.

TABLE 1
SPECIFIC SURFACE AREA

Catalyst	Surface area (m^2/g)
Bi–Mo(1/1)/SiO_2	202
Sn–P(10/1)	47.2
Bi–W(1/1)	14.6
Sn–Sb(10/1)	14.6
Sn–Sb(4/1)	12.8
MoO_3	3.2
Sb–Mo(2/3)	2.5
Bi–Mo(1/1)	2.2

Electrical-Conductivity Measurements

The electrical conductivity of the catalyst was measured under an atmospheric pressure using the apparatus shown in Fig. 3. The powder was compressed into a disk about 5 mm thick and 2 cm in diameter under a pressure of 1 ton/cm^2; four electrodes of platinum wire were buried in a line. A direct current of 90 V was charged between the outside electrodes. The resistance of greatest value (about 1 MΩ) was connected in a series circuit in order to avoid any fluctuation in the current with the variation in the resistance in the disk. The response of the potential difference between the inside electrodes with the

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* Represents the atomic ratio.

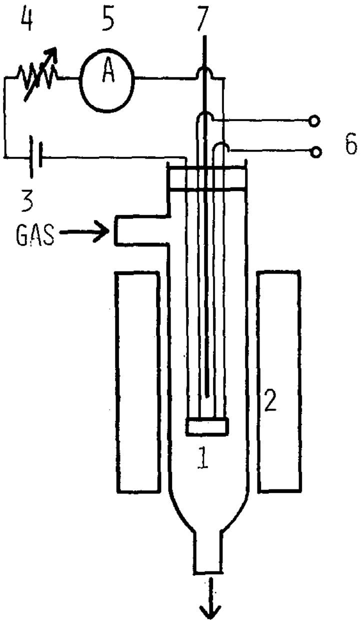

FIG. 3. Apparatus for measurements of the electrical conductivity of the catalyst: (1) catalyst; (2) electric furnace; (3) dry battery (d.c. 90 V); (4) variable resistance; (5) ammeter; (6) terminal for recorder; (7) thermocouple.

TABLE 2

SEPARATIVE ANALYSIS OF CO AND CO_2 WHEN O-R(30, 30)

	CO_2		CO	
Catalyst	total amount[a]	O[b] (%)	Total amount[a]	O[b] (%)
Bi-W(1/1)	5.08	78.7	0.991	79.1
Sn-P(10/1)	1.97	70.9	0.979	70.4
MoO_3	0.160	51.6	—	—
Bi-Mo(1/1)	2.20	83.7	0.427	79
Bi-Mo/SiO_2	6.02	83.3	—	—
Bi-Mo/SiO_2[c]	6.66	81.0	—	—
Sn-Sb(10/1)	0.945	32.9	0.194	31.5
Sb-Mo(2/3)	0.329	30.4	0.235	13.4

[a] Represents one-third of them (μmoles/period g catalyst).

[b] Percentage at the O-pulse with respect to the total amount; that at the R-pulse is 100 minus O (%).

[c] P_O in the O-pulse is 0.67 atm.

change in the atmosphere was recorded, and the electrical resistance was accounted for by the ammeter value. The streams were then dried, and the nitrogen was deoxygenated by the use of a reduced copper chromite catalyst.

RESULTS

Separative Analysis

Each gaseous product of the O-pulse and the R-pulse was sampled and analyzed separately. In order to avoid error resulting from gas mixing, an N-pulse of 15 sec was inserted between the O- and R-pulses. As shown clearly in Table 2, about 70% of the combustion reactions over the Sb–Mo and Sn–Sb catalysts belonged to the R-pulse; they were directly contrary to those of the Bi–Mo, Bi–Mo/SiO_2, Bi–W, and Sn–P catalysts. Over the MoO_3 catalyst, with a small formation of carbon oxides (carbon monoxide and carbon dioxide), half of the products were formed at the O-pulse. In addition, the carbon monoxide formation was accompanied by the formation of carbon dioxide over all the catalysts.

A similar experiment with regard to acrolein formation was carried out with a one-shot pulse technique in which deoxygenated helium was used as the carrier gas. A propylene pulse gave acrolein, but the next air pulse gave only carbon oxides. This means that adsorbed species of hydrocarbon do not react with molecular oxygen to form acrolein. From these experiments, it seems that acrolein is formed from propylene and surface oxygen at the R-pulse by the periodic-pulse technique.

Comparison of the Periodic-Pulse Reaction with the Continuous-Flow Reaction

The dependence of the rate of formation on the period was examined over the Bi–Mo catalyst (cf. Fig. 4). The rates when the period was zero sec were obtained from the continuous-flow reaction at a normalized pressure. The acrolein formation increased with a shortening of the period, although the formation of carbon oxides was not much increased. As shown in Fig. 4, by the extrapolation of the period to zero sec, the rates in the periodic-pulse technique coincide with those in the continuous-flow technique. Consequently, the continuous-flow reaction may be regarded as like the peri-

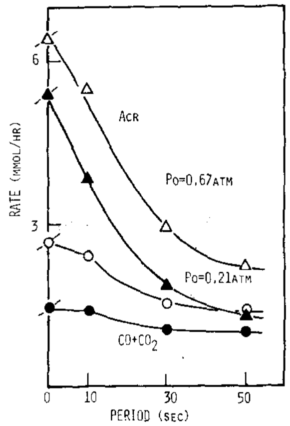

FIG. 4. Dependence of the rate of formation on the period over an unsupported Bi–Mo catalyst: $t_O/t_R = 1$ and $P_R = 0.25$ atm in the periodic-pulse technique. The results when period is zero sec show those in the continuous-flow technique at a normalized pressure.

TABLE 3

COMPARISON BETWEEN THE PERIODIC-PULSE AND CONTINUOUS-FLOW REACTIONS

		(mmoles/hr)		
Catalyst	Technique	CO_2	CO	Acrolein
Bi–Mo(1/1)	p[a]	0.836	0.21	1.86
	f[b]	1.06	0.39	5.42
Bi–Mo(1/1)[c]	p	1.17	0.35	2.93
	f	1.69	1.00	6.44
Bi–W(1/1)	p	2.02	0.488	0.306
	f	2.15	0.543	1.11
Sb–Mo(2/3)	p	0.245	0.265	0.518
	f	0.740	1.01	0.925
Sn–Sb(10/1)	p	0.732	0.194	3.48
	f	1.00	0.288	5.25
Sn–Sb(4/1)	p	0.628	0.179	3.46
	f	0.886	0.296	5.46
Sn–P(10/1)	p	0.720	0.434	0.368
	f	0.756	0.484	0.388
MoO_3	p	0.120	0.069	0.362
	f	0.094	0.063	0.342

[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.

[c] 0.67 atm of P_O in the O-pulse.

odic-pulse technique when the period becomes zero sec. This relation will be discussed below in more detail.

The rates obtained in the periodic-pulse technique over other oxide catalysts have been compared with those obtained in the continuous-flow technique at a normalized pressure (cf. Table 3). For reference, the results on the Bi–Mo catalyst are also listed in Table 3. The amount of acrolein on the Bi–W catalyst was greater in the continuous-flow technique than in the periodic-pulse technique, although those of carbon monoxide and carbon dioxide were nearly equal for both the techniques, as with the Bi–Mo catalyst. On the other hand, all of these amounts over the Sb–Mo and Sn–Sb catalysts were greater in the continuous-flow technique than in the periodic-pulse technique. On the Sb–Mo catalyst, a discrepancy was found in the combustion reaction in particular. Furthermore, the results over the Sn–P and MoO_3 catalysts were found to be similar for the two techniques.

On the basis of a comparison of the two reactions, the catalysts can be classified into the following three groups;

(a) Bi–Mo, Bi–W (b) Sn–Sb, Sb–Mo

(c) MoO_3, Sn–P

Although the Bi–W and Sn–P catalysts possessed similar activities and selectivities, a discrepancy was found in the acrolein formation over the Bi–W catalyst, but not in any reaction over the Sn–P catalyst. On the other hand, the Bi–Mo and Bi–W catalysts had the same tendency with regard to acrolein formation irrespective of their different selectivities, 79 and 29%, respectively. The results show that the discrepancy is found not only on the product with the greatest yield or on that with the highest selectivity. Accordingly, these differences between the results obtained by the two techniques do not depend on the levels of conversion and/or selectivity.

Furthermore, it is remarkable that the grouping was supported by the results of separative analysis. A discrepancy was found only in the combustion of the Group (b) catalyst, which took place at the R-pulse more than at the O-pulse. On the contrary, almost the same amount of carbon oxides was obtained from both the techniques over Group (a) and Group (c) catalysts, on which combustion took place mainly at the O-pulse.

P_R *Dependence*

Figure 5 shows the dependence of the rates on P_R in the R-pulse (partial pressure of propylene) over the Bi–Mo catalyst at O–R(15,15) (the pulse widths of the O- and R-pulses are both 15 sec), as the reaction temperature was varied. The amounts of acrolein were most when P_R = 0.10–0.20 atm, although those of carbon oxides increased in proportion to the partial pressure at any reaction temperature. It is evident that the decrease in acrolein formation when P_R in the R-pulse is 0.25 atm or more is fully compensated for by the increase in carbon oxides formation. As is shown by the dotted line, the sum of products does not have a maximum value relative to P_R in the R-pulse.

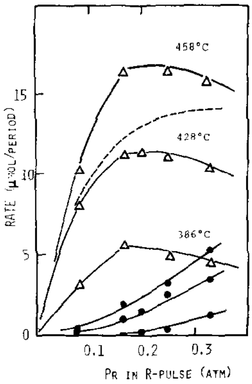

FIG. 5. Dependence of the rate of formation on P_R in the *R*-pulse over 0.8 g of an unsupported Bi–Mo catalyst, with 2.72 g of fused alumina as a diluent: (△) acrolein; (●) CO + CO_2; (– –) the sum of the products at 428°C.

Electrical-Conductivity Measurements

The electrical conductivity of the catalyst was measured by the d.c. method. It seems difficult to compare the absolute values of the electrical conductivity, because they are profoundly influenced by the method of a disk preparation and by the other procedures. In order to avoid any trouble arising from the experimental techniques, we measured the variation in the electrical conductivity with an atmospheric change.

For example, the results on the Bi–W catalyst are shown in Fig. 6. Preceding the measurements, a disk was oxidized by an air stream for a few hours at about 400°C. The measurement temperature was set at 386°C, and then the stationary value was obtained in the air stream (1). The gaseous stream was changed from air to nitrogen (2), and then the reaction was done under the same conditions as in the continuous-flow reaction shown above (P_R = 0.125 atm, P_O = 0.105 atm) (3). After it had reached the stationary state, the disk was reoxidized by the air stream (4). Finally, the disk was reduced with propylene (P_R = 0.25 atm) (5).

The ordinate in Fig. 6 represents the logarithm of the resistance, and so the difference in the ordinate corresponds to the relative ratio of the values. The measurements were also carried out by the a.c. method, in which an alternating current of 10 V and 5 kHz were used. The possibility of any peculiar action by the direct current may be eliminated, because the result

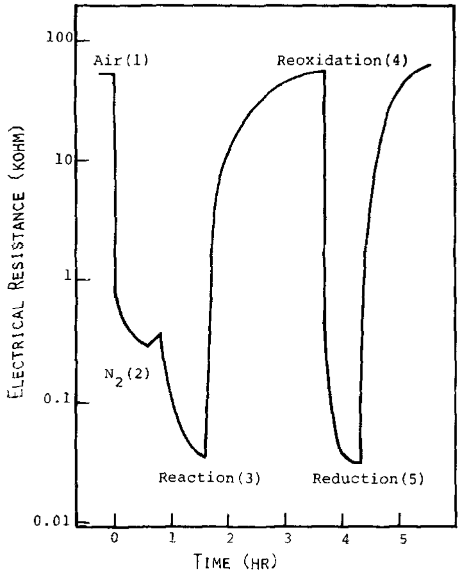

FIG. 6. Transition of the electrical resistance with an atmospheric change for the Bi–W(1/1) catalyst. The experimental conditions of (1, 4), (2), and (5) correspond to the O-, N-, and R-pulses respectively; reactions are carried out by the continuous-flow method at a normalized pressure.

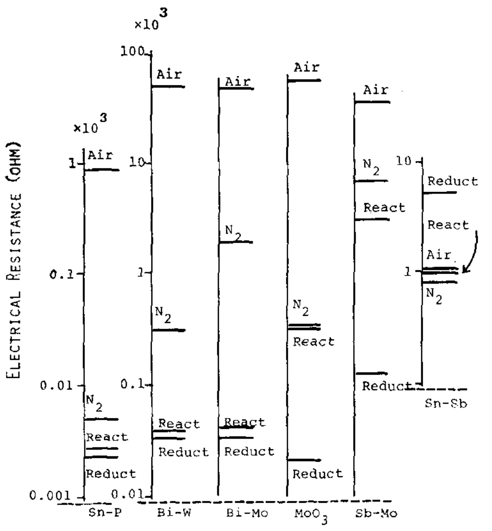

Fig. 7. Comparison of the oxidation states of various oxide catalysts, based on the electrical resistance.

obtained by the two methods on the Sn–Sb catalysts accorded well.

The values under various atmospheres for all the catalysts are shown in Fig. 7. The results show that all the catalysts behave as *n*-type semiconductors except for the Sn–Sb catalyst, because the electrical conductivity increases with the adsorption of the olefin-electron donor, or with the desorption of the oxygen-electron acceptor, and that it decreases with the reoxidation of the catalyst. Furthermore, the following conclusions were drawn.

1. By the exchange from air to nitrogen in the atmosphere, perhaps weakly held oxygen can be desorbed from the catalyst surface. It was found that this phenomenon became remarkable over the Bi–Mo, MoO_3, Bi–W, and Sn–P catalyst in that order, while there was scarcely none over the Sn–Sb catalyst.

2. The surface state in the reaction can be surmised by comparing the value of the electrical conductivity with the resistances in air and propylene, because the catalyst surface reaches its highest oxidation state in air and its lowest state in propylene. As is clear from the results, the Bi–W, Bi–Mo, and Sn–P catalysts were severely reduced under the reaction conditions. Contrarily, the Sn–Sb catalyst was not reduced at all; it remained in almost the same state as in the air. Over the MoO_3 catalyst, the value of the electrical conductivity under the reaction agreed with that in nitrogen. The Sb–Mo catalyst also seems to maintain a higher oxidation state.

It is found that there is a close relationship between the separative analysis and electrical conductivity. Combustion is found at the O-pulse over the catalysts which are severely reduced, but at the R-pulse over the catalysts which maintain higher oxidation states.

DISCUSSION

Separative Analysis and Electrical-Conductivity Measurements

As is clear from the results of the separative analysis, the catalysts can conceivably be roughly divided into two groups. Since the combustion took place mainly at the O-pulse over the Bi–Mo and Bi–W catalyst, etc., it may be suggested that the surface is covered with an adsorbed residue connected with the combustion rather than with active oxygen. On the other hand, since the higher amounts of carbon oxides were formed at the R-pulse over the Sn–Sb and Sb–Mo catalysts, there may be some active oxygen with a small amount of the irreversibly adsorbed residue. It is considered that the pulse at which the combustion reaction proceeds is determined largely by the reactivity of the adsorbed residue and by the activity of the surface oxygen. Accordingly, the results obtained by this method imply a relative situation concerning the surface oxidation states.

On the other hand, electrical-conductivity measurements have been carried out in order to estimate the oxidation state during the reaction in comparison with those in air and propylene. The results obtained by these two methods are very consistent with each other as to the surface-oxidation states.

In view of the above evidence, the combustion in the oxidation of propylene may be described as follows. When propylene flows into the reactor at the R-pulse, it gives carbon oxides by the action of surface oxygen if its amount is sufficient to follow the combustion. When there is not enough oxygen to produce carbon oxides, the propylene is adsorbed irreversibly on the catalyst surface. The adsorbed residue left on the catalyst surface can then be attacked by oxygen from the gas phase at the O-pulse.

The electrical conductivity suggests that the state of the catalyst surface contributes only to the combustion not to the acrolein formation, because acrolein formation in the periodic-pulse technique has no relation to the conductivity of the catalyst. Peacock *et al.* (*7*) have said that by means of the electrical-conductivity measurement the reaction on the Bi–Mo catalyst proceeds when the surface is reduced 10%. The divergent results may result from the difference in experimental techniques, i.e., the static apparatus at the low pressure and the continuous-flow-type apparatus under the atmosphere.

For the selection of a catalyst with high selectivity, Sachtler and de Boer (*3*) have proposed a reducibility parameter as the controlling activity of some oxides. Their proposal is based on the assumption that the activities of oxide catalysts are determined by the bond energy of the oxygen and the metal. From this point of view, carbon oxides, by-products, are formed by the oxygen which is combined weakly to the metal, while acrolein is formed by oxygen of a suitable activity. As is clear from the separative analysis, however, carbon oxides are not formed from propylene and catalyst oxygen in any of the catalysts. Not enough oxygen that can produce carbon oxides exists on the selective catalysts, such as bismuth molybdate. Thus, the combustion reaction is sometimes closely related to the irreversible adsorption of hydrocarbon. In order to decrease the combustion reaction in such cases, attention should be paid not to controlling the oxygen activity, but to decreasing the amount of irreversibly adsorbed hydrocarbon.

It has been common knowledge, on the basis of the zeroth order to oxygen in kinetic studies of the acrolein formation, that the coverage of surface oxygen is constant at the surface of the Bi–Mo catalyst. If all the sites are homogeneous, it follows that the surface is almost covered by oxygen. However, this is in conflict with our conclusion that a reducible catalyst, such as the Bi–Mo catalyst, is covered by an adsorbed residue rather than by oxygen. It may, therefore, be concluded that the active surface available for the acrolein formation is only a small part of the surface; that is, the heterogeneity of catalyst-active sites must be taken into account in order to understand the oxidation completely.

Comparison of the Periodic-Pulse Reaction with the Continuous-Flow Reaction (Period Dependence)

The suitability of the normalized pressure in the continuous-flow technique when it is compared with the periodic-pulse technique can be understood kinetically as follows.

It is assumed that the oxidation reaction proceeds according to the reduction–reoxidation mechanism;

$$\mathrm{R} + (\mathrm{O}) \rightarrow \mathrm{RO} + (\ \ ) \qquad (1)$$

$$(\ \ ) + 1/2\,\mathrm{O}_2 \rightarrow (\mathrm{O}) \qquad (2)$$

where R, RO, (O), and ( ) denote the olefin reactant, the oxidation product, the available oxygen, and the bare active site, respectively. In the periodic-pulse technique, the coverage of the available oxygen θ is decreased at the R-pulse and is increased at the O-pulse, as depicted in Fig. 8. The differential equations are obtained

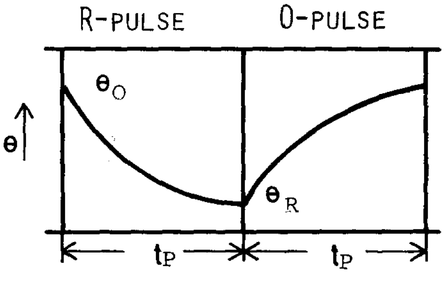

FIG. 8. Variation in the concentration of surface oxygen with time-on-stream in the periodic-pulse technique.

on the basis of Eqs. (1) and (2);

only during the R-pulse,

$$-\frac{d\theta}{dt} = k_R \theta P_R \qquad (3)$$

only during the O-pulse,

$$\frac{d\theta}{dt} = k_O(1 - \theta)P_O \qquad (4)$$

where k and P denote the rate constant and the partial pressure in each pulse, respectively. When the initial conditions of the coverage are θ_O at the R-pulse and θ_R at the O-pulse, as shown in Fig. 8, the amount of oxidation product per period, M, may be written under the condition of an equal pulse width at the O- and R-pulses as follows;

$$M = (\theta_O - \theta_R)/2t_p \qquad (5)$$

where t_p is the pulse width; therefore, $2t_p$ equals the period. By solving Eqs. (3) and (4) in terms of θ, and by substituting them in Eq. (5), we obtain;

$$M = \frac{[1 - \exp(-k_O P_O t_p)][1 - \exp(-k_R P_R t_p)]}{2t_p[1 - \exp\{(-k_O P_O - k_R P_R)t_p\}]}. \qquad (6)$$

When t_p approaches zero, the expression (6) can be written as follows;

$$\lim_{t_p \to 0} M = \frac{k_O k_R \frac{P_O}{2} \frac{P_R}{2}}{k_O \frac{P_O}{2} + k_R \frac{P_R}{2}}. \qquad (7)$$

On the other hand, it is assumed that the continuous-flow reaction proceeds under a steady state; therefore, M is obtained as follows:

$$M = \frac{k_O k_R P_O P_R}{k_O P_O + K_R P_R}. \qquad (8)$$

Equation (8) may be understood to coincide perfectly with (7) by replacing partial pressures by $P_R/2$ and $P_O/2$, i.e., the normalized pressures. This means that the periodic-pulse technique coincides with the continuous-flow one under the normalized pressure when the period is extrapolated to zero sec, as is shown in Fig. 4. Moreover, the reaction can be regarded as taking place according to the same mechanism, irrespective of the reaction techniques; the mechanism is supported by the above evidence. If the reaction proceeds under the conditions of the competitive-reversible adsorption in the Langmuir-Hinshelwood mechanism, no reaction can proceed in the periodic-pulse technique. Therefore, our findings suggests that the reversible adsorption mechanism can be disregarded.

The amount of surface oxygen available for acrolein formation on the Bi–Mo catalyst may be calculated from Fig. 4 to be less than 3.3 μmoles/g catalyst. On the other hand, the total amount of lattice oxygen at the surface can be approximately accounted to be of the order of 50 μmoles/g catalyst; this is about 10 times the available oxygen. It is considered that this speculation adds support to the heterogeneity of the catalyst activity, discussed above. Furthermore, it might be possible to regard the available oxygen as adsorbed.

Because it can be considered that the shortening of the period corresponds to the collecting of the frontal parts of the O- and R-pulses, the greater formation in the short period may imply that the reaction proceeds faster in the frontal part of O- and/or R-pulses. Consequently, the inclination observed in the period dependence is consistent with that of the variation in the rate with the time-on-stream in the pulse to which the reaction belongs.

Since acrolein is formed only at the R-pulse, the period dependence in acrolein formation over the Group (a) catalysts suggests that the acrolein formation proceeds fast in the frontal part of the R-pulse, and that it decreases gradually as time passes. On the other hand, over the Group (c) catalysts, the rate of acrolein formation is found to be nearly constant during the R-pulse. It seems that the latter has a large amount of surface oxygen with a lower activity, while the former possesses a small amount of more active surface oxygen. In other words, it may be considered that the period dependence is determined largely by the activity and the concentration of surface oxygen. Because oxygen is always present in the gas phase in the continuous-flow reaction, the active site on the Group (a) catalyst can be immediately reoxidized to react with propylene and to contribute repeatedly to the acrolein formation. This brings a greater yield of acrolein than in the periodic-pulse reaction.

The period dependence in the combustion reaction can be explained in a similar way. It may be determined by the rate of combustion and by the concentration of the adsorbed species. A combustion reaction over the Sn–Sb and Sb–Mo catalysts with a small amount of surface oxygen proceeds quickly at the R-pulse, while that over the Sn–P, Bi–W, and Bi–Mo catalysts, with great amounts of adsorbed residue, proceeds slowly at the O-pulse. It may be considered that the combustion occurs by following the fast reoxidation over the Group (b) catalysts, much as in the acrolein formation in the Group (a) catalysts.

Characterization of the Catalysts and Catalytic Actions of Bismuth and Antimony

It may be considered that the catalyst properties mentioned above may be attributed to some actions of the element, because it happens that the Group (a) and (b) catalysts contain bismuth and antimony, respectively, in their compositions. The role of each component in the catalytic actions of the binary oxide catalysts has not yet been made completely clear. For example, the main properties controlling their activities have been discussed in connection with the crystallization in the Bi–Mo system (*8*) or in connection with the change in the electrical conductivity in the Sn–Sb system (*9*). These considerations have been based on the assumption that the catalytic function is uniformly dispersed. On the other hand, the Batist, Lippens and Schuit (*2*) proposal regarding the Bi–Mo catalyst is considered to indicate that each component contributes to the different functions, in which each consists of a bi-function of molybdenum as an anion vacancy and of bismuth, close to molybdenum as an oxidizing reagent. It seems that the grouping of elements by Alkhazov, Belenky and Alekseyeva (*10*) is based on the same idea.

The properties of Group (a) catalysts can also be explained according to this proposal. As discussed above, the characteristics of Group (a) and (b) catalysts can be attributed to the fast reoxidation possible for acrolein and carbon oxide formations, respectively, in spite of the small concentration of surface oxygen. The fast reoxidation may be described as in the following equations. For example, the bismuth appears to play this role;

$$Bi^{3+} + 1/2\ O_2 \rightarrow Bi^{5+}O^{2-}$$

$$Bi^{5+}O^{2-} + (\ \ ) \rightarrow Bi^{3+} + (O)$$

where ( ) denotes the bare active site.

That is, it may be presumed that the bismuth adjacent to the active site which belongs to the molybdenum and tungsten atoms contributes to the activation of molecular oxygen, and that it results in a fast reoxidation of the active sites available for acrolein formation. Consequently, it may be also explained by Group (a) catalyst with highly mobile oxygen controlling the concentration of active oxygen at the surface, while Group (c) catalysts have a low bulk mobility. The role of antimony seems to be similar for the combustion reaction. The idea mentioned above is the same as that of Kominami (*11*) with regard to the selenium of the Cu–Se system catalyst; Ishikawa and Hayakawa (*12*) tried to explain the role of arsenic in the Fe–As system catalyst by the same idea. Furthermore, Alkhazov, Belenky and Alekseyeva (*10*) characterized the bismuth atom as a fair oxidizing reagent; this is consistent with the expectation stated above.

P_R Dependence and Irreversibly Adsorbed Species

The following explanation can be made of the maximum value of acrolein formation in Fig. 5 with respect to the partial pressure of propylene over the Bi–Mo(1/1) catalyst. As stated above, acrolein is formed from catalyst oxygen and gaseous propylene at the R-pulse. Since oxygen is not contained in the R-pulse, the reduced sites on the catalyst cannot be reoxidized and the hydrocarbon seems to be adsorbed irreversibly. The hydrocarbon adsorbed irreversibly reacts with gaseous oxygen to produce carbon oxides. If irreversible adsorption is predominant to the reoxidation of the catalyst, the catalyst surface reaches a more reduced state with an increase in the partial pressure of hydrocarbon, thus resulting in a decrease in the acrolein formation. The compensation relation between the formations of acrolein and carbon oxides implies that the identical active sites contribute to each reaction in proportion to the concentration of surface oxygen.

It is difficult at present to estimate in detail the adsorbed species connected with the combustion. Further investigations are needed to determine whether it is dehydrogenated propylene, acrolein, or a further oxidized material.

Belousov and Gershingorina (*13*) examined the oxidation of propylene into carbon dioxide over various kinds of metal oxides by the pulse microcatalytic method, and reported that the activities were poisoned by the irreversible adsorption of propylene. Although their remarks are important in understanding the adsorption of propylene, it is necessary to consider that the experiment was performed in a nonstationary state. Taking into consideration the differences in experimental technique, the irreversible adsorbed propylene, noted by Belousov and Gershingorina can be thought to be none other than that which leads to a combustion reaction with the action of molecular oxygen.

Taking into consideration the characteristics of the periodic-pulse technique, it seems that it can be utilized as a research method for oxidation reaction. In conclusion, the characteristics of the periodic-pulse technique can be regarded as follows; (1) oxidation and reduction are performed separately, thus giving the advantage of examining the reaction steps, the condition of the catalyst surface, etc., and (2) the results of the periodic-pulse reaction are closely related to those of the continuous-flow reaction with an enlarging of the rate of reduction or oxidation. It is conceivable that the reaction mechanisms are nearly the same for the two techniques.

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