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Interactions of Oxygen with Olefins Adsorbed on Zinc Oxide

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The interaction of oxygen with olefins adsorbed on ZnO was investigated by analysis of the reaction products in the gas phase. It was found that the oxygen uptake had occurred before the adsorbed olefin was oxidized to CO_2 and H_2O. This oxygen uptake was attributed to the formation of a surface olefin-oxygen complex. The reactivities for such complex formation increased in the order $C_2H_4 < 1{,}3\text{-}C_4H_6 < C_3H_6 < 2\text{-}C_4H_8 < 1\text{-}C_5H_{10}$. From these results it was concluded that the catalytic oxidation of olefins over ZnO proceeds via such surface complex formation.

INTRODUCTION

As regards the oxidation of propylene to acrolein it has been established by Adams and Jennings (*1*), and Sachtler and de Boer (*2*) that the oxidation proceeds via π-allylic intermediate. According to Morooka and Ozaki (*3*), nondissociative π-complex is a reaction intermediate in the oxidation of olefins on NiO. Existing data seem insufficient to clarify the intermediate in the oxidation of olefin. Especially, the part played by such intermediates in determining the selectivity of the oxidation is very far from a complete understanding. The information on the mechanism of the complete oxidation seems necessary for understanding the selectivity of oxidation. The complete oxidation is a complicated process, involving a number of consecutive steps. It seems very difficult to clarify the mechanism of such reaction only from kinetic studies. The situation will be much improved by direct study of the reaction of adsorbed species. Work along this line has been carried out by one of the present authors (*4*). It has been undertaken, therefore, to investigate the interaction of oxygen with olefins adsorbed on various oxides in order to obtain information on the mechanism of the oxidation. The results with ZnO are described below.

EXPERIMENTAL METHODS

Materials. Zinc oxide used was of extra pure grade from the Hayashi Junyaku Co. Its surface area determined by the BET method was 3.05 m²/g. Propylene was obtained from the Takachiho Co. and purified by fractional distillation. As to *trans*-2-butene, 1-pentene, ethylene, 1,3-butadiene and propane, materials 99.9% pure were obtained from the Takachiho Co. and used without further purification. Oxygen was obtained from a cylinder and purified by passing through silica gel immersed in liquid nitrogen.

Apparatus and procedure. A closed circulation system was used. The interaction of oxygen with olefins adsorbed on ZnO was investigated over a wide temperature range as follows: After adsorption of a known amount of olefin at 0°C, the olefin remaining in the gas phase was removed by immersing the trap attached to the reaction vessel in liquid nitrogen. Then, a known amount of oxygen was admitted to the system and circulated over the catalyst for 3 hr at 0°C. At high reaction temperatures the oxidation of adsorbed olefin occurs. In this case the oxidation products

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such as CO_2 and H_2O were condensed in the liquid nitrogen trap. By using two traps alternatively, trapping was carried out uninterruptedly. The amounts of oxygen uptake or consumed by the reactions were determined by measuring the pressure in the system. After the experiment at 0°C was finished, the temperature of the catalyst was raised in stages, at each of which similar experiments were carried out. In the study of the desorption of olefin adsorbed, desorption was carried out by means of a mercury diffusion pump and liquid nitrogen traps. Noncondensable gases were collected by a Töpler pump. The experiments were carried out over a wide range of temperature by raising the catalyst temperature in stages from 0 to 400°C.

In all the runs 5 g of the ZnO catalyst was used. Prior to the experiments the catalyst was evacuated at 450°C to a residual pressure of 10^{-4} mm Hg or less.

RESULTS AND DISCUSSION

Interaction of oxygen with propylene adsorbed on ZnO. Before the study of interaction of propylene adsorbed on ZnO, the adsorption of propylene on it was investigated. As shown in Fig. 1 the amount adsorbed at about 30 mm Hg decreases with increasing temperature. The remaining amounts adsorbed after desorption for 10 min at each adsorption temperature are shown in the same figure. It is seen that most of the propylene adsorbed at room temperature can be removed by evacuation around 100°C. Such behavior is essentially the same as those observed by Dent and Kokes (*5*) and also one of the present authors (*6*).

In the study of interaction of propylene adsorbed, oxygen was admitted at 0°C to the catalyst which had adsorbed propylene. Then, the catalyst temperature was raised up in stages, successively T_1, T_2, T_3 . . . . The amounts of oxygen uptake or consumed by the reactions and those of CO_2 and H_2O formed at each stage are shown in Fig. 2, where the amount of oxygen uptake at T_3 refers to the uptake during the temperature rise from T_2 to T_3 and after the temperature became constant at T_3. It is seen that an appreciable amount of oxygen uptake is observed in the temperature range where no formation of CO_2 takes place. As shown in Fig. 3, the amount of oxygen uptake at 85°C increases in proportion to the amount of propylene previously adsorbed. Furthermore, in the desorption experiment after oxygen was admitted to the catalyst which had adsorbed propylene, no propylene was found in the desorption products, in contrast to the result of desorption where only propylene was adsorbed (Fig. 1). Such behavior suggests that this oxygen uptake results from the interaction of oxygen with propylene to form an adsorption complex.

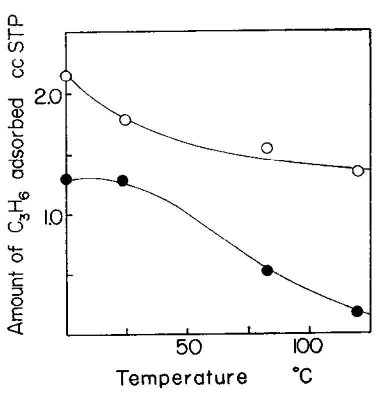

FIG. 1. Adsorption of propylene on ZnO: (○) amount adsorbed at about 30 mm Hg; (●) remaining amount adsorbed after desorption.

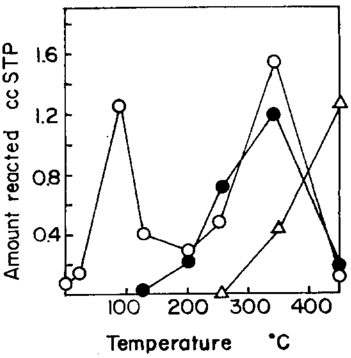

FIG. 2. Reaction of oxygen with adsorbed propylene: (○) O_2 uptake or consumed by the reactions; (●) CO_2 formed; (△) H_2O formed. Amount adsorbed of propylene at 0°C was 1.37 ml.

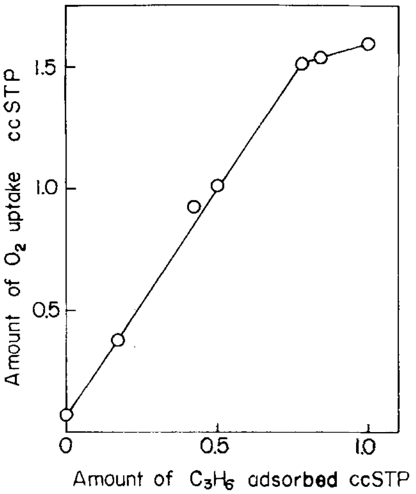

FIG. 3. Correlation between amounts of oxygen uptake and propylene preadsorbed. Temp, 85°C.

Figure 2 shows that the amount of oxygen uptake or consumed by the reactions at each stage passes through two maxima, one corresponding to the uptake at 85°C with the formation of the complex and the other corresponding to the reaction with formation of CO_2. This suggests that the oxidation of propylene adsorbed on ZnO proceeds in two consecutive steps, i.e., the propylene–oxygen complex formation and the oxidation of the complex to CO_2 and H_2O.

Comparison of the reactivities of various olefins for the complex formation. Similar experiments were carried out with olefins such as ethylene, *trans*-2-butene, 1-pentene and 1,3-butadiene. By analogy with propylene, the amounts of oxygen uptake and those of CO_2 and H_2O formed at each stage of the temperature elevation are shown in Figs. 4 and 5. As shown, similar two maxima are observed in the plots of the oxygen uptake against the catalyst temperature. Note that even at 0°C an appreciable amount of oxygen uptake occurs in the case of *trans*-2-butene. Similar results were obtained with 1-pentene. In the case of ethylene the catalyst temperature was raised in the presence of gaseous ethylene as well as of oxygen, since all the ethylene adsorbed had been removed before it was converted to the ethylene–oxygen complex.

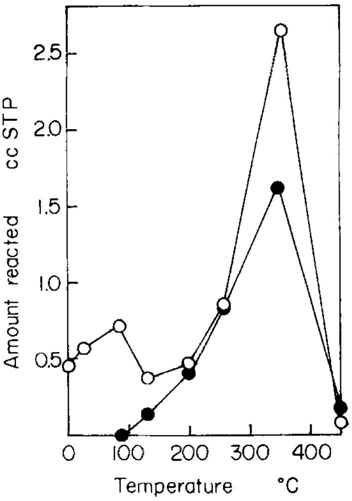

FIG. 4. Reaction of oxygen with adsorbed *trans*-2-butene. Symbols are the same as for Fig. 2. Amount adsorbed at 0°C was 1.58 ml.

In order to compare the relative reactivities of various olefins for the oxygen uptake, the increase in the amounts of oxygen uptake with increasing the catalyst temperature is shown in Fig. 6, where the total amount of oxygen uptake at T refers to the uptake during the temperature rise from 0 to T°C. It is seen that the relative rates of the oxygen uptake are in the following order: 1-pentene > *trans*-2-butene > propylene > butadiene > ethylene. This

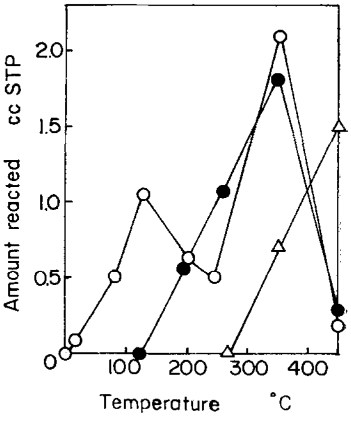

FIG. 5. Reaction of oxygen with adsorbed 1,3-butadiene. Symbols are the same as for Fig. 2. Amount adsorbed at 0°C was 1.25 ml.

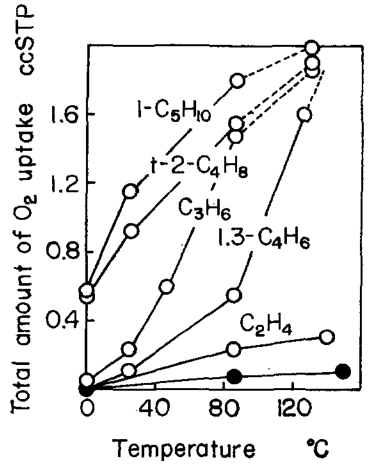

FIG. 6. Increase in the amount of oxygen uptake with temperature: (●) in the absence of hydrocarbons. Amounts adsorbed at 0°C were 0.80 ml for C_3H_6; 0.76 ml for t-2-C_4H_8 and 1-C_5H_{10}; and 0.80 ml for 1,3-C_4H_6. In the range of broken curves the uptake includes the amount of O_2 consumed as CO_2.

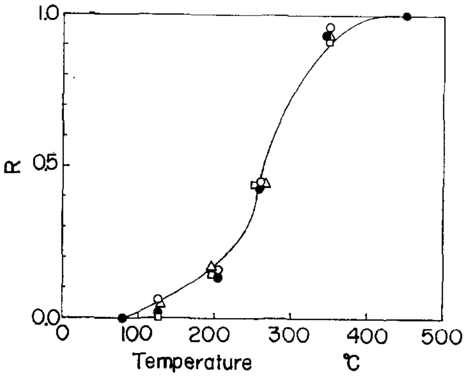

FIG. 7. Increase in the amount of CO_2 formed with temperature: (●) C_3H_6; (○) t-2-C_4H_8; (△) 1-C_5H_{10}; (□) 1,3-C_4H_6.

suggests that the relative rates of oxygen uptake increases with increasing carbon number for monoolefins.

The olefin–oxygen complex formed at lower temperatures is oxidized to CO_2 and H_2O at higher temperatures. The amount of CO_2 formed increases with increasing the catalyst temperature. Such increase is shown as the plots of R = (the amount of CO_2 formed during the temperature rise from 0 to T°C)/(the corresponding amount from 0 to 450°C) against the catalyst temperature T (Fig. 7). It is seen that the plots of various olefins lie on the same curve, suggesting that the olefin–oxygen complexes formed from various olefins exhibit similar reactivities for their oxidation to CO_2 and H_2O. Considering that there is a marked difference between the reactivities of olefins for the complex formation, it is concluded that the step of the complex formation determines the reactivities of olefins for complete oxidation.

The ratio of the amount of oxygen uptake at 85°C after contact for 3 hr to that of olefin previously adsorbed was about 2 for propylene (Fig. 3) and *trans*-2-butene, and was about 3 for 1-pentene. After contact for 24 hr these ratios increased to 2.5 and 3.5, respectively. In the case of butadiene the ratio was determined as 2.5 at 135°C. As shown in Fig. 3, the plot of the oxygen uptake shows a break at a large amount of propylene adsorbed; a trend reaching a saturation value was observed.

Reactive species in the complex formation. During the measurements of oxygen uptake at a constant temperature, the pressure in the reaction system was abruptly changed. From comparison of the rates of oxygen uptake before and after the pressure change, the pressure dependence of the rate of the complex formation was determined. The temperature dependence of the rate was also determined in a similar manner. The rates of oxidation of the complex to CO_2 and H_2O were determined by measuring the pressure decrease due to the reaction. (The products of CO_2 and H_2O were frozen in a liquid nitrogen trap.) Its pressure and temperature dependencies were determined in the manner described above. The results are shown in Table 1. Note that the rate varies approximately as $(p)^{1/2}$ for the oxidation of the complex while as p for the complex formation. This suggests that molecular adsorbed oxygen or gaseous oxygen participates in the formation of the complex. Participation of molecular adsorbed species seems to be more probable than that of gaseous oxygen, since the results obtained with other oxides

TABLE 1

PRESSURE AND TEMPERATURE DEPENDENCIES OF THE RATES OF THE COMPLEX AND CO_2 FORMATION

	Value of n[a] (rate $\propto p^n$)				Activation energy E[b] (kcal/mole)			
	Complex formation		CO_2 formation		Complex formation		CO_2 formation	
	Temp	n	Temp	n	Av temp[c]	E	Av temp	E
C_3H_6	52	1.2	293	0.44	50	15.0	295	23.1
t-2-C_4H_8	25	0.8	298	0.55	40	13.4		
1-C_5H_{10}	52	0.9	298	0.50	40	12.1		
1,3-C_4H_6					108	16.6		

[a] The measurements were carried out in the pressure range 5–50 mm Hg.

[b] An upper limit of the error was 7–10%.

[c] The mean of the temperatures before and after the abrupt change.

are explicable by assuming that the activities of adsorbed oxygen are different on various oxides. Details will be described in a forthcoming paper.

According to the work of Dent and Kokes (*5*), the remaining propylene adsorbed after desorption at 0°C consists of mainly π-allyl species, suggesting that the propylene–oxygen complex forms from interaction of π-allyl species with oxygen. The rise in the reactivity for oxygen uptake with increasing carbon number described above may be attributed to the increase in the electron concentration of the conjugated double bond of π-allyl species with increasing alkyl substitution, similar to that observed with the electrophilic addition reactions (*7*). The initial step in the complex formation may be the formation of a peroxyradical from π-allyl species. The complex finally formed, of course, has a somewhat different structure, since the ratio of oxygen to propylene in the complex is not equal to 1 as described above. Since π-allyl species is removed by evacuation at 180°C, reversibly adsorbed propylene is converted to irreversibly adsorbed species in the complex formation. It appears that the complex formation is confined to a limited number of sites, since in the plot of the oxygen uptake against the propylene adsorbed (Fig. 3) a trend approaching a saturation value is observed.

The complex formation in the catalytic oxidation of propylene and of propane. In the study of the catalytic oxidation of olefins by usual flow method, the experiments are carried out at higher temperatures than those used in the present work and also in the presence of gaseous olefins as well as of oxygen. In order to obtain information whether or not the conclusion described above is applicable in the experiments by usual flow method, the following experiments were carried out: An equimolar mixture of propylene and oxygen was circulated over the catalyst at a constant temperature. The change in the total pressure with reaction time was examined (Fig. 8). At 85°C only a decrease in the pressure was observed, while at 260°C an instantaneous decrease in the pressure was followed by a gradual increase. Such behavior suggests that at 260°C an instantaneous formation of the adsorption complex and its oxidation to CO_2 and H_2O takes place consecutively, thus confirming that the same conclusion is applicable in the catalytic oxidation of propylene.

It seemed of interest to find out whether or not the oxidation of saturated hydrocarbons such as propane involves the for-

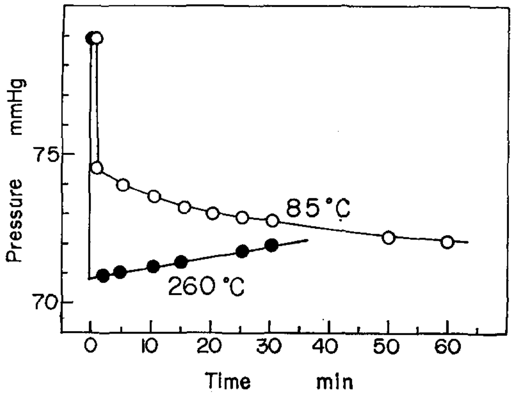

FIG. 8. Pressure change during circulation of propylene–oxygen mixture over ZnO.

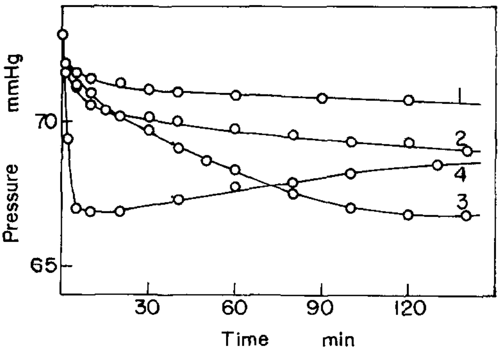

FIG. 9. Pressure change during circulation of propane–oxygen mixture over ZnO. Temp: (1) 164; (2) 206; (3) 260; (4) 300°C.

mation of an adsorption complex similar to that with olefin oxidation. Since the adsorption of propane on ZnO is very weak, i.e., the amount of propane adsorbed after desorption at 0°C is very small, the experiments of the oxidation of adsorbed propane are unfeasible. Circulation of an equimolar mixture of propane and oxygen over the catalyst was carried out in a similar manner to that described above. As shown in Fig. 9, the pressure decrease is observed, its extent being increased with temperature up to 260°C. Above 260°C the pressure decrease is followed by a gradual increase. The amount adsorbed during the experiment at 260°C after 120 min was 0.59 ml for propane and 1.81 ml for oxygen, being much greater than the propane adsorption in the absence of oxygen (0.14 ml). Furthermore, this adsorption was not removed by evacuation at room temperature. Such behavior suggests that a similar adsorption complex will form in the oxidation of propane on ZnO.

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