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Interactions of Oxygen with Propylene Adsorbed on Metal Oxide Catalysts

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The interaction of oxygen with propylene adsorption was investigated over a wide range of oxides as an extension of the previous work on zinc oxide. On Co_3O_4, after propylene adsorption the oxygen uptake due to formation of a surface propylene–oxygen complex occurred even at −78°C. Almost the same oxygen uptake was observed after ethylene adsorption on Co_3O_4. On NiO, CuO and Fe_2O_3, the oxygen uptake induced by propylene occurred at 0°C. On the other hand, on Cr_2O_3, V_2O_5, TiO_2 and MoO_3, such phenomenon was not observed. The activity order for the oxidation of propylene adsorbed on oxides was essentially the same as that found for the catalytic oxidation of propylene over the corresponding oxides. In addition, the propylene adsorption was examined on Co_3O_4 subjected to various pretreatments such as water vapor adsorption.

INTRODUCTION

In order to obtain the information on the mechanism of the catalytic oxidation of olefins on oxides and on the role of the intermediates in the selectivity of the oxidation, the interaction of oxygen with olefins adsorbed on zinc oxide was investigated in the previous paper (*1*). It was found that the oxidation proceeds in the two consecutive steps, i.e., the formation of an olefin–oxygen complex and its oxidation to CO_2 and H_2O. In addition, the characteristics of the two processes were clarified. It seems of interest to extend such investigation to other oxides and to find out whether or not this conclusion is applicable. In the present work, therefore, the interactions of oxygen with propylene adsorbed on various oxides such as Co_3O_4, NiO, Fe_2O_3, CuO, Cr_2O_3, V_2O_5, TiO_2 and MoO_3 were investigated in a similar manner.

EXPERIMENTAL METHODS

Materials

Chromic oxide (Cr_2O_3) was prepared by controlled ignition of CrO_3 in a stream of dry air at 450°C.

Ferric oxide (α-Fe_2O_3) was prepared by precipitation from the solutions of ammonium carbonate and ferrous nitrate. The resulting precipitate was washed, dried and heated to 500°C in air.

Co_3O_4 was prepared by precipitation with ammonia from a cobalt nitrate solution. The washed and dried material was heated in air at 450°C. The X-ray analysis showed only spinel structure of Co_3O_4 to be present.

V_2O_5 was prepared by precipitation from the solutions of ammonium metavanadate and nitric acid. The precipitate was washed, dried at 120°C and heated at 450°C.

MoO_3 was prepared by heating ammonium molybdate in air at 450°C.

NiO was prepared by heating nickel nitrate in air at 500°C.

TiO_2 and CuO were of extra pure grade and obtained from the Merck and the Nihonshiyaku Co., respectively.

All reagents used in the present work were of extra pure grade. The surface area of the catalysts determined by the BET method using argon were as follows: Co_3O_4, 10.0;

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Fe_2O_3, 16.2; Cr_2O_3, 10.9; V_2O_5, 2.0; MoO_3, 1.3; NiO, 3.3; TiO_2, 2.0; CuO, 12.5 m^2/g.

The preparation of the gases used in the present work was the same as described previously (*1*).

Apparatus and Procedure

Details were described in the previous paper (*1*). A closed circulation system was used. The temperature of the catalysts which had already adsorbed a known amount of propylene was raised up in stages in the presence of oxygen. The amounts of oxygen consumed and of the reaction products were determined as described previously.

Prior to the experiments all the catalysts were evacuated at 450°C except for CuO, which was evacuated at 300°C.

RESULTS AND DISCUSSION

Interaction of Oxygen with Propylene Adsorbed on Co_3O_4

Oxygen was admitted to the catalyst which had already adsorbed propylene at 0°C. Then, the temperature of the catalyst 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. 1, 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 even at 0°C. As shown in Fig. 2, this oxygen uptake increases with increasing amount of propylene previously adsorbed. After the oxygen uptake the desorption experiments were carried out. It was found that there was no reversible desorption of propylene. In the case where only propylene was adsorbed, about 15% of propylene adsorbed was desorbed as such. In addition, when, instead of oxygen, hydrogen was admitted to the catalyst which had adsorbed propylene, 50% of propylene adsorbed was hydrogenated to propane at 0°C. Similar hydrogenation experiments were carried out with the catalyst which had been subjected to the propylene adsorption followed by the oxygen uptake. No hydrogenation occurred. Such behavior suggests that this oxygen uptake results from the interaction of oxygen with propylene to form an adsorption complex by analogy with zinc oxide described in the previous paper (*1*). It was found that at −78°C the oxygen uptake proceeded at a similar rate to that observed at 0°C. This suggests that the activity of Co_3O_4 for formation of the propylene–oxygen complex is much higher than that of ZnO, the activation energy of the complex formation being very small. The pressure dependence of the rate of formation was determined by changing the pressure abruptly during the rate measurements, the rate being proportional to $p^{0.5-0.6}$.

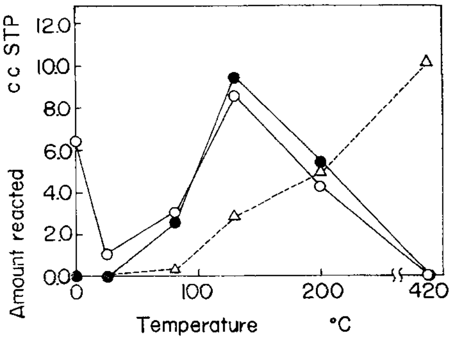

FIG. 1. Reaction of oxygen with propylene adsorbed on Co_3O_4. Catalyst, 5 g; Amount adsorbed of propylene, 5.06 cc; (○—) O_2 uptake or consumed by the reactions; (●—) CO_2 formed; (△- -) H_2O formed.

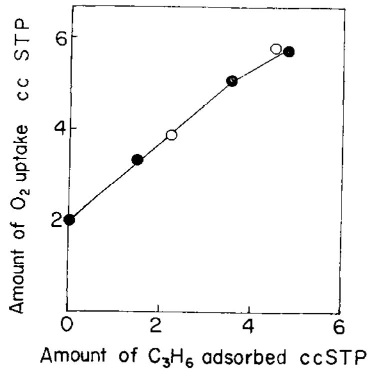

FIG. 2. Correlation between the amounts of oxygen uptake and olefin preadsorbed. Catalyst, Co_3O_4 5 g; Temp, 0°C; (●—) C_3H_6; (○—) C_2H_4.

Similar experiments were carried out with ethylene in place of propylene. It was found that a similar oxygen uptake occurred after the adsorption of ethylene. The amount of oxygen uptake induced by ethylene was almost the same as that with propylene (Fig. 2). Furthermore, the behavior of oxidation of the complex was similar to that with propylene. It is to be noted that such similarity is in contrast to a marked difference between the behavior for both olefins obtained with ZnO (*1*).

Effects of Pretreatments on the Propylene Adsorption on Co_3O_4

It is well known that the characteristics of the oxide surface are markedly changed after various treatments such as the reduction and oxidation treatments (*2*). Furthermore, in the study of the catalytic oxidation by the usual flow method, the experiments are carried out in the presence of water vapor and other reaction products. It seems of interest to obtain the information on the propylene adsorption under such experimental conditions. The experiments for this purpose were carried out with the results shown in Table 1. After the water vapor adsorption at 200°C, the amounts of propylene adsorbed at 0°C as well as the remaining amount adsorbed after desorption at 0°C (the amount of the strong adsorption) are decreased. Although such a decrease would be expected, it is to be noted that an appreciable amount of the strong adsorption still remains after adsorption of a large amount of water. A similar decrease in the amount of the strong adsorption is observed with the catalyst after the reduction treatment. In the case of preadsorption of oxygen, there is little or no change in the amount of propylene adsorbed strongly.

TABLE 1

EFFECT OF PRETREATMENTS ON THE PROPYLENE ADSORPTION ON Co_3O_4[a]

	Amount adsorbed at 0°C (cc)	Remaining amount adsorbed after desorption at 0°C (cc)
Before treatment	5.09	4.38
After 3.24 cc of H_2O adsorption at 200°C	4.14	2.10
After H_2 reduction treatment at 450°C	4.19	2.65
After 0.83 cc of O_2 adsorption at 25°C	6.70	4.50

[a] 5 g of catalyst was used.

It was found that the amount of the strong adsorption with propylene was almost the same as that with ethylene. Such a behavior is in contrast with the results obtained with ZnO, where the strengths of adsorption for both olefins are markedly different from each other. In the case of ZnO, there appears sufficient evidence for the formation of π-allyl in the propylene and of π surface complexes in the ethylene adsorption (*3*). It has been proposed that π-complex is formed in the adsorption of propylene as well as of ethylene on Co_3O_4 (*4*). Such conclusion, however, is applicable to the intermediate in hydrogenation reactions on it. The work concerning the nature of the overall olefin adsorption on Co_3O_4 is now in progress. Details will be published in the near future.

The oxidation of propylene adsorbed after various treatments was carried out by raising the catalyst temperature T in stages as described above. Values of R = (the amount of CO_2 formed from 0 to T°C)/(the corresponding amount from 0 to 450°C) were plotted against T (Fig. 3). The plots after various treatments lie on the same curve, suggesting that although the amounts of the strong adsorption vary according to the pretreatment, its reactivity for the oxidation exhibits no marked difference.

Interaction of Oxygen with Propylene Adsorbed on Various Oxides

Similar experiments were extended to other oxides. In the case of Fe_2O_3, after the adsorption of propylene the oxygen uptake occurred at 0°C, its amount of uptake being approximately equal to that of propylene adsorbed (Fig. 4). In this case little or no oxygen adsorption took place before the propylene adsorption, leading to a reliable ratio of the oxygen uptake to the propylene

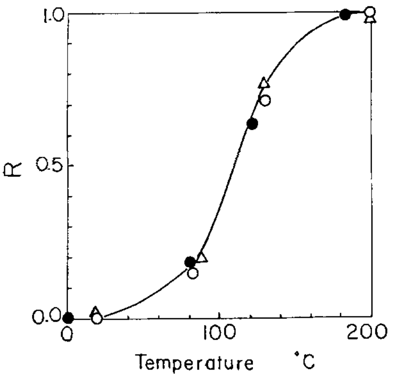

FIG. 3. Increase in the amount of CO_2 formed with temperature. Catalyst, Co_3O_4, 5 g; (●—) after H_2O adsorption; (△—) after reduction treatment; (○—) after O_2 adsorption.

adsorption. The temperature and pressure dependencies of the rate of oxygen uptake were determined as described above. The activation energy for the complex formation and that for the oxidation of the complex were 13 and 25 kcal/mole, respectively. The rate of the complex formation varied as $p^{0.8-0.9}$, similar to that observed with ZnO. The activity of Fe_2O_3 for the complex formation is higher than that of ZnO, since with Fe_2O_3 the oxygen uptake occurred at much lower temperatures.

Similar results were obtained with NiO and CuO, i.e., the oxygen uptake induced by the propylene adsorption occurred again at 0°C, its amount being equal to the amount of propylene adsorbed (Fig. 4). In the case of V_2O_5 and Cr_2O_3, somewhat different behavior was observed. As shown in Figs. 5 and 6, there is no oxygen uptake at 0°C. With increasing the catalyst temperature, disappearance of oxygen is observed, but simultaneously formation of CO_2 and H_2O takes place. As a result, the amounts of oxygen retained by the catalyst are much smaller than those obtained with other oxides. In the case of V_2O_5, the H_2O formation occurs in a lower temperature range than the CO_2 formation. Such a behavior is quite different from those obtained with other oxides. For TiO_2 and MoO_3 with a negligible amount of the strong propylene adsorption, no oxygen uptake was observed. The fact that the oxygen uptake occurs easily with Co_3O_4, NiO and CuO, and not with TiO_2 and MoO_3 suggests that there is some similarity in the activity pattern ob-

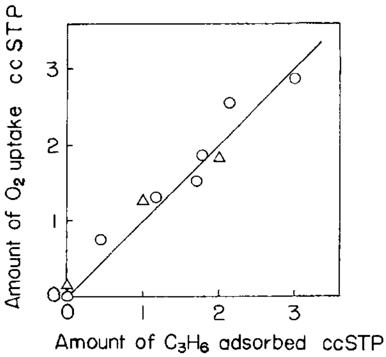

FIG. 4. Correlation between the amounts of oxygen uptake and propylene preadsorbed. Catalyst, 5 g; Temp, 0°C; (○—) Fe_2O_3; (△—) CuO.

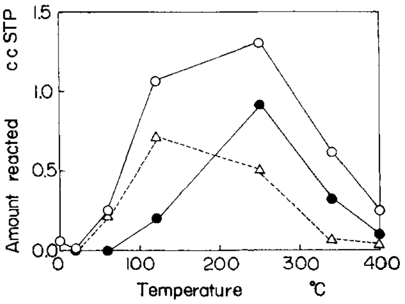

FIG. 5. Reaction of oxygen with propylene adsorbed on V_2O_5. Catalyst, 15 g; Amount adsorbed, 0.52 cc; Symbols are the same as for Fig. 1.

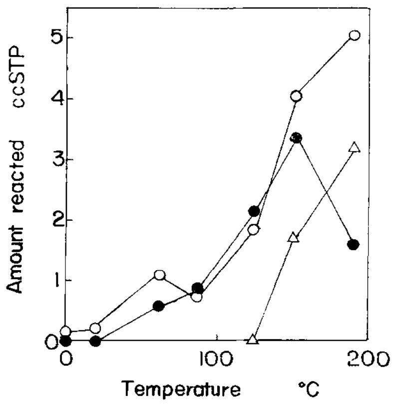

FIG. 6. Reaction of oxygen with propylene adsorbed on Cr_2O_3. Catalyst, 5 g; Amount adsorbed, 3.98 cc; Symbols are the same as for Fig. 1.

tained for the propylene–oxygen complex formation and for the catalytic oxidation of propylene on oxides. The activity pattern in the oxidation of hydrocarbons on oxides has been discussed by various workers (*5*). From the standpoint of the oxygen–catalyst bond energy, such a change in the activity of oxides for the propylene–oxygen complex formation might be explicable by assuming that the reactivity of adsorbed oxygen is higher on the oxide with a lower oxygen bond energy. An appreciable activity for the complex formation with ZnO and no activity with Cr_2O_3, however, appears to be unexplicable on such basis, since the oxygen bond energy increases with the order $Co_3O_4 < CuO < NiO < Cr_2O_3 < Fe_2O_3 < V_2O_5 < ZnO < TiO_2$ according to the work of Sazonov, Popovskii and Boreskov (*6*).

Oxidation of Propylene Adsorbed and Catalytic Oxidation of Propylene

The conclusion such that the oxidation proceeds via the two consecutive steps, i.e., the complex formation and its oxidation to CO_2 and H_2O is obtained with the reaction of olefin adsorbed, and not with the catalytic oxidation of olefins. In order to check its applicability to catalytic reactions, the following experiments were carried out with Co_3O_4. During the rate measurements of the oxidation of propylene adsorbed, the composition of the gas phase was abruptly changed from pure oxygen to a mixture of propylene and oxygen (Fig. 7). Little or no change in the reaction rate was observed, while a slight increase in the amount of propylene adsorbed took place. This suggests that weakly adsorbed propylene which is expected to form in the presence of gaseous propylene, has no significant role in the reaction. On the basis of these results together with those for ZnO described previously (*1*) the conclusion described above is applicable to the catalytic oxidation of olefins as well as to the oxidation of olefins adsorbed.

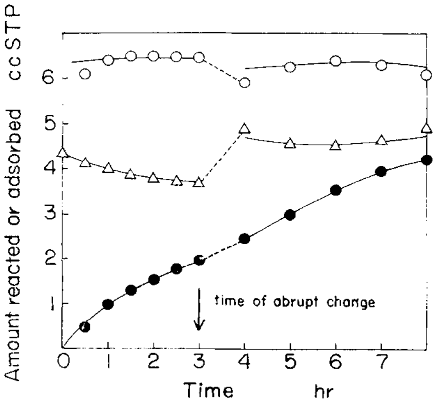

FIG. 7. Oxidation of propylene adsorbed on Co_3O_4 at 82°C. Catalyst, 5 g; initial, O_2, 30 mm Hg; after 3 hr, mixture of C_3H_6 and O_2 (1:3), 80 mmHg; (●—) CO_2 formed; (△—) C_3H_6 adsorbed; (○—) O_2 adsorbed.

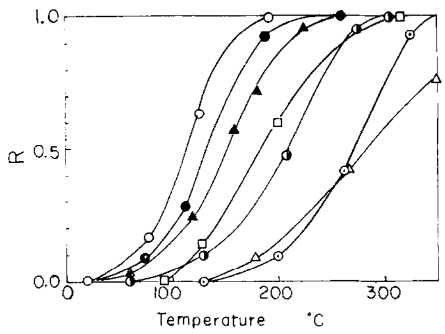

FIG. 8. Increase in the amount of CO_2 formed with temperature. (○—) Co_3O_4; (●—) CuO; (▲—) Cr_2O_3; (□—) V_2O_5; (◑—) Fe_2O_3; (⊙—), ZnO; (△—) TiO_2.

The relative rates of oxidation of the complex to CO_2 and H_2O were determined from the experiments when the catalyst temperature T was raised up in stages during the oxidation of propylene adsorbed. Values of R described above were plotted against the catalyst temperature T. The results are shown in Fig. 8. The activity of oxides for the oxidation decreases in the order $Co_3O_4 > CuO > Cr_2O_3 > V_2O_5 > Fe_2O_3 > ZnO > TiO_2$, being essentially the same as that obtained with usual flow experiments (*7*). This suggests that the rate of the catalytic oxidation of olefins on oxides is determined by the second step, i.e., the oxidation of the olefin–oxygen complex.

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