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Oxidation of Propylene Adsorbed on Metal Oxides. Oxygen Species in Catalytic Oxidation

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Adsorption of ethylene and propylene has been investigated volumetrically with various oxide catalysts. From the results together with those of oxidation of propylene adsorbed on oxides, it is concluded that the difference between the characteristics of oxidation of propylene adsorbed on the oxide catalysts for complete or selective oxidation is attributable to the difference in the oxygen species responsible for oxidation rather than that in the adsorbed state of propylene. A comparison of characteristics of the oxidation of adsorbed propylene in the presence of gaseous oxygen and in a vacuum suggests that on the catalysts for complete oxidation, adsorbed oxygen plays a significant role in the oxidation because of its higher activity as compared to that of lattice oxygen.

In order to obtain information on the mechanism of catalytic oxidation, investigation was carried out on the oxidation of olefins adsorbed on oxide catalysts by analysis of reaction products as well as by IR techniques.[1-3] In the case of ZnO, adsorbed propylene was converted into surface formate and acetate ions as well as OH groups with oxygen uptake, which were oxidized successively to CO_2 and H_2O. A marked difference in the oxidation of adsorbed propylene was observed with catalysts for selective oxidation such as V_2O_5[2] and Sn–Mo oxide.[4] For understanding the difference between the characteristics of oxidation of olefins adsorbed on oxides, it seems necessary to obtain information on how the oxygen species responsible for the oxidation as well as the nature of adsorbed state of olefins varies on going from one oxide to another. Work along this line has been undertaken in the present study.

As regards the adsorbed state of olefins, IR studies seem to be most promising. However, IR data are available only for a limited range of oxides such as ZnO,[5] Sn–Mo oxide,[4] and copper oxides[6] because of the inherent difficulties in the IR measurements of adsorbed species. Accordingly, volumetric adsorption measurements have been carried out for all the oxide catalysts for which the oxidation of adsorbed propylene was examined.[1,2]

Experimental

Details of apparatus, procedure and materials were reported.[1,2] The adsorption of ethylene and propylene as well as the oxidation or desorption was investigated with a closed circulation apparatus. In the case of the oxidation of adsorbed propylene, the temperature of the catalysts containing a known amount of adsorbed propylene was raised stepwise in the presence of oxygen. The amount of oxygen consumed and that of the reaction products were determined.

The surface area of the catalysts determined by the BET method using argon were as follows; Co_3O_4, 10.0; NiO, 3.3; CuO, 12.5; V_2O_5, 2.0; ZnO, 3.1; Fe_2O_3, 16.2; TiO_2, 2.0; MoO_3, 1.3 m^2/g.

Results and Discussion

Adsorption of Ethylene and Propylene on Oxides. The results of olefin adsorption experiments with various oxide catalysts are shown in Fig. 1. The amount of olefins adsorbed per unit area of the catalyst surface at 0 °C and 30 Torr as well as that of olefins remaining after evacuation at 0 °C are given. From these data we can obtain information on the activity of oxides toward the chemisorption of olefins. The strength of adsorption can be estimated from the remaining amount of adsorbed propylene after evacuation to the total amount adsorbed at 30 Torr. It is seen that both Co_3O_4 and ZnO exhibit the highest activity towards olefin chemisorption. The highest strength of adsorption of propylene is observed with Co_3O_4 and the lowest strength of adsorption with TiO_2 and MoO_3.

For the oxides such as ZnO, Fe_2O_3, and TiO_2 the amount of adsorbed propylene remaining after evacuation is larger than the corresponding amount of ethylene, while for the oxides such as Co_3O_4, NiO, CuO, and V_2O_5 the amounts of both olefins remaining are roughly the same. This suggests that the nature of the strong adsorption of olefins differs between both groups of oxide catalysts. Dent and Kokes[5] found that propylene undergoes adsorption to form π-allyl on ZnO while ethylene undergoes adsorption to form π-complex. They explained the difference between the remaining amounts of adsorbed propylene and ethylene.

On increasing the desorption temperature olefins adsorbed on ZnO desorbed as such without undergoing oxidation, while most olefins adsorbed on Co_3O_4 desorbed as CO_2 and H_2O. Thus, the difference between the nature of olefins adsorbed on both groups of oxides is confirmed.

Oxidation of Propylene Adsorbed on Oxides. The behavior of catalysts containing adsorbed propylene in the presence of oxygen, observed on raising the temperature, was described in previous papers.[1,2] In the case of ZnO one mole of the strongly adsorbed propylene took up two moles of oxygen to form surface formate and acetate ions,[1,3] which were oxidized successively to CO_2 and H_2O. A similar oxygen uptake was observed with other oxides such as Co_3O_4, NiO, Fe_2O_3, and CuO. On NiO, formation of carboxylate ions similar to that on ZnO was confirmed by IR techniques.[7] On the other hand, the interaction of oxygen with strongly adsorbed propylene on V_2O_5 led to little or no oxygen uptake, formation of water being observed at lower temperatures as compared to the cases of oxides such as Co_3O_4, ZnO, *etc.*[2] IR studies on Sn–Mo oxide[4] show that the interaction of oxygen with strongly adsorbed propylene causes formation of surface OH groups alone, no surface carboxylate ions being observed. The results indicate that the behavior observed with the catalysts for complete oxidation, such as Co_3O_4 and ZnO, differs from that with the catalysts for selective oxidation, such as V_2O_5 and Sn–Mo oxide.

The results of oxidation of the propylene adsorbed are compared with those of the adsorption of olefins. Although there is a striking difference in the nature of propylene adsorbed on Co_3O_4 and ZnO, both exhibit a similar behavior in the oxidation of adsorbed propylene, *i.e.*, formation of carboxylate species with oxygen uptake occurs during the course of oxidation. Irrespective of a marked difference in the behavior of Co_3O_4 and V_2O_5 in the oxidation of adsorbed propylene, there seems little difference in the features of olefin adsorption, *e.g.*, for both oxides the amount of adsorbed ethylene remaining is roughly the same as the corresponding amount of propylene (Fig. 1).

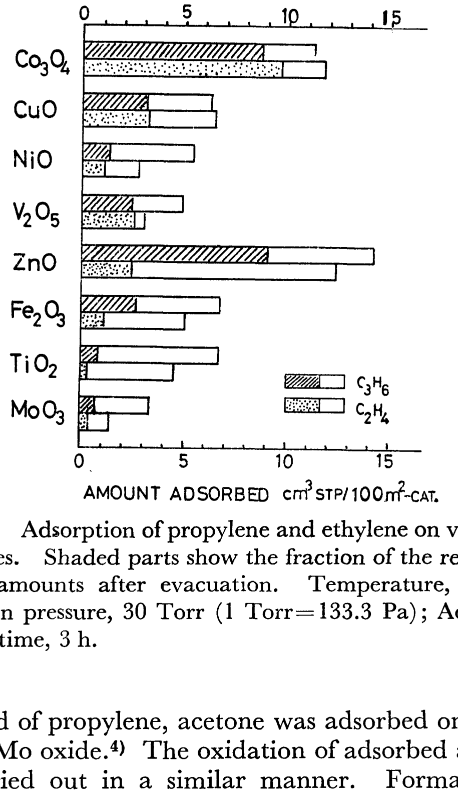

Fig. 1. Adsorption of propylene and ethylene on various oxides. Shaded parts show the fraction of the remaining amounts after evacuation. Temperature, 0 °C; Olefin pressure, 30 Torr (1 Torr = 133.3 Pa); Adsorption time, 3 h.

Instead of propylene, acetone was adsorbed on NiO[8] and Sn–Mo oxide.[4] The oxidation of adsorbed acetone was carried out in a similar manner. Formation of surface carboxylate ions was observed for NiO, but not for Sn–Mo oxide. Essentially the same difference between the behavior of both oxides in the oxidation was observed as that with propylene adsorbed. It seems that the features of the oxidation of adsorbed propylene are not closely associated with its adsorbed state. Such a difference in the features of the oxidation could be attributed to the difference in the oxygen species responsible for oxidation.

Oxygen Species Responsible for Catalytic Oxidation. A number of workers[9] have discussed the difference between the characteristics of the oxide catalysts for selective oxidation such as V_2O_5, MoO_3, and Bi–Mo oxide and for complete oxidation such as Co_3O_4, NiO, and Fe_2O_3 from the viewpoint of the type of metal–oxygen bonds.

The present paper is concerned with the relative roles of adsorbed and lattice oxygen in the oxidation on these oxide catalysts. The following experiments were carried out: The temperature of catalysts containing the strongly adsorbed propylene was raised stepwise in a vacuum, *i.e.*, desorption experiments were carried out. The amount of CO_2 formed during the course of temperature rise was compared with the corresponding amount in the presence of oxygen at 30 Torr. The results are shown by plots R *vs.* T, where R = (the amount of CO_2 formed during the temperature rise from 0 to T °C)/(the amount of propylene strongly adsorbed at 0 °C) × 3.

In the case of Co_3O_4 the plots R *vs.* T in the presence of oxygen shift to a lower temperature by about 150 °C as compared with that in a vacuum, suggesting participation of adsorbed oxygen in the oxidation (Fig. 2). A similar behavior is observed with Fe_2O_3 (Fig. 3). On ZnO, most part of adsorbed propylene was removed in a vacuum without undergoing oxidation, in contrast

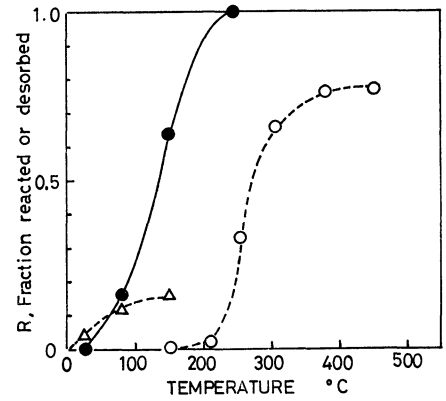

Fig. 2. Comparison of oxidation with desorption of propylene adsorbed on Co_3O_4.
—●—, CO_2 formed in the oxidation; ···○···, CO_2 formed in the desorption; —△—, C_3H_6 desorbed in the desorption. Experimental conditions in Figs. 2, 3, 4, and 5; Reaction time at each temperature in the oxidation, 3 h; oxygen pressure, 30 Torr; desorption time, 3 h; amounts of propylene adsorbed are shown in Fig. 1.

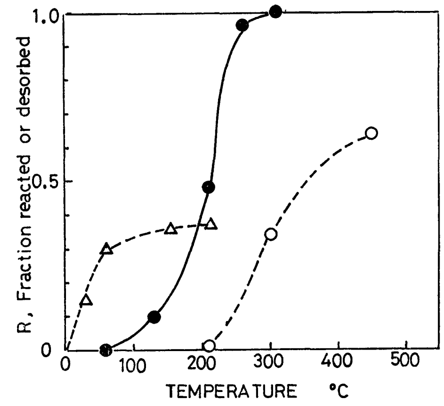

Fig. 3. Comparison of oxidation with desorption of propylene adsorbed on Fe_2O_3.
Symbols are the same as Fig. 2.

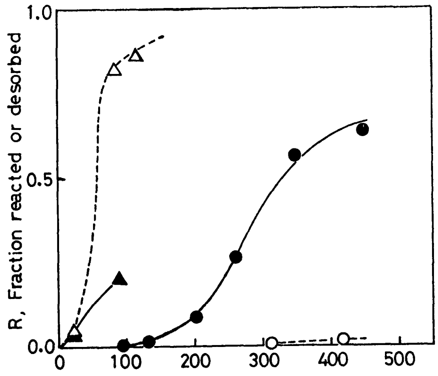

Fig. 4. Comparison of oxidation with desorption of propylene adsorbed on ZnO.
-▲-, C_3H_6 desorbed in the oxidation; other symbols are the same as Fig. 2.

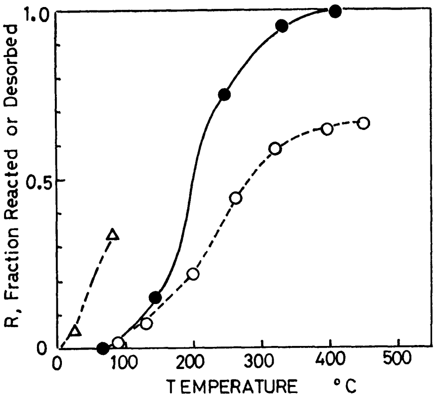

Fig. 5. Comparison of oxidation with desorption of propylene adsorbed on V_2O_5.
Symbols are the same as Fig. 2. Since in the case of V_2O_5 CO is formed in addition to CO_2, R values refer to formation of $CO+CO_2$. The amount of oxygen required for the oxidation of adsorbed propylene corresponded to about 30% of the surface oxygen layer.

with the case in the presence of oxygen where most part of adsorbed propylene was oxidized to CO_2 and H_2O (Fig. 4). Such a behavior suggests that surface lattice oxygen has no oxidizing power, *i.e.*, the oxidation proceeds *via* adsorbed oxygen alone.

For V_2O_5, the oxidation of adsorbed propylene in a vacuum occurs in about the same temperature range in the presence of oxygen (Fig. 5). The presence of gaseous oxygen has no effect on oxidation, *i.e.*, the surface lattice oxygen participates in the oxidation, in line with the conclusion reached by various workers.[10,11]

On the oxides which are effective for complete oxidation, active adsorbed oxygen is formed, which attacks olefins to form carboxylate ions, leading to the oxygen uptake by the catalysts. The absence of adsorbed oxygen on the catalysts for selective oxidation has been demonstrated by Seiyama,[14] who carried out the thermal desorption of oxygen adsorbed on various oxides. Haber and Grzybowska[15] reached similar conclusions from available data on the activity in oxygen isotopic exchange of various oxide catalysts. The general characteristic feature of the oxides effective for complete oxidation is that adsorbed oxygen plays a significant role in the oxidation because of its higher activity as compared with that of surface lattice oxygen.

References

1) Y. Kubokawa, T. Ono, and N. Yano, *J. Catal.*, **28**, 471 (1973).

2) T. Ono, T. Tomino, and Y. Kubokawa, *J. Catal.*, **31**, 167 (1973).

3) K. Hata, S. Kawasaki, Y. Kubokawa, and H. Miyata, *Proc. 6th Int. Cong. Catal.*, London, (1976), Vol. 2, p. 1102.

4) T. Ono and Y. Kubokawa, *J. Catal.*, **52**, 412 (1978).

5) A. L. Dent and R. J. Kokes, *J. Am. Chem. Soc.*, **92**, 6709, 6718 (1970).

6) S. V. Gerei, E. V. Rozhkova, and Ya. B. Gorokhovatsky, *J. Catal.*, **28**, 341 (1973).

7) S. Kawasaki, H. Miyata, and Y. Kubokawa, unpublished results.

8) H. Miyata, M. Wakamiya, and Y. Kubokawa, *J. Catal.*, **34**, 117 (1974).

9) E. R. S. Winter, *J. Chem. Soc.*, *A*, **1968**, 2889; J. Novakova, *Catal. Rev.*, **4**, 77 (1971); F. Trifiro and I. Pasquon, *J. Catal.*, **12**, 412 (1968).

10) *E.g.*, K. Hirota, Y. Kera, and S. Teratani, *J. Phys. Chem.*, **72**, 3133 (1968); W. M. H. Sachtler, G. J. H. Dorgero, J. Fahrenfort, and R. J. H. Voorhoeve, *Proc. 4th Int. Cong. Catal.*, Moscow, (1968), Vol. 1, p. 454.

11) In the case of supported V_2O_5 catalysts, adsorbed oxygen participates in the oxidation of olefins.[12] A similar behavior has been observed with another group of catalysts for selective oxidation such as Ag_2O and Cu_2O. For Ag_2O, participation of adsorbed oxygen appears to be established.[13]

12) S. Yoshida, T. Matsuzaki, T. Kashiwazaki, K. Mori, and K. Tarama, *Bull. Chem. Soc. Jpn.*, **47**, 1564 (1974).

13) P. A. Kilty, N. C. Rol, and W. M. H. Sachtler, *Proc. 5th Int. Cong. Catal.*, Florida, (1972), Vol. 2, p. 929.

14) "Kinzoku-sankabutsu To Sono Shokubai-sayo," ed by T. Seiyama, Kodansha, Tokyo (1978), p. 169.

15) J. Haber and B. Grzybowska, *J. Catal.*, **28**, 489 (1973).