The Study of Selective Oxidation of Propylene on Complex Oxides by Means of Temperature-Programmed Desorption[1]

L. D. KRENZKE,[*2] G. W. KEULKS,[*] A. V. SKLYAROV,[†] A. A. FIRSOVA,[†]
M. YU. KUTIREV,[†] L. YA. MARGOLIS,[†] AND O. V. KRYLOV[†]

[*] *Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201, and* [†] *Institute of Chemical Physics, Academy of Science of the USSR, Moscow, USSR*

The interaction of propylene with a number of complex oxide catalysts has been investigated by means of thermal desorption. The results indicate that propylene is adsorbed on only one type of active site and that this site is energetically similar for all the selective oxidation catalysts tested. The adsorbed propylene can react at the site to form acrolein via two different mechanisms. One of the mechanisms involves lattice oxygen, and the other, adsorbed oxygen, but in both cases the acrolein is derived from a common hydrocarbon intermediate. On one catalyst, a modified cobalt molybdate, evidence is given which shows that the rate-determining step in the selective oxidation of propylene is the desorption of acrolein and not the surface reaction.

INTRODUCTION

During the past few decades, many investigations have been devoted to the study of the selective oxidation of propylene to acrolein over transition metal oxide catalysts. Several recent publications (1) have reviewed this process, and it is now generally accepted that the oxidation of propylene proceeds via the formation of a symmetrical allylic intermediate. This allylic species reacts with oxygen from the oxide lattice after a second hydrogen abstraction to form acrolein or with gas-phase or adsorbed oxygen to form acrolein via the decomposition of an allyl peroxide or hydroperoxide (2).

This scheme indicates that acrolein can

[1] Work done at the Institute of Chemical Physics, Moscow, USSR.

[2] Exchange Fellow, USA–USSR Cooperative Program in Chemical Catalysis.

be produced by two different pathways and, consequently, may involve more than one type of active site. If the active centers are energetically heterogeneous, it is difficult to obtain any information about them or their relative contribution to the catalyst activity from steady-state reaction kinetics. This is particularly true if the rate of reaction is influenced or controlled by the desorption of the product. There is some evidence for the existence of a desorption-controlled reaction in the work of Keizer et al. (3) and Batist et al. (4) on the oxidative dehydrogenation of 1-butene to butadiene over bismuth molybdates. They observed a break in the Arrhenius plot and attributed the higher activation energy at lower temperatures to inhibition by strongly adsorbed butadiene.

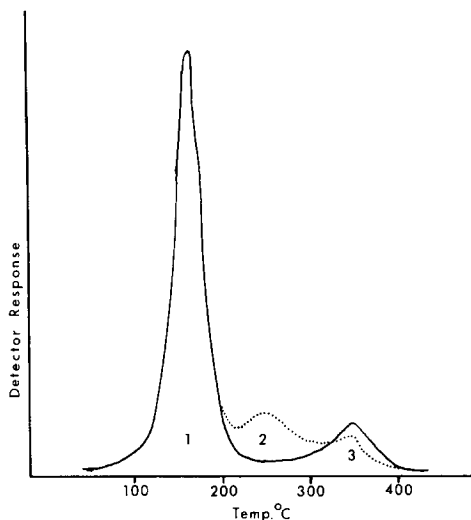A reasonable approach to the investigation of different types of active centers in

418

FIG. 1. Desorption spectra of propylene as a function of carrier gas: (——) He and ($\cdots$) air over $Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$ at a heating rate of 27°C/min. Peak 1 is C_3H_6, $T_m = 167°C$; peak 2 is C_3H_4O (form I), $T_m = 257°C$; and peak 3 is C_3H_4O (form II), $T_m = 365°C$.

a catalyst system is the temperature-programmed desorption (TPD) technique developed and reviewed by Cvetanovic and Amenomia (5). Using this method, we have studied the interaction of propylene with a wide variety of selective oxidation catalysts.

EXPERIMENTAL

The preparation of the catalysts used in this study has been previously described in the literature: $Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$ (6), Bi_2MoO_6 (7), $Bi_2Mo_3O_{12}$ (8), 5 atom% Sb in SnO_2 (9), USb_3O_{10} (10), $BiFeMoO_x$ and $Bi_3FeMo_2O_x$ (11), Cu_2O (pure reagent grade) and $CoMoO_4$ (prepared by coprecipitation of cobalt nitrate and ammonium paramolybdate, washed, dried, and calcined for 5 hr at 500°C).

All experiments were carried out in a U-shaped quartz reactor made of small-bore tubing to minimize diffusional broadlining of the desorption peaks. The catalyst samples, except Cu_2O, were pretreated *in situ* at 450°C for 1 hr in flowing air and

then cooled in air to the temperature at which the propylene adsorption would be carried out. The Cu_2O sample was pretreated in He for 1 hr at 450°C to avoid oxidation to CuO. Propylene was then adsorbed at atmospheric pressure for 15 min and 150°C for all catalysts except for one series of experiments with the modified cobalt molybdate sample. In that case, the adsorption temperature was varied between 70 and 150°C. After the adsorption was completed, the reactor was cooled rapidly to room temperature in flowing propylene, and then the carrier gas, either He or air, was passed through the reactor at a rate of 100 cm³/min to remove the weakly bound propylene. The carrier gas was allowed to flow over the catalyst for at least 30 min or until the recorder baseline was stable.

A flame detector was used instead of the conventional thermal conductivity cell for several reasons: high sensitivity, selectivity for hydrocarbons, stable baseline during temperature programming, and the ability to use a reactive carrier gas such as air. After the chromatogram was recorded and the peak locations were known, the experiment was repeated without the flame detector, and the various peaks were trapped and analyzed by conventional gas chromatography.

In several preliminary experiments, the flow rate of the carrier gas and the quantity of adsorbed propylene were varied, and neither had any effect on the position of the peaks. Therefore, readsorption is negligible, and the desorption of propylene and acrolein follow first-order kinetics. The energy of activation for the desorption process was then calculated by applying the following equation at various heating rates:

$$2 \log T_m - \log B = E_d/2.303RT_m \\ + \log (E_d/RA), \quad (1)$$

where T_m = temperature at peak maximum, B = the heating rate in degrees

Centigrade per second and A = the temperature-independent constant in the Arrhenius equation.

RESULTS AND DISCUSSION

$Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$

The majority of the desorption experiments were carried out on the modified cobalt molybdate catalyst. Initial tests were run to determine the effect of carrier gas composition and adsorption temperature on the TPD chromatogram. Figure 1 shows the difference between the desorption chromatograms of propylene when the carrier gas is changed from helium to air. These chromatograms have several significant features. First, propylene desorbs as a single symmetrical peak. This indicates that propylene interacts with only one type of active site and that these sites are energetically homogeneous. Second, a portion of the adsorbed propylene can react at this site during either the adsorption cycle or the TPD cycle to form acrolein. The third and perhaps most interesting feature is that the weakly bound form of acrolein is absent when helium is used as the carrier gas. This indicates that the weakly bound form of acrolein is produced via the interaction of adsorbed propylene and gas-phase or adsorbed oxygen during the TPD cycle. On the other hand, the formation of the strongly bound acrolein is independent of the presence of gas-phase oxygen and must therefore be produced via the

TABLE 2

Energy of Activation for the Desorption of
Propylene and Acrolein

Catalyst/carrier gas	E_d(kcal/mole)		
	C_3H_6	C_3H_4O(I)	C_3H_4O(II)
$Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$			
Air	17 (169°C)[a]	13 (257°C)	30 (363°C)
He	17 (169°C)	—	31 (387°C)
$CoMoO_4$			
Air	16 (154°C)	—	28 (325°C)
He	16 (154°C)	—	29 (348°C)
Bi_2MoO_6			
Air	17 (176°C)	11 (200°C)	31 (390°C)
He	17 (176°C)	11 (200°C)	32 (400°C)
$Bi_2Mo_3O_{12}$			
Air	18 (186°C)	13 (268°C	31 (390°C)
He	18 (186°C)	13 (268°C)	32 (400°C)
5% Sb in SnO_2			
Air	18 (200°C)	12 (250°C)	32 (400°C)
He	18 (200°C)	12 (250°C)	— •
USb_3O_{10}			
Air	18 (200°C)	13 (266°C)	—
He	18 (200°C)	—	—
$Bi_2Fe_2Mo_2O_{12}$			
Air	17 (170°C)	11 (212°C)	31 (383°C)
He	17 (170°C)	11 (212°C)	32 (400°C)
$Bi_3FeMo_2O_{12}$			
Air	18 (187°C)	11 (220°C)	31 (385°C)
He	18 (187°C)	11 (220°C)	32 (413°C)
Cu_2O			
Air	—	—	—
He	13 (81°C)	—	—
	14 (104°C)	9 (146°C)	23 (225°C)

[a] Value within parentheses is the T_m at $B = 27°C/min$.

interaction of adsorbed propylene with lattice oxygen during the adsorption and/or the TPD cycle.

Figure 2 illustrates the effect of the propylene adsorption temperature on the TPD chromatograms using air as the carrier gas. The fact that propylene does not chemisorb below 70°C indicates that the adsorption process is activated. The total quantity of hydrocarbon adsorbed was determined by integrating the area under the desorption peaks and using the appropriate response factors. This quantity was almost constant for the adsorption temperatures of 90, 110, 130, and 150°C and corresponded to a surface coverage by propylene of ~12%. The value is, however, somewhat lower than the actual coverage because carbon dioxide formation could not be taken into account. As the adsorption temperature is increased, the amount
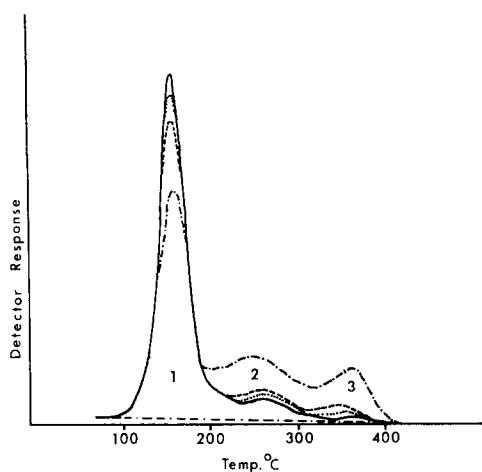
TABLE 1

Kinetic Parameters for the Desorption of Propylene
and Acrolein from $Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$

Heating rate (°C/min)	T_m (°C)		
	C_3H_6	C_3H_4O(I)	C_3H_4O(II)
28	169	257	363
12.5	156	217	346
5	135	188	325
A (sec^{-1})	5.5×10^6	1.2×10^3	3.7×10^8
E_d(kcal/mole)	17	12	30

FIG. 2. Desorption spectra as a function of propylene adsorption temperature: (– – ·– –) 70°C, (———) 90°C, (· · · · ·) 110°C, (– – – –) 130°C, and (– · – · –) 150°C over $Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$ at a heating rate of 27°C/min with air as the carrier gas. Peak 1 is C_3H_6, $T_m = 168$°C; peak 2 is C_3H_4O-(form I), $T_m = 260$°C; and peak 3 is C_3H_4O (form II), $T_m = 360$°C.

of propylene converted to both forms of acrolein is increased. It has already been noted that the weakly bound form of acrolein is produced only during the TPD cycle when gas-phase oxygen is present, whereas the strongly bound form can be produced during adsorption and/or TPD. This indicates that both forms are derived from a common hydrocarbon intermediate which is formed during the adsorption cycle and that the quantity of this intermediate is dependent on the temperature of propylene adsorption. This observation is in good agreement with the mechanistic information cited earlier (2).

The TPD technique can be used to study the energetics of a surface reaction if the appearance of the product peak is controlled by the surface reaction and not by the product desorption. Therefore, the desorption chromatogram of preadsorbed acrolein was obtained for comparison with the propylene desorption chromatograms run at the same conditions. The results showed two forms of acrolein which desorb at the same temperatures as the acrolein produced from adsorbed propylene. This suggests that the appearance of acrolein in the gas phase is controlled by the rate of desorption and not by the surface reaction. This also indicates that the two acrolein peaks correspond to two different chemisorbed species attached to a single type of site. Consequently, the positions of the acrolein peaks cannot yield any information about the kinetics of the surface reaction. The quantity of each type of acrolein is, however, directly related to the rate of formation. A comparison of the relative amounts of C_3H_4O (I) to C_3H_4O (II) at different adsorption temperatures indicates that the ratio C_3H_4O (I)/C_3H_4O (II) decreases with increasing adsorption temperature. This means that the energy of activation for the formation of C_3H_4O (I) using adsorbed oxygen is lower than the activation energy for the formation of C_3H_4O (II) with lattice oxygen.

The TPD data have indicated that the rate of appearance of acrolein in the gas phase is controlled by the rate of desorption. If this is indeed true, then the kinetics of acrolein desorption should be closely related to the kinetics of acrolein formation during a steady-state reaction. Table 1 gives the results of desorption experiments carried out at different heating rates in air with the modified cobalt molybdate catalyst and the kinetic parameters calculated from this data by use of Eq. (1). Comparing the rate constants calculated from the data in Table 1, it can be easily seen that the rate of desorption of the weakly bound form of acrolein in the temperature range of 450 to 350°C is from 50 to 1000 times greater than the rate of desorption of strongly bound acrolein. Therefore, the observed rate of formation of acrolein should approximate the kinetics for the desorption of the weakly bound acrolein. The kinetic data for the steady-state oxidation of propylene to acrolein have been previously determined (12). The apparent
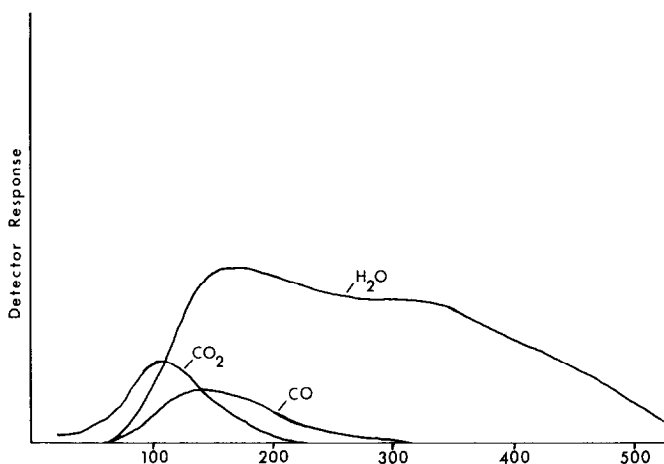
FIG. 3. Desorption spectra of propylene from Pt/Al$_2$O$_3$ in the presence of adsorbed oxygen.

energy of activation for the formation of acrolein was found to be 10 kcal/mole, and the preexponential factor, 1×10^7 sec^{-1}. This is in excellent agreement with the desorption data for C$_3$H$_4$O(I) which has an E_d of 12 kcal/mole and a value of 1.2×10^3 sec^{-1} for A. It was also reported (*12*) that even small quantities of acrolein in the feed gas would suppress the conversion of propylene. This behavior is consistent with the idea that the rate of reaction is controlled by the desorption of the product.

Only two desorption experiments were carried out on each of the other catalysts, one in a helium carrier and the other in air. The results are listed in Table 2. The energies of activation for desorption were calculated from data obtained at only one heating rate by using the preexponential factors determined for the modified cobalt molybdate catalyst.

The results given in Table 2 show a remarkable consistency in the values for the energy of activation for desorption of propylene and the two forms of acrolein. This means that propylene is adsorbed on these various catalysts in the same form and that the active site for acrolein formation is energetically similar. This result is supported by the work of Mikhalchenko

and co-workers (*13*). They ran thermal desorption experiments with supported π-allyl nickel and π-ally molybdenum and observed almost identical desorption chromatograms. The positions of the propylene and product peaks were also in excellent agreement with those observed in this work. This seems to indicate that the mechanism or mechanisms for the oxidation of propylene to acrolein are the same for these catalysts.

It does seem surprising, however, that for all of the oxides we studied, the thermal desorption spectra are almost identical. In order to be sure that our data truly reflect the properties of partial oxidation catalysts, we carried out a similar experiment with a known complete oxidation catalyst, Pt/Al$_2$O$_3$. The catalyst was reduced and then reoxidized so that the surface was covered by oxygen. After propylene adsorption a TPD spectrum was obtained using a mass spectrometer on the detector. The TPD spectrum, Fig. 3, is completely different from the spectra observed for partial oxidation catalysts, showing only deep oxidation products. Therefore the data in Table 2 really do reflect the properties of catalysts for partial oxidation.

Another trend which can be noticed from the data in Table 2 is that the energy of

TABLE 3

Comparison of the Energies of Activation for the Desorption and Formation
of Acrolein over Oxide Catalysts

Catalyst	E_d (kcal/mole)		E_A for the formation of C_3H_4O (kcal/mole)	Reference
	C_3H_4O (I)	C_3H_4O (II)		
$Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$	12	30	10	(12)
Cu_2O	9	23	20	(17)
Bi_2MoO_6	11	32	13–31	(16)
$Bi_2Mo_3O_{12}$	13	32		
5% Sb in SnO_2	12	32	12	(9)

activation for the desorption of strongly bound acrolein is dependent upon the carrier gas, whereas that for the weakly bound acrolein is not. This difference is due to the effect of catalyst reduction. The catalyst is reduced during propylene adsorption but can be completely reoxidized at temperatures over 300°C in the presence of air. At the temperature at which weakly bound acrolein desorbs, most catalysts are not yet completely reoxidized, so the acrolein is desorbing from a reduced surface with either the helium or air carrier gas. However, at temperatures over 300°C, the catalysts in the air stream are reoxidized, and the strongly bound acrolein observed is desorbing from a completely oxidized surface. This apparently leads to a decrease in the energy of activation for desorption. This effect has also been proposed by Haber and co-workers (14). On the basis of ESCA measurements, they predicted that acrolein would be more strongly adsorbed on a reduced surface.

With Bi_2MoO_6, $Bi_2Mo_3O_{12}$, $Bi_2Fe_2Mo_2O_{12}$, $Bi_3FeMo_2O_{12}$, and Sb in SnO_2 catalysts, the appearance of the weakly bound form of acrolein is independent of carrier gas used. This indicates that, with these catalysts, the strongly bound form of acrolein which is associated with the lattice oxygen pathway is able to equilibrate with the weakly bound form during the adsorption or TPD cycle. On the other hand, the $CoMoO_4$ catalyst yields acrolein in only the high-temperature form and the appearance of product is again independent of the carrier gas composition. Pure cobalt molybdate is known to have a poor selectivity to acrolein (15). Consequently it seems that the strongly adsorbed form of acrolein is susceptible to further oxidation unless it can easily rearrange to the weakly bound form. With USb_3O_{10}, acrolein is produced only in the weakly bound form and only when gas-phase oxygen is present. It, therefore, appears that only the hydroperoxide pathway is active with this catalyst.

Considering the similarities in the desorption data of the catalysts used in this study, it is possible that the reaction kinetics of the other catalysts may be influenced by the desorption of acrolein particularly at lower temperatures. Table 3 compares the energies of activation for desorption with the apparent energies of activation for the formation of acrolein reported in the literature. There appear to be some similarities; however, more extensive data would have to be obtained before any definite conclusions could be drawn.

ACKNOWLEDGMENTS

REFERENCES

1. (a) Margolis, L. Ya., *Catal. Rev.* **8**, 241 (1973). (b) Sampson, R. J., and Shooter, D., *Oxid. Combust. Rev.* **1**, 223 (1965). (c) Voge, H. H., and Adams, L. R., *Advan. Catal.* **17**, 151, (1967). (d) Sachtler, W. M. H., *Catal. Rev.* **4**, 27 (1970). (e) Hucknall, D. J., "Selective Oxidation of Hydrocarbons," Chap. 3, p. 23. Academic Press, New York/London, 1974.

2. Daniel, C., and Keulks, G. W., *J. Catal.* **24**, 529 (1972).

3. Keizer, K., Batist, Ph. A., and Schuit, G. C. A., *J. Catal.* **15**, 256 (1969).

4. Batist, Ph. A., Prette, H. J., and Schuit, G. C. A., *J. Catal.* **15**, 267 (1969).

5. Cvetanovic, R. J., and Amenomia, J., *Advan. Catal.* **17**, 103, (1967).

6. Isaev, O. V., and Margolis, L. Ya., *in* "Preparation of Catalysts," (B. Dalmon, P. A. Jacobs, and G. Poncelet, Eds.), Elsevier Scientific, Amsterdam, 1976. p. 177.

7. Batist, Ph. A., Bouwens, J. Z. H., and Schuit, G. C. A., *J. Catal.* **25**, 1 (1972).

8. Keulks, G. W., Hall, J. L., Daniel, C., and Suzuki, K., *J. Catal.* **34**, 79 (1974).

9. Godin, G. W., McCain, C. C., and Porter, E. A., *Proc. 4th Int. Congress Catalysis* **1**, 271 (1971).

10. Grasselli, R. K., and Suresh, D. D., *J. Catal.* **25**, 273 (1972).

11. Notermann, T., Keulks, G. W., Skliarov, A., Maximov, Yu., Margolis, L. Ya., and Krylov, O. V., *J. Catal.* **39**, 286 (1975).

12. Vinogradova, O. M., Vytnov, G. Z., Luiksaar, I. V., and Al'tahuler, O. V., *Kinet. Katal.* **16**, 671 (1975).

13. Mikhalchenko, V. G., Davydov, A. A., Budneva, A. A., Kuznetsov, B. N., and Sokolovskii, V. D., *React. Kinet. Catal. Lett.* **2**, 163 (1975).

14. Haber, J., Marczewski, W., Stock, J., and Ungier, L., *Proc. 6th Int. Congress Catalysis* **2**, 827 (1977).

15. Keulks, G. W., and Krenzke, L. D., *Proc. 6th Int. Congress Catalysis* **2**, 806 (1977).

16. Peacock, J. M., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15**, 398 (1969).

17. Belousov, V. M., Gorokhovatskii, Ya. B., and Rubanik, M. Ya., *Kinet. Katal.* **3**, 221 (1962).