

## Adsorption and Heat of Adsorption of Propylene on a Bi-Mo Oxide Catalyst

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The adsorption isotherms of propylene were determined on a Bi-Mo/SiO<sub>2</sub> oxide catalyst in the range of 37–150°C and on a Bi-Mo oxide catalyst without carrier at 35°C. For the individual propylene doses, the adsorption heats were also determined calorimetrically. The adsorption heat of propylene on the Bi-Mo/SiO<sub>2</sub> catalyst is equal to 8 kcal/mole, independently of the surface coverage, whereas the adsorption heat on the Bi-Mo catalyst decreases with the coverage of the surface from 12 to 2 kcal/mole.

In measurements carried out at 170°C, the adsorption of propylene is followed by a consecutive process, i.e., the oxidation of propylene to acrolein, which is accompanied by reduction of the catalyst. Oxygen is adsorbed from this catalyst at the same temperature with a high heat of adsorption, 75 kcal/mole, in an amount exceeding the preceding amount of adsorbed propylene by about 13%. Moreover, the adsorption of propylene from a propylene-oxygen mixture was also investigated.

The results obtained are discussed with regard to the interaction between propylene and the surface of the Bi-Mo/SiO<sub>2</sub> oxide catalyst, and an attempt has been made to evaluate the reaction mechanism of the oxidation of propylene to acrolein from the viewpoint of thermochemical data.

### INTRODUCTION

Catalytic oxidation of olefins has attained considerable significance in the last 20 years, in particular after the discovery of the properties of the bismuth molybdate catalyst. This catalyst is employed on a carrier and without carrier; it is very selective for the oxidation of propylene to acrolein or, in the presence of NH<sub>3</sub>, to acrylonitrile, or for the oxidation of *n*-butenes to butadiene.

Only a small number of papers concerned with the field of oxidation catalysis, however, has dealt with the study of the adsorption and with the determination of the heats of adsorption of propylene and oxygen on the bismuth-molybdenum oxide catalyst. Gel'bshtein *et al.* (1) measured the adsorption of oxygen in the range from 100 to 450°C and that of propylene between 150 and 300°C. Krylov and Margolis (2) report that both propylene and oxygen are adsorbed on a Bi-Mo oxide catalyst and give the ratio of

both adsorptions determined at one temperature in the range of 100–200°C for a number of oxide catalysts. The adsorption of propylene is higher than that of oxygen. The latter authors give for the heat of adsorption of propylene on MoO<sub>3</sub> on a carrier (γ-Al<sub>2</sub>O<sub>3</sub>) at room temperature the value of 6–11 kcal/mole.

The significance of these values, determined especially in the temperature range of the beginning reaction, is obvious, e.g., from the viewpoint of judging the suitability of the suggested reaction mechanism. For this reason, we were concerned with the measurement of the adsorption of propylene and the determination of the adsorption heats by the calorimetric method on a bismuth-molybdenum oxide catalyst with and without carrier mainly in the temperature range of the beginning oxidation of propylene. The present paper is the continuation of that listed in Ref. (3).

## EXPERIMENTAL

**Adsorption apparatus.** The adsorption of propylene was measured in a volume adsorption apparatus connected with gas reservoirs and a vacuum source. Low pressures ( $p < 12$  Torr) were measured with a McLeod manometer, higher pressures with a mercury U-manometer. The adsorption vessel with the catalyst was located during the measurement in a calorimeter. The dead volume of the adsorption vessel was determined at the individual measuring temperatures by means of helium.

**Catalyst employed.** The measurements were carried out on two specimens of a precipitated mixed oxide catalyst on a carrier, Bi-Mo/SiO<sub>2</sub>, and without carrier, Bi-Mo. The atomic ratio of both components Bi:Mo is near unity. The surface areas of the specimens, determined by means of adsorption of argon at the temperature of liquid nitrogen, were 93 m<sup>2</sup>/g and 1.75 m<sup>2</sup>/g, respectively. The catalyst employed for the adsorption measurements had a grain size of 0.3–0.6 mm.

Before the measurement, the catalyst in the adsorption vessel was always heated *in vacuo* to 450°C for 4 hr and then in an oxygen atmosphere ( $p = 150$ – $200$  Torr) at the same temperature for 30 min (activated catalyst). After completed heating, the adsorption vessel was sealed off, placed into the calorimeter and joined to the adsorption apparatus through the glass valve. Before the measurement, the glass valve was broken, and the catalyst was evacuated at the temperature of the experiment for 30 min. As will be pointed out later, the heating of the catalyst *in vacuo* did not result in a reduction of its surface.

**Gases employed.** Propylene was withdrawn from a steel cylinder, and before its introduction into the gas reservoir of the apparatus, it was purified by freezing in an evacuated glass tube cooled with liquid nitrogen. Acrolein was purified by vacuum distillation. The vessel with the liquid acrolein was cooled down to  $-10^{\circ}\text{C}$ , and the distillate was condensed in a storage vessel cooled by solid CO<sub>2</sub>. The distillation was repeated several times, and the specimen

obtained was colorless. Hydroquinone was added as a stabilizer to the liquid acrolein. Oxygen was prepared by thermal decomposition of KMnO<sub>4</sub> and dried by passing it through a trap cooled by solid CO<sub>2</sub>.

**Calorimeter.** The heat evolved in the adsorption was measured by means of a calorimeter of the Wittig type (4). The adsorption vessel with about 10 g of the catalyst was located in the calorimeter. The catalyst was packed in a layer of 2 mm, between the wall of the adsorption vessel, and a Ni mesh wound into the form of a cylinder and placed in the center of the vessel. The Ni mesh is seated on a glass spiral sealed to the bottom of the vessel (Fig. 1). This permits the contact of the gas with the entire surface of the catalyst and at the same time facilitates the transfer of the heat from the catalyst to the calorimeter. Inside the calorimeter, in close contact with the adsorption vessel, there is also a calibration resistor consisting of a constantan wire wound on a mica plate and placed in a copper casing. The water value of the calorimeter was determined after each measurement in an atmosphere of the investigated gas. Temperature changes inside the calorimeter were indicated by means of Fe-constantan thermocouples and recorded by an electronic

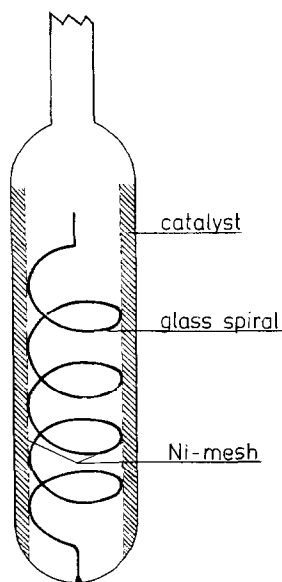


FIG. 1. Diagram of adsorption vessel.

compensation recorder type EZ 2 (Laboratorní Potfeby-Laboratory Equipment, Prague) with a sensitivity of  $100 \mu\text{V}$  over the entire scale (28 cm).

## RESULTS

### A. Adsorption of Propylene on the Bi-Mo/SiO<sub>2</sub> Oxide Catalyst

The adsorption of propylene was measured on the Bi-Mo/SiO<sub>2</sub> oxide catalyst at temperatures of 37, 61, 103, 150, and 170°C. According to the time-dependent course of adsorption, the results can be divided into three groups: (1) the adsorption of propylene ends within a few minutes and does not further change with time—temperature range 37–103°C; (2) transitional region—temperature 150°C; at lower pressures as adsorption (1); at higher pressures the behavior approaches that defined adsorption (3); (3) small, rapid drop of the propylene pressure in the burette at the beginning of the measurement, followed by a permanent, moderate pressure drop with time—temperature 170°C.

**1. Adsorption of propylene on the Bi-Mo/SiO<sub>2</sub> oxide catalyst in the range of 37–103°C.** Figure 2 presents the isotherms for 37, 61, and 103°C, measured on the activated catalyst and on the same specimen of the catalyst after preceding long-term (about 2 hr) desorption of propylene into vacuum at the temperature of the experiment (used catalyst). The difference of the adsorptions measured on both specimens, the activated and the used one, increases with rising temperature approximately from 3 to 12%. This difference of the adsorptions indicates that a small part of the adsorbed propylene is bound irreversibly. For this

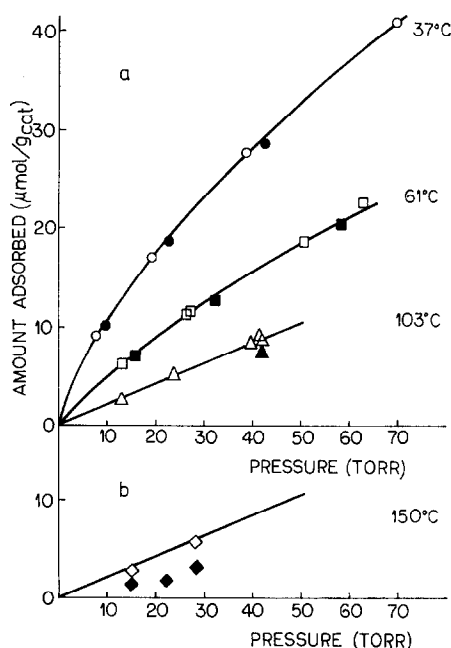


FIG. 2. (a) Adsorption isotherms of propylene on activated ( $\circ$ ) and used ( $\bullet$ ) Bi-Mo/SiO<sub>2</sub> catalyst at 37, 61, and 103°C. (b) Adsorption isotherms of propylene on activated ( $\diamond$ ) and used ( $\blacklozenge$ ) catalyst at 150°C.

reason, the amount of desorbed propylene was measured after completed adsorption at the individual temperatures in such a way that the propylene was desorbed into an evacuated gas burette with a cold finger at liquid nitrogen temperature. The pressure in the burette was practically zero during the desorption.

Table 1 presents the values of the adsorption of propylene on the activated catalyst determined at the individual temperatures, further the values of the desorbed amount found after 30 min of desorption at the tem-

TABLE 1  
 ADSORPTION OF PROPYLENE ON Bi-Mo/SiO<sub>2</sub> OXIDE CATALYST AT 37–150°C

Temp (°C)	Adsorption ( $\mu\text{mole/g}_{\text{cat}}$ )	Pressure (Torr)	Desorption ( $\mu\text{mole/g}_{\text{cat}}$ )	Irreversible part (%)	Irreversible part ( $\mu\text{mole/g}_{\text{cat}}$ )
37	40.7	69.4	37.9	6.9	2.8
63	22.5	62.8	20.2	10.2	2.3
103	8.6	41.9	4.8	44.2	3.8
103	9.1	41.4	5.6	38.5	3.5
150	5.7	28.0	2.3	60.0	3.4

perature of the experiment, and the percentage of the irreversibly bound propylene. These values are about three times as high as the values read from the adsorption isotherms. A considerable part of the irreversibly bound propylene can be removed from the catalyst by several hours' evacuation.

The adsorption was pursued for a total time of about 40 min, and after an initial rapid drop the pressure in the burette did not change during this time interval.

**2. Adsorption of propylene on the Bi-Mo-SiO<sub>2</sub> oxide catalyst at 150°C.** Figure 2b shows the values of the propylene adsorbed on the activated catalyst at 150°C. These values, read after about 50 min, are in agreement with the values measured at 103°C (Fig. 2b, solid line). The course of the adsorption at this temperature, at a lower pressure, is the same as at lower temperatures, whereas at a higher pressure a moderate pressure drop with time can be observed (Fig. 3, curve 1). When the measurement of the adsorption of propylene was repeated on the used catalyst, the measured

values of the adsorption were almost half of those measured on the activated catalyst.

After completed adsorption of propylene on the activated catalyst, the amount of the desorbate was ascertained in the same way as at lower temperatures. It was found that 60% of propylene remained irreversibly bound on the catalyst (Table 1). A comparison of the values of the irreversibly adsorbed propylene, read from Table 1 and Fig. 2b, reveals that long-term evacuation at 150°C can remove only a small part of the irreversibly bound propylene from the surface of the catalyst.

**3. Adsorption of propylene on the Bi-Mo/SiO<sub>2</sub> catalyst at 170°C.** The curve of the pressure of propylene in the burette in dependence on time at 170°C is presented in Fig. 3, curve 2. Since in this case no equilibrium values of the adsorption of propylene can be read, no adsorption isotherm is given. After completed adsorption of propylene within 60 min, the amount of the desorbate was again determined. It was found that 90–93% of the adsorbed propylene remained bound on the catalyst.

After a comparison of the curves 1 and 2 (Fig. 3) it can be stated that the pressure drop with time is more distinct at rising propylene pressure in the burette and rising temperature of the catalyst.

**4. Heat of adsorption of propylene on the Bi-Mo/SiO<sub>2</sub> oxide catalyst.** The course of the adsorption was also investigated in the calorimeter, and the heat effects of the adsorption of the individual doses were evaluated. The value of the heat of adsorption of propylene on the Bi-Mo/SiO<sub>2</sub> oxide catalyst is independent of the occupation of the surface and the temperature of the catalyst in the range of 37–103°C (Fig. 4). The average value is 8 kcal/mole, the same on both the activated and the used catalyst.

The adsorption heat of propylene at 170°C on the activated catalyst amounted to 22.3 kcal/mole (Table 2). The values measured on the used specimen, only evacuated at 170°C, were lower, the lowest was 11.4 kcal/mole.

The heat of adsorption of propylene was also calculated from the adsorption iso-

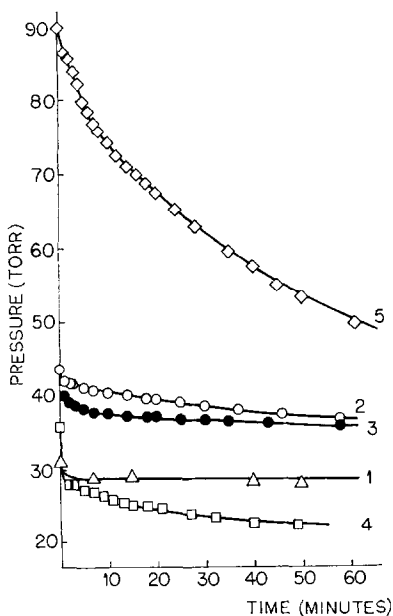


FIG. 3. Time-dependent course of the pressure of propylene, acrolein, and oxygen during the adsorption: 1, propylene, 150°C; 2, propylene, 170°C; 3, oxygen, 170°C; 4, acrolein, 170°C; 5, propylene-oxygen mixture, 170°C.

TABLE 2  
 ADSORPTION OF PROPYLENE AND OXYGEN AND HEAT OF ADSORPTION ON  
 Bi-Mo/SiO<sub>2</sub> OXIDE CATALYST AT 170°C

Adsorption ( $\mu\text{mole/g}_{\text{cat}}$ )			Heat of adsorption (kcal/mole)			
			Propylene		Oxygen	
Propylene	Oxygen	$\Delta\%$	$\Delta H$	$\Delta\%$	$\Delta H$	$\Delta\%$
21.85	14.7	—	—	—	78.8	+4.8
—	3.1	—	—	—	41.3	—
7.3	7.7	+5.5	21.9	-1.8	75.2	0.0
7.9	9.3	+17.7	21.0	-5.8	71.2	-5.3
6.8	7.9	+16.2	24.1	+8.0	75.6	+0.5
			22.3 <sup>c</sup>		75.2 <sup>c</sup>	
35.0 <sup>a</sup>	19.0 <sup>b</sup>				76.4 <sup>b</sup>	

<sup>a</sup> Adsorption of acrolein.

<sup>b</sup> Measured after the desorption of acrolein.

<sup>c</sup> Average value.

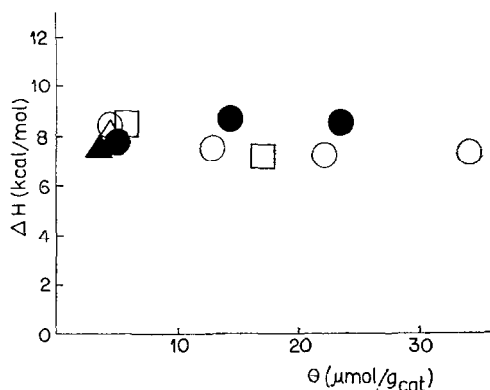


FIG. 4. Dependence of heat of adsorption of propylene on the occupation of the surface of the catalyst at 37°C, ○, 61°C, □, and 103°C, Δ.

therms for 37, 61, and 103°C, as given in Fig. 2a, according to the Clausius-Clapeyron equation, and the values for the individual degrees of occupation of the surface were also calculated: 7.7 kcal/mole ( $\theta = 2.5 \mu\text{mole/g}$ ), 6.9 kcal/mole ( $\theta = 5.0 \mu\text{mole/g}$ ) and 6.2 kcal/mole ( $\theta = 7.5 \mu\text{mole/g}$ ).

#### B. Adsorption of Propylene on a Bi-Mo Oxide Catalyst\*

Figure 5a presents the adsorption isotherm for propylene determined at 35°C on a

\* These measurements were carried out in the Institute of Technical Chemistry, Technical University, Berlin.

mixed Bi-Mo oxide, without carrier, activated at 450°C. The corresponding values of the heat of adsorption are given in Fig. 5b in dependence on the occupation of the surface of the catalyst. The heat of adsorption of propylene decreases rapidly from 12 to 2 kcal/mole.

#### C. Adsorption of Oxygen on the Bi-Mo/SiO<sub>2</sub> Oxide Catalyst at 170°C

After desorption of propylene, the catalyst was evacuated for another 30 min at 170°C by direct connection to the vacuum source, whereupon an oxygen dose was admitted onto the catalyst. The oxygen pressure decreased rapidly to a value which then changed with time only negligibly (Fig. 3, curve 3). The measured heat of adsorption of an oxygen dose approximately equalling that of the adsorbed propylene amounted to 75.2 kcal/mole. The measured values are listed in Table 2.

It is interesting that the adsorption of oxygen was always higher than the preceding adsorption of propylene. A further dose of oxygen did not lead to additional adsorption. However, when the first oxygen dose is lower than the preceding adsorption of propylene, oxygen is adsorbed also in further doses, but with a lower heat of adsorption.

The adsorption of oxygen was also in-

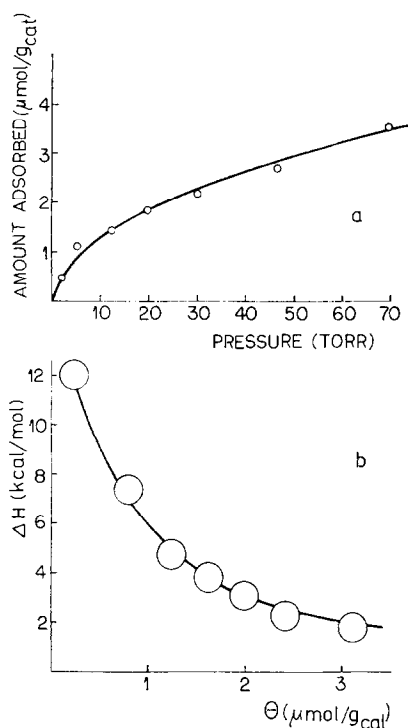


Fig. 5. (a) Adsorption isotherm of propylene on activated Bi-Mo catalyst—adsorption at 35°C. (b) Heat of adsorption of propylene on Bi-Mo catalyst, determined at 35°C, in dependence on the occupation of the surface.

vestigated on an activated catalyst which was evacuated at 450°C and a pressure of  $10^{-3}$  Torr for about 20 hr, in order to determine whether the surface is not reduced during the evacuation. No adsorption of oxygen was observed.

#### D. Adsorption of Propylene from a Propylene-Oxygen Mixture on the Bi-Mo/SiO<sub>2</sub> Oxide Catalyst at 170°C

Curve 5 in Fig. 3 represents the time-dependent course of the total pressure in the adsorption of a propylene-oxygen mixture (1:1) on the activated catalyst. The break found on the curve has obviously its significance. If the pressures of oxygen and propylene, as given in the paper by Peacock, are added up, the curve of the total pressure exhibits a similar break. The course of the adsorption is also represented by the relation  $\log p_0/p$  vs  $t$  (min), where  $p$  is the

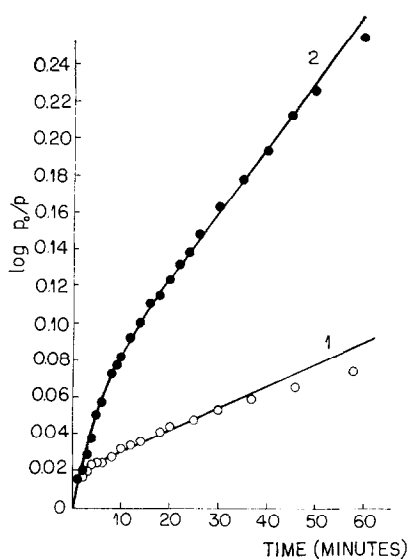


Fig. 6. Semilogarithmic dependence of pressure on time in the adsorption of propylene (Curve 1) and propylene-oxygen mixture (Curve 2) at 170°C.

pressure of the gas at the time  $t$ , and  $p_0$  is the pressure at the beginning of the measurement (Fig. 6, curve 2). The graph presents for comparison also the course of the adsorption of pure propylene on the same catalyst (curve 1).

According to the analysis of the gas mixture at the end of the measurement, the catalyst retained nearly twice as much propylene as oxygen. The composition of the gas mixture, however, changes during the adsorption from 1:1 to 2:1 (oxygen:propylene), and this change is already small in the last phase of the measurement. The value measured for the adsorption heat of propylene amounted in this case to 43.5 kcal/mole.

#### E. Adsorption of Acrolein on the Bi-Mo/SiO<sub>2</sub> Oxide Catalyst at 170°C

Besides the adsorption of propylene on the activated catalyst, the adsorption of acrolein at 170°C was also investigated. The time-dependent course of the pressure of acrolein in the burette is analogous to the course of the propylene pressure (Fig. 3, curve 4). The amount of adsorbed acrolein and the corresponding heat of adsorption could not be established due to the complicated course of the adsorption, because the acrolein was

partly spontaneously eliminated from the gaseous phase by a side reaction.

#### F. Analysis of the Gaseous Phase

After completed adsorption of propylene, acrolein, and the propylene-oxygen mixture, the gas phase in the burette was analyzed in a chromatographic column, and no desorption products were found. The analysis of the desorbate after adsorption of propylene and the propylene-oxygen mixture at 170°C revealed traces of acrolein and CO<sub>2</sub>. In the analysis of the desorbate after the adsorption of acrolein, CO<sub>2</sub> and CO were found as desorption products.

### DISCUSSION

#### A. Adsorption of Propylene on the Bi-Mo and Bi-Mo/SiO<sub>2</sub> Oxide Catalysts at 35-150°C

The adsorption of propylene on the Bi-Mo/SiO<sub>2</sub> oxide catalyst in the range of 37-103°C is practically reversible (see Fig. 2a). The heat of adsorption determined in this temperature range is 8 kcal/mole and independent of the occupation of the surface. This value is in good agreement with the value determined from the adsorption isotherms (7.7 kcal/mole) as well as with the value ascertained chromatographically (3), 7.7 kcal/mole, in the range of 30-200°C.

The heat of adsorption of propylene on Bi-Mo oxide decreases from 12 to 2 kcal/mole. We assume that this value is not in disagreement with the value of 3.8 kcal/mole, as determined chromatographically (3), because this value is near the mean value of the calorimetrically established heat of adsorption of propylene, which is near 4 kcal/mole. The value of the heat of adsorption of propylene measured on both specimens of the catalyst supports the conclusion expressed in Ref. (3), according to which the adsorption of propylene on Bi-Mo/SiO<sub>2</sub> oxide proceeds on two different centers, SiO<sub>2</sub> and the active constituent Bi-Mo. Calorimetric measurements of the heat of adsorption show that the adsorption of propylene on SiO<sub>2</sub> predominates, mainly at temperatures below 100°C, over the adsorption on the active constituent Bi-Mo.

The overall adsorption of propylene at 103 and 150°C is equal. Since the adsorption of propylene on silica gel is of physical nature and decreases with rising temperature, this means that the adsorption of propylene on the active constituent Bi-Mo in the range of 103-150°C increases with rising temperature, obviously in consequence of a change in the character of the bond of the adsorbed propylene. This change of the bond leads probably to irreversible adsorption as well as to an increase in the value of the heat of adsorption of propylene.

In agreement with this concept are the results of some authors, according to whom the adsorption isobar of propylene passes through a minimum near the temperature of 100°C (2, 5, 6).

#### B. Adsorption and Reaction of Propylene on the Surface of the Bi-Mo/SiO<sub>2</sub> Catalyst at 170°C

According to the time-dependent course of the pressure during the adsorption at 170°C (Fig. 3, curve 2) it can be concluded that the adsorption to which corresponds only the initial rapid pressure drop is accompanied by a slow subsequent reaction, whose course satisfies the equation for a monomolecular reaction. This process can be explained by the reaction of the adsorbed propylene with the lattice oxygen leading to the reduction of the surface of the catalyst. Peacock (10) investigated the interaction between propylene and the Bi-Mo/SiO<sub>2</sub> catalyst in dependence on time in the range of 225-500°C by means of a Mo<sup>5+</sup> signal in the ESR spectra. The dependence on time of this signal at 225°C exhibits qualitatively entirely the same course as that of the time-dependent adsorption of propylene in our case. Table 3 presents the values of the amounts of the Mo<sup>5+</sup> ions (2nd column) as read for various times from the graph given by Peacock, as well as the values of the adsorbed amounts of propylene for the same times from our measurements (3rd column). The ratio of both values is practically constant, and this indicates that the same process takes place in both cases.

Propylene reacts with lattice oxygen to form acrolein and water, and these products

TABLE 3  
CHANGE OF  $\text{Mo}^{5+}$  SIGNAL AND ADSORPTION OF  
PROPYLENE WITH TIME ON  $\text{Bi-Mo/SiO}_2$   
OXIDE CATALYST

Time (min)	$\text{Mo}^{5+} \cdot 10^{-16}$	$\text{C}_3\text{H}_6 \cdot 10^{-16}$	$\text{C}_3\text{H}_6/\text{Mo}^{5+}$
0.5	1.7	50.5	29.4
5.0	7.1	160.0	22.4
10.0	8.1	201.5	24.7
26.0	10.3	284.8	27.7

should be desorbed from the surface of the catalyst and appear in the gaseous phase. In our case, however, acrolein is completely removed due to the spontaneous polymerization (?), and also water disappears due to the adsorption on the surface, probably bound by silica gel, since the analysis of the adsorption products reveal always only traces of acrolein besides a small amount of  $\text{CO}_2$ . On the basis of the measurements performed it cannot be directly said whether the polymerization of acrolein takes place on the surface of the catalyst or only after desorption of the gaseous phase. In consequence of the instantaneous removal of acrolein by polymerization and of water by adsorption it was possible to pursue the time-dependent course of the adsorption of propylene.

The oxidation of propylene consumes oxygen from the surface of the catalyst. This decrease in oxygen was ascertained by measuring the amount of adsorbed oxygen after preceding desorption of propylene and evacuation of the catalyst. According to the data in Table 2, the amount of adsorbed oxygen is on an average 13% higher than the amount of adsorbed propylene.

The measured heat of adsorption of oxygen amounted to 75.2 kcal/mole. This value approaches the reaction heat of  $\text{MoO}_2 + \frac{1}{2} \text{O}_2 = \text{MoO}_3$ , which according to the tables (8) is equal to 100.8 kcal/mole  $\text{O}_2$ . Nearly the same value is given for the reaction heat of  $2 \text{Bi} + \frac{3}{2} \text{O}_2 = \text{Bi}_2\text{O}_3$ , i.e., 92 kcal/mole  $\text{O}_2$ . This difference between the measured and the calculated value can be explained by the circumstance that the heat of adsorption of oxygen characterizes the bond between oxygen and the metal ion on the surface, whereas

the reaction heat characterizes the bond between oxygen and the metal in the bulk. Another explanation of this difference is presented by the concept of Krylov and Margolis, who assume that the formation of the  $\text{Mo}^{5+}$  ions, observed in the ESR spectra during the oxidation of propylene on the surface of the catalyst without oxygen in the gaseous phase, results from the reaction between  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  ions,  $\text{Mo}^{4+} + \text{Mo}^{6+} = 2 \text{Mo}^{5+}$ . Consequently, the surface of the reduced catalyst would contain  $\text{Mo}^{5+}$  ions, so that the adsorption of oxygen would be accompanied by the oxidation of these ions only, and this could lead to a lower value of the heat of adsorption of oxygen.

The approximately equal values of the heat of oxidation of  $\text{Mo}^{4+}$  and Bi indicate that during the oxidation of propylene both surface ions,  $\text{Mo}^{6+}$  and  $\text{Bi}^{3+}$ , could be reduced. According to the results obtained by Kamran Aykan (9), who studied the reduction of the  $\text{Bi-Mo/SiO}_2$  oxide catalyst during the oxidation of propylene in the absence of oxygen in the gas phase,  $\text{MoO}_2$  and metallic Bi are formed during the reaction. The reduction of  $\text{Bi}^{3+}$  in this reaction is also assumed by other authors (2, 10).

According to the value of the adsorption heat of oxygen, the reduction of the surface is of the same type also in the case of the adsorption of acrolein (see Table 2), which is oxidized to  $\text{CO}_2$  and CO.

In view of the fact that the adsorption of propylene and its oxidation proceed almost simultaneously on the surface of the catalyst, the value of the heat of adsorption of propylene, as given in Table 2, is de facto given by the sum of the adsorption and the reaction heat of propylene. Consequently, the value of the heat of adsorption of propylene at 170°C cannot be specified unambiguously on the basis of our results.

According to the chromatographic determinations of the heat of adsorption of propylene, given in Ref. (3), this heat is constant in the range of 30–200°C and equal to 7.7 kcal/mole; it relates rather to the reversible adsorption on the carrier, i.e.,  $\text{SiO}_2$ . Consequently, the conclusion following from our adsorption measurements is more probable that at a temperature above 100°C



the type of bond between propylene and the surface undergoes a change. However, we do not know the corresponding heat of adsorption.

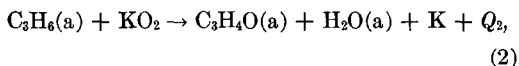
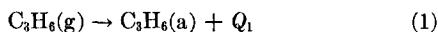
The heat of adsorption of propylene adsorbed from a propylene-oxygen mixture at 170°C has a higher value (43.5 kcal/mole) than that found in the adsorption of propylene in the absence of oxygen in the gas phase (22.3 kcal/mole). This difference is just due to the presence of oxygen in the gas phase, whose consumption during the reaction partly compensated the decrease in the lattice oxygen.

The rate of the reaction of propylene with oxygen, expressed by the drop of the propylene pressure in unit time, is in this case higher than that of the reaction of propylene with the surface of the catalyst without oxygen in the gaseous phase (see Fig. 3). (We assume on the basis of the results obtained by Peacock (11) that the drop of both the propylene and the oxygen pressure proceeds at equal rate at the beginning of the reaction.)

The values of the heats measured in the interaction of propylene with the surface of the catalyst involve the heat effects corresponding to the individual steps of the reaction. Now we shall attempt to indicate the course as well as the individual steps of the reaction and to verify them by means of the measured or already known heat effects.

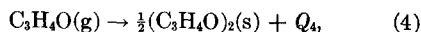
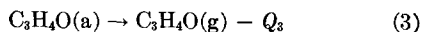
### C. Heat Effects and Partial Steps of the Oxidation of Propylene

According to Voge and Adams (12), the molecule of propylene reacts with the oxygen atom adsorbed on the surface of the Bi-Mo/SiO<sub>2</sub> oxide catalyst either directly from the gaseous phase or in the adsorbed state. This process can be represented by following equations:

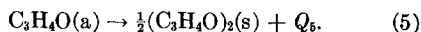


where  $Q_1$  and  $Q_2$  are the heat effects of the individual processes.  $\text{KO}_2$  denotes the catalyst in the oxidized state, K in its reduced state. In our case it was found that neither

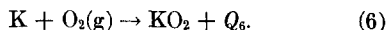
acrolein nor water appears in the gaseous phase. The water is bound by the catalyst carrier, and acrolein is removed by polymerization, which can proceed either after preceding desorption anywhere in the reaction system



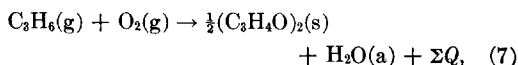
or directly on the surface of the catalyst



In the reactions (1-5), the catalyst is reduced and can be returned into its initial state by adsorption of oxygen

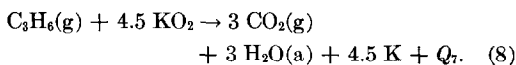


The result is the equation of the over-all reaction

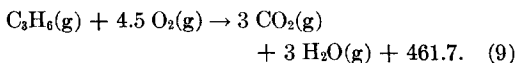


where  $\Sigma Q = Q_1 + Q_2 - Q_3 + Q_4 + Q_5$  or  $Q_1 + Q_2 + Q_5 + Q_6$ .

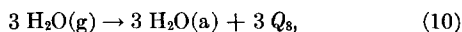
From the data listed in Table 2 it follows that the consumption of oxygen for returning the catalyst into its initial state (Eq. (6)) is on an average 13% higher than the consumption of propylene. We assume that this higher oxygen consumption is due to the oxidation of propylene to  $\text{CO}_2$ . From the calculation it follows that about 3.7% of propylene is oxidized to  $\text{CO}_2$ . (We do not take into consideration that part of this propylene can be oxidized only to CO.)



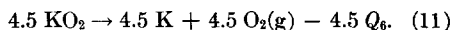
For the homogeneous oxidation of propylene to  $\text{CO}_2$  we obtain from the tables (8) the reaction heat of 461.7 kcal/mole.



An appropriate adjustment of this equation leads to the following equations (8)



and



The sum of Eqs. (9), (10), and (11) gives Eq. (8), and for the value of  $Q_7$  we obtain

$$Q_7 = 461.7 + 3 Q_8 - 4.5 Q_6.$$

For  $Q_8$  we have selected the value of the heat of condensation of water, i.e., 9 kcal/mole (13), and for  $Q_6$  the measured value of the heat of adsorption of oxygen, i.e., 75.2 kcal/mole:

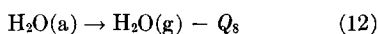
$$Q_7 = 461.7 + 27.0 - 338.4 = 150.3.$$

A 3.7% conversion of propylene to  $\text{CO}_2$  liberates a heat amount of 5.6 kcal. If we now subtract from the heat of adsorption of propylene (22.3 kcal/mole) the contribution of 5.6 kcal corresponding to the oxidation of propylene to  $\text{CO}_2$  (and convert this difference to a 100% conversion of propylene to acrolein), we obtain for  $\Sigma Q$  the value

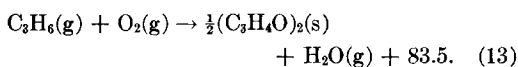
$$\Sigma Q = 17.3 + 75.2 = 92.5 \text{ kcal/mole}$$

as the over-all heat effect of the adsorption of propylene and its oxidation to acrolein.

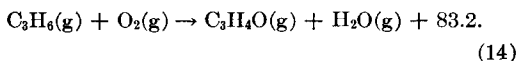
For the sum  $Q_1 + Q_2 + Q_5$ , or  $Q_1 + Q_2 - Q_3 + Q_4$ , we have obtained the value 17.3 kcal/mole. Now we shall try to subdivide this value into the individual partial steps. To Eq. (7) we coordinate the equation of the desorption of water



and after summing up Eqs. (7) and (12) we obtain



Now we compare this equation with the equation for the homogeneous oxidation of propylene, where the reaction heat has been calculated from the tables (8)



From a comparison of both equations it follows that the transfer of acrolein from the gaseous into the solid phase (polymer) proceeds without a heat effect. This is possible only in such a way that acrolein is desorbed from the surface of the catalyst and polymerizes from the gaseous phase outside the adsorption vessel. According to this conclusion, the heat of adsorption of propylene

at 170°C is given by the sum of the three heats  $Q_1 + Q_2 - Q_3 = 17.3$  kcal/mole. On the assumption that the heat of adsorption of propylene will be near to the heat of adsorption of acrolein (as it is the case in the region of physical adsorption (3)), the difference  $Q_1 - Q_3$  will be relatively small. From this would follow that the value of 17.3 kcal/mole would for the greatest part correspond to the heat  $Q_2$ .

In the oxidation of propylene from a propylene-oxygen mixture, a heat of adsorption of propylene of 43.5 kcal/mole was measured. According to an analysis of the gaseous phase, 218  $\mu$ moles of propylene and 120  $\mu$ moles of oxygen were retained on the catalyst. If we now add to the measured value of 43.5 kcal/mole the heat liberated by the adsorption of oxygen, 98  $\mu$ moles, necessary for returning the catalyst into its initial, oxidized state, (33.8 kcal) and if we subtract the heat of adsorption of water (because the water remains adsorbed on  $\text{SiO}_2$ ), 9 kcal/mole, we obtain the value of the over-all heat of the reaction  $43.5 + 33.8 - 9 = 68.3$  kcal/mole.

This value is about 17% lower than the theoretical value, 83.2 kcal/mole. In this case we did not take into account the possible formation of CO and  $\text{CO}_2$ , because according to the results obtained by Peacock (11), the formation of these products of the oxidation of propylene from a mixture with oxygen is strongly suppressed, in comparison with the oxidation of propylene on the surface of the catalyst without oxygen in the gaseous phase. The somewhat lower value of the calculated heat, 68.3 kcal/mole, can be partly explained by the low accuracy of the analysis of the propylene-oxygen mixture carried out at the end of the measurement.

In a similar way it would be possible to represent in detail also the course of oxidation of acrolein and to calculate the heat effects for the individual steps. At present, however, we still need some experimental data necessary for verifying the calculated values.

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