JOURNAL OF CATALYSIS 23, 253–258 (1971)

Chromatographic Determination of Adsorption Heats of Propylene, Propane, Acrolein, and CO_2 on Oxides of Bi, Mo, Bi–Mo, Bi–Mo/SiO_2, and on SiO_2

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Received March 5, 1971

The chromatographic method was employed for determining the adsorption heats of some reactants in the oxidation of propylene to acrolein: propylene, propane, acrolein, and CO_2. The measurements were carried out on a Bi–Mo oxide catalyst with and without carrier and on the basic constituents of this catalyst, i.e., Bi_2O_3, MoO_3, and SiO_2. The measured results are discussed from the viewpoint of the interaction between propylene and the surface of the catalyst.

INTRODUCTION

The selective oxidation of lower olefins on mixed oxide catalysts, of which the best known is the mixed Bi–Mo oxide with the atomic ratio Bi:Mo near unity, has in recent time received considerable attention. Its significance is ever increasing, since it is very attractive for industrial purposes. This relates first of all to the oxidation of propylene to acrolein by air oxygen (*1*, *2*), and in the presence of NH_3 to acrylonitrile (*3*).

In the literature, attention is paid first of all to the study of the kinetics and the mechanism of the oxidation on the two best known oxide catalysts, Cu and Bi–Mo oxides. The kinetics of the oxidation of propylene on both catalysts is today already well known (*1*), and even mechanisms of the reaction are suggested (*2*, *4*, *5*). It is important, however, to know also the energy balance of the individual suggested steps of the reaction. For this reason, we have measured first the adsorption of propylene in connection with the determination of the adsorption heats by the chromatographic and the calorimetric method at various temperatures, including that of the beginning of the slow oxidation of propylene.

In this part of our study we were first concerned with the determination of the adsorption heats of the individual reactants of the oxidation of propylene on a Bi–Mo oxide catalyst, with and without carrier, and on its pure constituents, namely Bi_2O_3, MoO_3, and SiO_2. For the determination of the adsorption heats we selected the chromatographic method (*6*), and, where possible, we extended the range of measurements to temperatures near those of the reaction.

EXPERIMENTAL

Catalysts employed. The measurement was carried out on a mixed Bi–Mo oxide catalyst (with the atomic ratio of Bi:Mo nearing 1:1) without carrier (1.7 m^2/g) as well as with an SiO_2 carrier (55% by weight, 93 m^2/g), and further on specimens of Bi_2O_3 (1.0 m^2/g) and MoO_3 (3.0 m^2/g). Moreover, a commercial specimen of SiO_2 was used, viz. "silica gel for chromatography CH." The determination of the specific surface was carried out on specimens preheated at 120°C *in vacuo*, by means of adsorption of argon at the temperature of liquid nitrogen with the use of the BET method. The grain size of the specimens employed was 0.3–0.6 mm. The individual specimens were packed in a glass column, 1 m long, i.d., 2.7 mm.

Gases employed. The propylene, which was to be injected into the column with the catalyst, was directly taken from a steel bottle. The purity of the propylene was 98%, the remainder was propane. The acrolein vapors were injected in a mixture with the carrier gas. The purity of both propylene and acrolein was controlled by chromatographic analysis. Gaseous CO_2 was obtained by distillation of solid CO_2. As an inert gas, spectroscopically pure argon was used.

The carrier gas was nitrogen or helium. Nitrogen was freed from oxygen traces (<0.5%) by passing it over reduced Cu wires heated to 400°C, whereupon it was dried by leading it through a trap cooled with solid CO_2. Helium was only dried by passing it through a trap with activated carbon, cooled with liquid nitrogen. The oxygen used for activation of the catalyst was dried in the same way as nitrogen.

Apparatus. The measurement was carried out in a chromatograph assembled in the laboratory and suitable for ascertaining the retention times of the adsorbed gases and completed by an analytical part. The diagram of the equipment is presented in Fig. 1. The carrier gas, helium or nitrogen, passes through the purification section, and by the two-way cock C it enters either the measuring part of the apparatus (with the column of the catalyst K) through the needle valve D, or it is led into the analytical section through the needle valve D′. The flow rate of the gas is controlled by means of the needle valves. In the determination of the retention times of the adsorbed gas, the carrier gas passes over the catalyst located in a bath at constant temperature. The injection of the absorbate into the flow of the carrier gas is carried out by means of an injection syringe through the glass extension G sealed with a circular plate of silicone rubber. The injected gas can be led after its passage through the catalyst by the two-way cock C″ into the trap B″ cooled by liquid nitrogen. This procedure was chosen when we wanted to determine the composition of the desorbate. The condensed desorbate (except, e.g., CO) was evaporated by rapid heating of the vessel B″ into the analytical part of the apparatus. The composition of the gaseous phase in both parts of the apparatus was ascertained by means of the thermal conductivity cells H_1, H_2, and H'_1, H'_2, which were connected by a Wheatstone bridge to an electronic recorder. The flow rate of the carrier gas was measured by the bubble flow meter L, L′.

Measuring procedure. Before the measurement, the catalyst was always heated in a stream of oxygen for 1 hr at 450°C, the flow rate of O_2 was 1.5 liter/hr. After this heating, the catalyst was cooled in an oxygen stream to room temperature. Only now, oxygen and carrier gas were interchanged, and the required temperature of the catalyst was set. At each temperature, doses of the inert gas argon and of the adsorbate were led on to the catalyst in a mixture or separately. The overpressure of the gas at the column inlet was measured by means of an open U-manometer, F. The measured retention times *t* were corrected for this overpressure

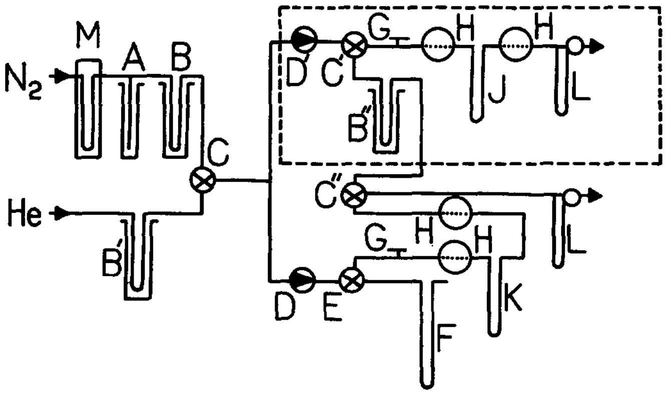

FIG. 1. Schematic view of the gas chromatographic apparatus.

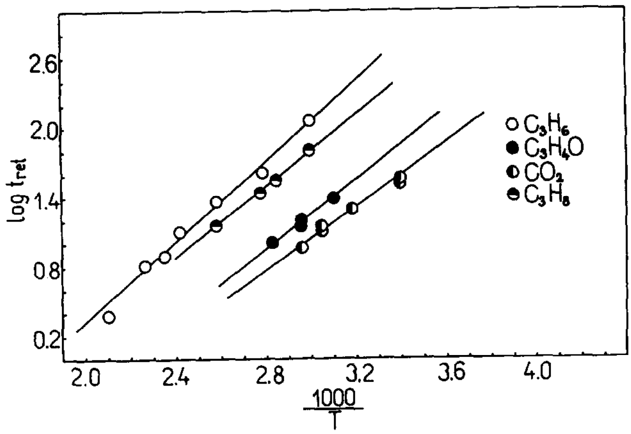

FIG. 2. Pulse flow retention times as a function of temperature for various gases on a Bi–Mo/SiO_2 catalyst. Helium was used as a carrier gas.

$-t_0$. The calculation of the adsorption heat was carried out by means of the relation (*4*)

$$\log t_0 = C - \frac{\Delta H}{2.303RT},$$

where C is a constant, ΔH is the adsorption heat (kcal/mole), R is the gas constant, and T is the absolute temperature at which the measurement was performed. The measurements were carried out for two different doses, 0.2 and 0.05 ml; in the case of acrolein, 0.5 ml of the carrier gas saturated with acrolein vapors at room temperature was injected. The flow rate of the carrier gas amounted in the majority of cases to 1.5 liter/hr.

RESULTS AND DISCUSSION

The retention times of the adsorbate in both carrier gases, nitrogen and helium, were determined on the oxide catalyst Bi–Mo/SiO_2. Figure 2 presents the values of the retention times in dependence on temperature, log t_0 vs $1/T$, for propylene, propane, acrolein, and CO_2 in helium. The calculated values of the adsorption heats and the temperature range in which the measurement was carried out are given in Table 1. The retention time of the adsorbate is in all cases independent of the number of doses. From the table it is evident that the value of the adsorption heat is independent of the carrier gas employed.

TABLE 1
ADSORPTION HEATS DETERMINED ON THE Bi–Mo/SiO_2 CATALYST (CARRIER GAS N_2 AND He)

	N_2		He	
Bi–Mo/SiO_2	ΔH (kcal/mole)	t(°C)	ΔH (kcal/mole)	t(°C)
Propylene	7.7	60–200	7.7	60–200
Propane	6.2	60–200	6.1	60–200
Acrolein			6.4	40–120
CO_2			5.9	20–65

Figure 3 shows the dependence of the retention time on temperature for propylene, propane, and acrolein on silica gel. These linear relations were employed for calculating the values of the adsorption heats given in Table 2.

The values of the retention times of the individual specimens of Bi–Mo/SiO_2 and silica gel were determined with a maximum error of 5%, because the surfaces of both specimens are sufficiently large. However, the accuracy was lowered in the reading of

TABLE 2
ADSORPTION HEATS DETERMINED ON SILICA GEL (CARRIER GAS N_2)

Silica gel	ΔH (kcal/mole)	t(°C)
Propylene	7.8	40–200
Propane	6.6	40–200
Acrolein	6.5	25–120

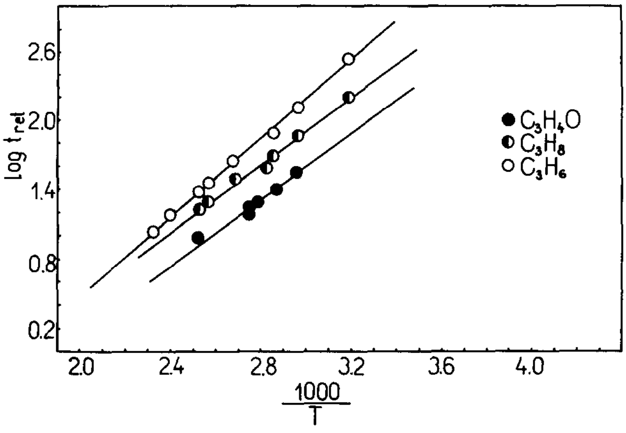

FIG. 3. Pulse flow retention times as a function of temperature for various gases on silica gel. Nitrogen was used as a carrier gas.

the retention times for the further specimens, which are without a carrier and whose surface is more than an order of magnitude smaller. For this reason, the values of the retention times plotted in Fig. 4 again in dependence on log t_0 vs $1/T$ exhibit also a wider scattering. Nevertheless, these values of the adsorption heats of propylene on the individual specimens can be ascertained with sufficient accuracy. These values are listed in Table 3. All the values of the retention times given in Figs. 2, 3, and 4 were measured for a dose of 0.2 ml. Equal slopes of the straight lines, however, were found also for a dose of 0.05 ml.

Some of the values of the adsorption heats measured by us are confirmed in the literature. For instance, the Japanese authors Kimiko Arita *et al.* (7) found for the adsorption heat of propane and propylene on silica gel the values 6.3 and 7.7 kcal/mole, which are in very good agreement with our results. In a further communication it will be reported that we measured the adsorption

TABLE 3

ADSORPTION HEATS OF PROPYLENE ON VARIOUS OXIDES (CARRIER GAS He)

Propylene	ΔH (kcal/mole)	t(°C)
Bi_2O_3	6.4	−8 to 31
MoO_3	3.3	0 to 65
Bi-Mo-O	3.8	−18 to 43

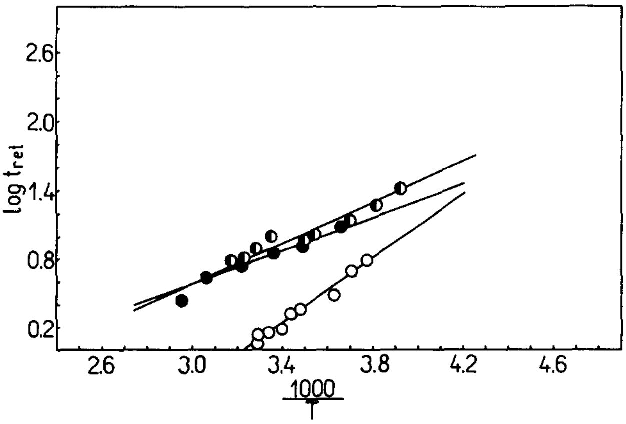

FIG. 4. Pulse flow retention times as a function of temperature for propylene on various oxides. ○, Bi_2O_3; ●, MoO_3; ◐, Bi-Mo oxide. Helium was used as a carrier gas.

heats of propylene on a specimen of Bi–Mo/SiO_2 also by the calorimetric method (in dependence on the coverage of the surface) and found the value 8.0 kcal/mole in the temperature range of 35–100°C, independently of the coverage of the surface. The measured adsorption isotherms were employed for calculating the adsorption heat of propylene according to the Clausius–Clapeyron equation, and 7.7 kcal/mole was found for a coverage of 2.5 μmole/g of the catalyst. All three values, 7.7, 8.0, and 7.7 (see Table 1) are in good agreement. From a comparison of the values of the adsorption heats listed in Tables 1, 2, and 3 it is possible to draw some conclusions.

(a) It is striking that the adsorption heats of the adsorbates on silica gel have the same values as on the Bi–Mo/SiO_2 catalyst, where SiO_2 is the carrier of the catalytically active constituent. From this fact it can be assumed that propylene adsorbed on the catalyst is for the greater part bound to SiO_2 surface. This holds at least in the temperature range up to 100°C, in which the adsorption heats of propylene on the oxides without carriers were measured (at higher temperature were the retention times unmeasurable). All the values of adsorption heats given in Table 3 are considerably lower than the heats measured on Bi–Mo/SiO_2. If the range of the adsorption of propylene on the active constituent of this catalyst were comparable with the adsorption on the SiO_2 carrier, this would have to manifest itself by a decrease in the value of the adsorption heat below the value determined on SiO_2.

The magnitude of the adsorption heat (Table 1) indicates the physical nature of the adsorption bond. On the basis of these results, however, it is not possible to exclude a change in the type of the bond of propylene to the active component, the oxides of Bi and Mo, at higher temperatures. A change in this bond is indicated by adsorption measurements of some authors (*8*), who report that the adsorption of propylene on MoO_3 is at 60°C lower than at 180°C. Similarly, Zhdanova and Popova (*9*) found in the study of the adsorption of propylene on CuO, Cu_2O, and Cu in the range of 20–150°C that the isobar of propylene (p = 10 Torr) passes through a minimum near 50°C. In view of the fact that the oxidation of propylene on CuO and on a Bi–Mo oxide catalyst proceeds according to the same mechanism, the same type of the bond with the surface can be assumed for both catalysts. According to this it is possible to imagine that on the Bi–Mo/SiO_2 catalyst, a reversible adsorption of propylene on the carrier proceeds in the range from 40 to 200°C with the adsorption heat of 7.7 kcal/mole and, whereas an adsorption of propylene on the active constituent of the catalyst, which is reversible to about 80°C and of a small extent, the adsorption heat being 3.8 kcal/mole cannot be excluded. This type of the bond of propylene with the oxides of Bi and Mo may be preserved at higher temperature, and at the same time, however, it is not possible to exclude a change in the bond of the adsorbed propylene with the surface that could lead to irreversible adsorption.

(b) From the results given in Table 3, however, it is possible to arrive at a rough picture of the composition of the active constituent in the surface of the catalyst. The adsorption heat of propylene on MoO_3 and Bi–Mo oxide is practically the same, whereas on Bi_2O_3 it is nearly double this value. From this it can be assumed that either the surface of the mixed oxide is predominantly occupied by Mo^{6+} ions or that the adsorption of propylene on the Bi^{3+} ions is negligible in comparison with the adsorption on the Mo^{6+} ions. Gel'bshtein *et al.* (*10*) measured the adsorption of propylene on Bi_2O_3, MoO_3, and Bi–Mo oxide at 170°C, in which case according to their report there proceeded no interaction between propylene and the surface. According to their results, the adsorption of propylene on Bi_2O_3 is higher than on MoO_3 and Bi–Mo oxide. Consequently, (from the data in Table 3) two conclusions can be drawn, viz., either that the surface of the active constituent is occupied predominantly by Mo^{6+} ions, or that propylene in contact with the surface of the Bi–Mo oxide is adsorbed only on the Mo^{6+} ions. The results obtained in the study of the properties of the Bi–Mo/SiO_2 catalyst by means of IR spectroscopy (*11*) show that the heating of the catalyst *in vacuo* and in oxygen results in the liberation of MoO_3 from the active constituent of the catalyst, which is converted into $Bi_2O_3 \cdot MoO_3$. The liberated MoO_3 manifests itself by an absorption band. Changes in the spectrum after adsorption of propylene on the catalyst preheated in such a way were observed only in this band, and this would support our second conclusion, following from the data in Table 3, that propylene is adsorbed on the surface of the Bi–Mo oxide catalyst only on the Mo^{6+} ions.

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