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Oxidation of Propylene by Means of SnO_2-MoO_3 Catalysts

I. The Effect of Combining SnO_2 and MoO_3

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The low partial pressure of $MoO_2(OH)_2$ existing over solid MoO_3 in the presence of water vapor was determined at temperatures from 400° to 500°C.

It was found that SnO_2, contacted around 450°C with a gas saturated with $MoO_2(OH)_2$, sorbs MoO_3 (or a hydrated form) to its surface. The sorbed molybdenum oxide constitutes what may be considered a monolayer. This coverage of the SnO_2 surface with molybdenum oxide is a reversible process.

In the oxidation of propylene with molecular oxygen at 370°C and atmospheric pressure, SnO_2 shows some catalytic activity; half or more of the reacted propylene is completely broken down to CO_2 and CO, while a considerable portion is converted to acrolein. MoO_3 is a much less active oxide.

However, SnO_2 covered with a monolayer of molybdenum oxide is 5 to 10 times more active in the oxidation of propylene than SnO_2 alone, and gives a completely different product distribution. The reaction yields mainly acetic acid along with acetone (in varying ratios), while total oxidation to CO and CO_2 is of minor importance. These results can only be obtained in the presence of water vapor (in the experiments with either SnO_2 or MoO_3 alone, water vapor was also used).

So, although MoO_3 did not form a bulk compound with SnO_2, it could be bound to the SnO_2 surface, which then exhibited a peculiar catalytic activity.

INTRODUCTION

Of late years, rather much attention has been given to the oxidation of propylene with molecular oxygen by means of heterogeneous catalysis. Nearly all publications deal with oxidation to acrolein. This type of oxidation takes place for example, on a bismuth molybdate catalyst.

Application of propylene labeled with ^{13}C (*1, 2*), ^{14}C (*3, 4*), or D (*5, 6*), revealed that the acrolein is formed by a mechanism in which first a hydrogen atom is abstracted from the methyl group and the resulting allyl group, CH_2CHCH_2, is oxidized with equal chances at either end.

As disclosed in some patent specifications (*7–10*), which are based partly on work done in this laboratory (*10*), there also exist catalysts characterized by their activity in the formation of acetic acid, acetone, and acetaldehyde. To warrant satisfactory results, it is considered necessary, or at least desirable, to execute this oxidation reaction in the presence of water vapor. Mention should also be made here of a patent specification (*11*) dealing with a process for conversion of propylene and water vapor into acetone and hydrogen.

Investigations in this laboratory revealed that a catalyst containing SnO_2 and MoO_3 is active in the oxidation of propylene, and that acetic acid is the main product of the reaction.* This catalyst was prepared by

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* After completion of the present paper, we came across an abstract of a recent article by Lazukin, Rubanik *et al.* (*20*), who also used SnO_2-MoO_3 catalysts for oxidizing propylene. The abstract does not mention whether the experiments were carried out in the presence of water vapor. One of the oxidation products is acetic acid, but this does not seem to be the main product; acetone is not mentioned.

Referring, among other things, to the results of X-ray analysis, the Russian authors state that their samples, which had been heated to 600°C, bringing SnO_2, MoO_3, and a commercial SiO_2 preparation (Aerosil) together in water, removing the water by evaporation and drying, and heating the dried mass at 450°. SnO_2 and MoO_3 in pure form are not good catalysts.

The outlined procedure of preparing the above catalyst does not seem to favor compound formation. This has been confirmed by an X-ray examination, in which no trace of a compound of the two oxides was observed in the catalyst. It would seem surprising, therefore, that a catalyst containing SnO_2 and MoO_3 shows such an outstanding activity and selectivity.

In the presence of water vapor, MoO_3 exhibits a certain degree of volatility, which is due to the formation of gaseous $MoO_2(OH)_2$* (*12*). This knowledge induced us to undertake the following experiment.

At 475°C water vapor was led through a flow reactor containing a bed of MoO_3/Aerosil pellets and (further downstream) a bed of SnO_2/Aerosil pellets. After this flow had been continued for a number of hours, the temperature was brought down to 375°C and a stream of propylene was fed in together with air and water vapor. The SnO_2 bed appeared to be active now, for the temperature in the bed rose owing to the heat of reaction, and an appreciable amount of acid was produced. (In an experiment in which the order of the oxide beds was reversed, no appreciable catalytic activity was observed upon the passage of water vapor.)

This test furnishes a clear indication that volatilized MoO_3 is sorbed to the SnO_2 surface, which thus acquires a marked catalytic activity. It was considered useful to undertake a further experimental study. This comprised (a) determining the volatility of MoO_3 in the presence of water vapor at temperatures around 450°C, and the MoO_3-sorbing capacity of SnO_2; (b) determining the nature and degree of the activities of SnO_2-MoO_3 combinations and of SnO_2 and MoO_3 alone (without SiO_2, to avoid complications) in the oxidation of propylene.

These points are dealt with in Part I. The following parts will deal with the mechanism of propylene oxidation on SnO_2/MoO_3.

To avoid drawing wrong conclusions, we used three types of SnO_2 and MoO_3, which differed as regards origin of the starting material and/or way of preparation.

EXPERIMENTAL

An electrically heated fluid bed of carborundum particles whose temperature could be controlled to within 1–2°C, was used as the heating medium [see Mars and Maessen (*15*)]. The flows of propylene and air were measured with capillary flow meters. In most of the experiments water vapor was fed in from a saturator. The amount of water vapor was determined by weighing the condensate.

According to gas-chromatographic analysis, the propylene contained 0.03% of propane, 0.0035% of butylene-1 and/or isobutylene, 0.0002% of ethane and/or ethylene, and a slight amount of acetone (in the order of 0.01%).

The air was freed of CO_2 by means of soda lime.

The experiments were carried out at atmospheric pressure.

Determination of the volatility of MoO_3 in the presence of water vapor. A flow of water vapor (0.4 mole/hr) and air was fed into a heated bed of crystalline MoO_3 (obtained by crushing a solidified melt of

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contained solid solutions of MoO_3 in SnO_2 and the compound $SnO_2 \cdot 2\,MoO_3$ (tin molybdate?). To our knowledge this is the first time that X-ray evidence for the existence of a compound or a solid solution in the system SnO_2/MoO_3 is advanced in the literature. The Russian results seem to conflict with those obtained by Doyle and Forbes (*21*), who, after heating SnO_2 and MoO_3 together at 700°C, could not observe a compound. Our own attempts at preparing a compound, in which we tried both the wet and the dry route (ultimate temperatures around 900°C) were likewise unsuccessful.

* The formula $MoO_2(OH)_2$ has not been established beyond doubt, but is very probably correct (see ref. *14*). A gaseous molybdenum compound of high molecular weight becomes noticeable only at elevated steam pressures (*13*).

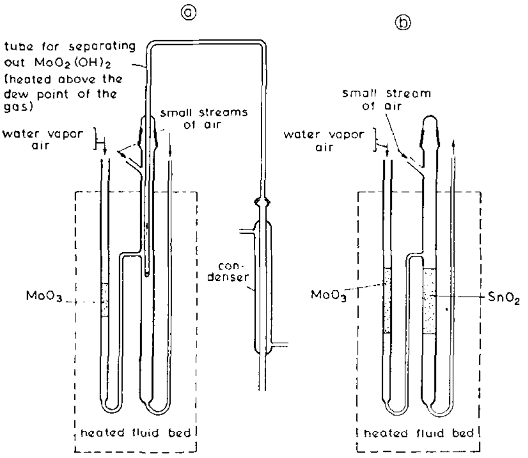

FIG. 1. (a) Apparatus for determining the volatility of MoO_3 in the presence of water vapor (schematic). (b) Apparatus for sorbing $MoO_2(OH)_2$ to SnO_2 (schematic).

MoO_3 and passing it through a 0.5-mm screen). The length of the bed was 5 cm, the diameter 0.7 cm. The gas was discharged through a removable tube (Fig. 1a), in the cooler part of which the $MoO_2(OH)_2$ deposited (in the form of MoO_3 as was shown by X-ray analysis). The lower end of the tube was sealed to prevent deposited particles dropping out (the gas entered through a perforation in the wall). Provisions were taken to prevent condensation of water vapor in the tube.

Deposited molybdenum oxide was dissolved in an NaOH solution, after which the molybdenum in the solution was determined. The molybdenum in the condensate was also determined. The amount invariably proved to be less than 1% of that deposited in the tube.

Sorption of $MoO_2(OH)_2$ to SnO_2; desorption of $MoO_2(OH)_2$. Part of the sorption experiments were performed as follows. A flow of air (60 nl[*]/hr) and water vapor (70 nl/hr) was passed in succession through a bed of crystalline MoO_3 and a bed of SnO_2 pellets (0.5 mm). The beds (each 10 cm long) being contained in the same apparatus (Fig. 1b), their temperatures were equal. After a given time, the apparatus was lifted out of the fluid bed and layers of approximately 1 cm thickness were drawn from the SnO_2 bed, through a tube with a constricted inlet, into a suction flask.

In other sorption experiments the $MoO_2(OH)_2$ was supplied exclusively by *diffusion*. These were carried out in 1-cm diameter tubes containing, in upward order, MoO_3 powder, a 2–3 mm high layer of carborundum, and a 1 cm high layer of SnO_2. The tubes were placed in a vessel in which an atmosphere of 90% water vapor and 10% oxygen was maintained (pressure 1 atm). The vessel itself was placed in a furnace. After a tube had been heated the required number of hours, it was taken out for determination of the molybdenum contents in the lower and upper halves of the SnO_2 bed.

Two experiments were carried out on the *desorption* of $MoO_2(OH)_2$. In one of these MoO_3-covered SnO_2 was in the left-hand leg of the apparatus shown in Fig. 1 (so at the place of the MoO_3 bed in Fig. 1a) so that no material could be drawn from the SnO_2 bed. However, the $MoO_2(OH)_2$ desorbed by the passing water vapor could at given intervals be collected in the removable tube mentioned above. In the other experiment the loaded SnO_2 was contained in the right-hand leg.

Oxidation of propylene. The oxide to be tested (0.5-mm pellets) was filled into the annular space (3 mm wide) between an inner tube in which a chromel-alumel thermocouple could be moved up and down, and an outer tube (1 cm inside diameter) surrounded by the fluid bed. The oxide bed was enclosed between layers of carborundum.

After the start of the experiment, conditions were allowed to settle for, say, 2 hr.

On leaving the oxide bed, the gas was normally passed through an ice-cooled glass coil opening at its lower end into a collecting vessel for the condensate. After being weighed, the condensate was analyzed for acids. In the tests executed with the combination SnO_2/MoO_3, the condensate was collected for 2 hr. In the other experiments, where the acid production was much

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[*] nl = liter (N.T.P.).

smaller, this period was prolonged to 4 or 6 hr (in test No. 1 even to 11 hr).

To isolate the volatile carbonyl compounds, such as acrolein, the gas was led through a train of three ice-cooled wash bottles provided with sintered glass distributor plates and containing 50 g of water each. Except in the tests at a low flow rate, the gas was led through the bottles for 2 hr. Substantially all of the acetone can thus be caught. A portion of the acetaldehyde and acrolein (some 7% and 11% of the amounts issuing from the reactor), however, is not absorbed (no correction was made for this). Carbon dioxide, being only very slightly soluble, passes through almost quantitatively. The gas issuing from the wash bottles was sampled for determination of CO and CO_2.

Preparation of the MoO_3 and SnO_2 masses.

MoO_3-A. A pure commercial preparation of MoO_3 powder, used as delivered.

MoO_3-B. MoO_3 crystals deposited from an air current passed over molten MoO_3 at 850°C, were dissolved in ammonia. The solution was evaporated till dryness. The pulverulent material obtained after heating at 500°C for 4 hr was used in unpelleted form.

MoO_3-C. Nitric acid was added to a solution of ammonium paramolybdate. The precipitate was dried, and heated at 500°C. Upon addition of water, the material was compressed under a high load and then broken to 0.5-mm pellets.

SnO_2-A. Granulated tin was oxidized with nitric acid. The liquid was evaporated on a steam bath after which the residue was dried at 140°C and heated at 950°C for 4 hr.

SnO_2-B. Granulated tin was oxidized with nitric acid. Following decantation, filtration, and washing, the precipitate was dried, and heated at 500°C for 16 hr.

SnO_2-C. Water was added to a commercial SnO_2 preparation. Following evaporation of the water, the oxide mass was heated at 900°C for 5 hr.

All SnO_2 preparations were used in the form of 0.5-mm pellets.

Determination of surface area. The surface area accesible to CH_4 or N_2 at -196°C was determined by means of the well-known BET method. The cross-sectional area per adsorbed molecule was taken equal to 16.0 Å^2 for CH_4 and to 15.4 Å^2 for N_2. Nitrogen was used only in the measurements on SnO_2-B and SnO_2-C.

Analyses

Acids. Total acid was determined by titration. The amounts of the individual acids (acetic acid, acrylic acid, maleic acid, and formic acid) were determined by liquid–liquid chromatography (silica gel column; stationary phase: 0.1 *N* H_2SO_4; mobile phase: benzene with varying percentages of *n*-butanol). Samples of low acid content were concentrated in a rotary evaporator at 40°C after addition of sodium hydroxide; acrylic acid proved to be stable under these conditions.

Nonacids. A mixture of a known portion of the condensate and an aliquot portion of the collective contents of the wash bottles was analyzed gas chromatographically for acetone, acrolein, and acetaldehyde (column: Carbowax 600 on Chromosorb W; detection: flame ionization); traces of propionaldehyde and other compounds, if present, were not determined.

CO and CO_2. CO and CO_2 in samples of the issuing gas were determined by measuring the change in electrical conductance of a dilute NaOH solution upon absorption of CO_2. The analysis was performed with an apparatus supplied by Wösthoff (Bochum, W. Germany).

Molybdenum. Mo-containing SnO_2 samples were fused with NaOH. (Although boiling with a sodium hydroxide solution had also proved adequate, fusing was chosen for greater certainty.) The molybdenum in the solution was transformed into the red thiocyanate complex, which was then determined colorimetrically. Protiva's (*16*) variant of this procedure (application of HNO_3) proved most satisfactory.

RESULTS

Volatility of MoO_3 in the presence of water vapor. Determinations of the volatility of MoO_3 in the presence of water vapor

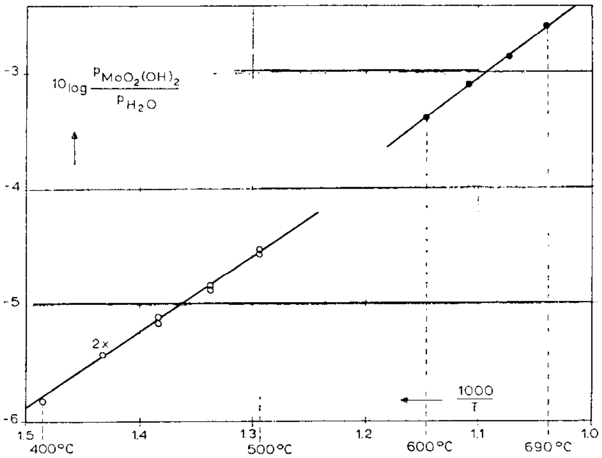

FIG. 2. The volatility of MoO_3 in the presence of water vapor: p, partial pressure; T, absolute temperature (°K); ○, this paper; ●, Glemser and von Haeseler (*12*).

were performed at 400°, 425°, 450°, and 500°C. The results are shown in Fig. 2, where the logarithm of the equilibrium constant of the reaction

$$MoO_3\ (\text{solid}) + H_2O \rightleftharpoons MoO_2\ (OH)_2$$

is plotted versus the reciprocal of the absolute temperature. The figure also gives the results of determinations in another temperature range by Glemser and von Haeseler (*12*).

Prior to the experiments referred to in Fig. 2, investigations were carried out at 450°C to examine whether the feed rate of the water vapor has an effect on the $MoO_2(OH)_2$ concentration in the issuing gas. An increase of this rate from 5 to 100 nl/hr gave a decrease in concentration of roughly 10%, which can hardly be called significant. The $MoO_2(OH)_2$-carrying gas streams used in the experiments referred to in Fig. 2 (low flow rate) and in those to be dealt with in the next paragraph (high flow rate) may therefore be considered to be saturated with $MoO_2(OH)_2$.

The equation for the straight line found by application of the method of least squares to our own data reads

$$\log_{10}(p_{\mathrm{Mo}}/p_{\mathrm{H_2O}}) = -(6450/T) + 3.80 \qquad (1)$$

where p is partial pressure and T is absolute temperature (°K).

Sorption of $MoO_2(OH)_2$ to SnO_2. An $MoO_2(OH)_2$-carrying gas stream was passed through a 10-cm long bed of 16.3 g SnO_2-A for 7 hr and at a temperature of 450°C. Next, ten 1-cm high layers were sucked up from the apparatus and analyzed for molybdenum. The weight percentages of molybdenum (calculated as metal) thus found were as follows: 1st layer, 0.21%; 2nd layer, 0.22%; 3rd layer, 0.18%; 4th layer, 0.04%; 5th and following layers, $\leqslant 0.01\%$. Evidently, the tin dioxide sorbs molybdenum (in oxidic form) up to a given limit (approx. 0.2%), so that a molybdenum front travels through the bed. The molybdenum-containing tin dioxide up to the front showed a light-green color. (The total amount of molybdenum sorbed by the bed was 11 mg. Judging from the temperature and the amount of infed water vapor, one might have expected a total sorption of 16.5 mg. The difference between the two figures is rather large. Perhaps, the actual temperature was considerably lower than 450°C, owing to some failure.)

To obtain material for catalytic experiments, the loading with molybdenum in the subsequent experiments was continued until after the front had broken through the bed; this could be established from the deposition of molybdenum trioxide (or dioxide dihydroxide?) in the outlet of the apparatus. Two 10-cm long beds of SnO_2-A were loaded with molybdenum for 48 hr at 437°. To check whether the bed had been equally loaded, samples were taken from top, middle, and bottom. The molybdenum percentages were found to be as follows:

Top	0.08	0.014 and 0.013 (2 successive layers)
Middle	0.23	0.13
Bottom	0.28	0.20

The molybdenum content of the top layers was unexpectedly low. The other percentages are less similar than we had hoped, but still come in the correct order of magnitude.

The two loaded masses were combined (code: I) and the molybdenum content was determined again; this proved to be 0.24 wt% of molybdenum. We also determined the specific surface area; this was 3.0 m^2/g, nearly the same as that of SnO_2-A.

We further loaded 3 g of SnO_2-B with molybdenum by passing a gas flow saturated with $MoO_2(OH)_2$ through it at 450°C for 36 hr. This loaded tin dioxide (code: II) was found to contain 1.6 wt% of molybdenum.

When loading by *diffusion,* we used a sample prepared along very much the same lines as the SnO_2-A. A duplicate run at 525°C for 78 hr gave molybdenum contents of 0.24 and 0.25 wt% for the lower half and 0.16 and 0.17 wt% for the upper half of the bed. After 7, 17, and 41 hr at 500°C, the molybdenum contents in the lower half were 0.056%, 0.090%, and 0.19%, while no or only little molybdenum was found in the upper half. In these experiments and in one other (in which the temperature was not kept constant) the molybdenum-containing part of the tin dioxide bed often showed a slight discoloration. This discoloration showed up after the material had been kept at room temperature for varying lengths of time.

From the data just mentioned we calculated the diffusion coefficient at 500°C of $MoO_2(OH)_2$ (in a gas of 1 atm pressure, substantially water vapor). In making these calculations, we assumed that a sharp molybdenum front, behind which the molybdenum content is 0.245%, moves through the bed, and employed Eq. (1). We further used reasonable values for porosity and labyrinth factors (*17*). The values found were 0.39, 0.40, 0.49, 0.38, and 0.35 cm^2/sec, the average being 0.40 cm^2/sec.

Desorption of $MoO_2(OH)_2$. To a bed of 4 g of SnO_2-A, which had been loaded with $MoO_2(OH)_2$ at 475°C, we supplied 35 nl/hr of $MoO_2(OH)_2$-free water vapor together with air, likewise at 475°C. The desorbed molybdenum was collected over several successive periods of suited duration and the quantities collected were determined. Molybdenum still present in the SnO_2 bed at the end of the test (i.e., after 20 hr) was also determined. The molybdenum concentration in the outflowing gas had decreased to 2% of the original concentration (which was only slightly greater than half the value following from Fig. 2), while the overall molybdenum content of the SnO_2 was 9% of the original one. Unfortunately, the molybdenum balance did not fit: the sum of the collected quantities of molybdenum was three quarters of the amount that had disappeared from the SnO_2 bed.

From a graph in which the molybdenum concentration in the gas phase was plotted against the amount of water vapor passed through, we derived the adsorption isotherm of $MoO_2(OH)_2$ at 475°C. (That $MoO_2(OH)_2$ is adsorbed to the SnO_2 is demonstrated in the Discussion section.) In making this derivation we assumed that adsorption equilibrium existed in the SnO_2 bed and that the original amount of molybdenum in the SnO_2 equaled the remainder left at the end of the experiment plus the total amount of the collected molybdenum. The adsorption isotherm found could very well be represented by an equation of the type $q = ac^n$ (Freundlich isotherm) in which q is the number of moles of $MoO_2(OH)_2$ or MoO_3) adsorbed per m^2, c is the number of moles of $MoO_2(OH)_2$ per mole of H_2O present in the gas phase, and a and n denote constants ($n < 1$). A Langmuir isotherm did not satisfy.

We also supplied a flow of $MoO_2(OH)_2$-free water vapor (70 nl/hr) to a bed of 10 g of preparation I at 450°C and took samples from the top, middle, and bottom of the bed after 41 hr. The molybdenum contents were 1%, 5%, and 18% of that of preparation I.

TABLE 1

OXIDATION OF PROPYLENE ON SnO_2, MoO_3, AND COMBINATIONS OF THESE OXIDES

Molar ratio of the amounts of propylene, air, and water vapor, 1:10:5. Propylene feed rate: 135 mmoles/hr, unless otherwise indicated. With regard to specific surface area and quantity, a catalyst containing, in addition to SnO_2, an MoO_3, preparation is considered to consist exclusively of SnO_2.

Test nr.	Catalyst			Temperature of the heating medium[10]	Reaction rate of propylene	Selectivities (%)							Mole % HCOOH in C_1[11]	Mole % CO in C_1[11]
	Type	Specific surface area (m^2/g)	Quantity[9] (g)	(°C)	($\frac{mmole}{h\ m^2}$)	Total breakdown	Acet-aldehyde	Acetone	Acrolein	Acetic acid	Acrylic acid	Maleic acid		
1[1]	MoO_3-A	0.7	1.7 (a)	497	0.06	24	10	5	50	7	1.5	2	10[12]	50
2[2]	MoO_3-B	1.7	10 (b)	497	0.25	69	0.5	0.2	20	2	6	2	3[12]	55
3[2]	MoO_3-B	1.7	10 (b)	497	0.06	44	1.5	0.5	45	4	4	1	3[12]	50
4[2][3]	MoO_3-B	1.7	10 (b)	497	0.08	57	0.5	0	40	0.5	1	1	1[12]	53
5	MoO_3-C	1.0	6 (c)	372	0.03	28	10	30	25	5	1.5	1	1	61
6	MoO_3-C	1.0	6 (c)	496	0.13	0	55	10	30	4	1.5	0	0	73
7	SnO_2-A	2.9	3 (d)	354	0.10	35	5	7	45	- - - - 3	- - - -	- - - -	-	36
8	SnO_2-A	2.9	3 (e)	372	0.12	58	6	7	20	- - - - 9	- - - -	- - - -	-	43
9	SnO_2-A	2.9	3 (e)	372	0.11	50	6	8	25	8	3	0	0.3	35
10	SnO_2-A[5]	2.9	5 (f)	372	0.16	58	3	3	30	- - - - 6	- - - -	- - - -	-	33
11[4]	SnO_2-A	2.9	15.5 (g)	373	0.14	74	0	25?	0?	1	0.3	0	0	36
12	SnO_2-B	25	2 (h)	297	0.003	22	<15	10	40	- - - ·13	- - - -	- - - -	-	43
13	SnO_2-B	25	2 (h)	349*	0.07	68	4	3	20	4	0.7	0	0.1	43
14	SnO_2-B	25	2 (i)	349*	0.07	68	3	4	20	4	0.8	0	0.1	42
15[4]	SnO_2-C	2.9	9 (j)	372	0.08	65	0	10	20	4	1.2	0	0	24
16	I	3.0	5 (k)	342	0.40	10	3	30	2.5	49	1.5	4	4	68
17	I	3.0	5 (k)	371*	0.81	31	2	8	8	44	3	4	0.5	51
18	I	3.0	5 (l)	373*	1.14	16	2	17	10	49	0.3	6	2	69
19[3]	I	3.0	5 (k)	373*	0.47	39	2	4	17	18	6	14	0.4	83
20	II	25[7]	1 (m)	272*	0.27	19	5	47	< 0.2	24	0.6	4	4	46
21	SnO_2-A + MoO_3 (cryst.)[6]	2.9	5 (n)	348	0.48	7	4	43	6	37	1	2	3	70
22	SnO_2-A + MoO_3 (cryst.)	2.9	5 (n)	372	0.63	14	5	14	13	49	2	3	1	79
23	SnO_2-A + MoO_3 (cryst.)	2.9	5 (n)	399*	0.83	22	2.5	6	13	49	5	2.5	0.3	79
24	SnO_2-A + MoO_3-C[6]	2.9	5 (o)	372	0.51	14	5	19	11	45	3	3	1.5	72
25	SnO_2-C + MoO_3 (cryst.)[6]	2.9	5 (p)	372	0.30	17	4	15	15	42	4	2.5	1.5	73
26	SnO_2-C + MoO_3 (cryst.)	2.9	5 (p)	396	0.45	16	4	16	19	38	5	1.5	1	74
27[3]	SnO_2-C + MoO_3 (cryst.)	2.9	5 (p)	372	0.25	48	3	3	26	8	3	9	1	60
28	I-des	3.9[8]	5.8 (q)	372	0.27	24	3	8	17	36	7	5	0.6	57
29	I-des	3.9[8]	5.8 (q)	397*	0.57	19	3	6	38	22	7	5	0.4	60

[1] Propylene feed rate: 9 mmoles/hr.

[2] Propylene feed rate: 18 mmoles/hr.

[3] No supply of water vapor.

[4] Collecting the carbonyl compounds in the wash bottles was done for only 15 min.

[5] Previously, a mixture of air (60 nl/hr) and water vapor (80 nl/hr) was passed through at 435°C for 16 hr.

[6] Weight ratio $MoO_3:SnO_2 = 1:2$. Previously, a mixture of air (5 nl/hr) and water vapor (3 nl/hr) was passed through at 475°C for one night.

[7] This is the value for SnO_2-B.

[8] Determined for the catalyst charge in Nos. 28 and 29 after completion of the tests.

[9] Equal letters in brackets behind the numbers in this column denote that the same charge was used.

[10] An asterisk denotes that the temperature rise caused by the heat of reaction was 10°C or more. In tests Nos. 18 and 20 the rise was as high as 24° and 16°C, respectively.

[11] C_1 means CO, CO_2, and HCOOH together.

[12] In tests Nos. 1–4, the amount of acid, determined by direct titration, was much smaller than the sum of the separately determined quantities. The deficit was approximately equal to the amount of formic acid. It may be supposed that formic acid is produced in bonded form, and is released during the concentration in alkaline medium before the analysis.

The material left after sampling will be referred to as I-des.

When dry air is passed through loaded tin dioxide, no desorption takes place. This appeared from a separate experiment.

Catalytic experiments. The experimental conditions and results are given in Table 1. Additional information is given below.

Experiments on the oxidation of propylene were done with MoO_3, SnO_2, and combinations of MoO_3 and SnO_2. These combinations were SnO_2 covered with molybdenum oxide (I, II, and I-des; see previous paragraphs), and mixtures of SnO_2 pellets with crystalline MoO_3 or pelleted MoO_3-C. Before the tests, a small flow of water vapor (3 nl/hr of water vapor with 5 nl/hr of air) was passed through the latter mixtures for one night at 475°C.

The gas flow rate was 48 nl/hr, except in the experiments with MoO_3-A and MoO_3-B, where it had to be kept low to avoid an unduly large pressure drop.

The degree of propylene conversion was normally low: less than 5% in the experiments with only MoO_3 and only SnO_2 (except in the experiments 2, 3, and 4 with MoO_3), and less than 10% in those with combinations of SnO_2 and MoO_3 (except in expt. 18). Hence, the reaction rate of propylene, i.e., the number of millimoles of propylene reacted per hour and per m^2 of catalyst surface area, is a suitable measure of the catalyst activity (in case the catalyst is a mixture of MoO_3 and SnO_2, the term catalyst surface area should be taken to denote the SnO_2 surface area). The reaction rate was calculated from the quantities of the various reaction products. In doing so, we reasoned that

(a) 1 molecule of acetone, acrolein, or acrylic acid comes from 1 molecule of propylene;
(b) 1 molecule of acetic acid or acetaldehyde plus 1 molecule of CO, CO_2 or HCOOH come from 1 molecule of propylene;
(c) 1 molecule of maleic acid plus 2 molecules of CO, CO_2 or HCOOH come from 2 molecules of propylene;
(d) in the case of total breakdown 3 molecules of CO, CO_2 or HCOOH come from 1 molecule of propylene.

The selectivity is defined as the percentage of the reacted propylene converted into a given product. On the basis of blank runs some minor corrections have been made in the results of the MoO_3 tests and one test with SnO_2 (No. 12).

No allowance has been made for formaldehyde (which may have been formed in slight amounts).

DISCUSSION

As appears from Fig. 2, there is no complete agreement between the results of our work on the volatility of MoO_3 in the presence of water vapor and those of Glemser and von Haeseler. The slope of the line drawn along our points is much weaker than that of the line along the points found by the above authors. The difference in slope suggests that there is a difference of +4 kcal/mole between the reaction enthalpies at 650° and 450°C. This would seem very unlikely; judged from specific heat values, the actual difference is —1 to —2 kcal/mole. For the rest, the points determined by us at 450°C, i.e., in the middle of the temperature range considered, deviate only slightly from the extension of the line representing Glemser and von Haeseler's data. The cause of the discrepancy between the inclinations is not clear to us.

Below 500°C the saturation concentration of $MoO_2(OH)_2$ is very low. Nevertheless, a flow of 50 nl/hr of water vapor at 450°C can entrain 40 mg of Mo (calculated as metal) in 24 hr.

It was found that if a gas flow saturated with $MoO_2(OH)_2$ is passed through an SnO_2 bed, the $MoO_2(OH)_2$ is adsorbed by the SnO_2 to a given limit. In SnO_2-A (2.9 m^2/g) this limit appeared to be at approx. 0.24 wt% of Mo; in SnO_2-B (25 m^2/g) at 1.6 wt% of Mo. So, the Mo percentage is approximately proportional to the specific surface area of SnO_2. Calculating the surface area corresponding to one Mo atom, we found 20 Å² on SnO_2-A and 25 Å² on SnO_2-B. These figures are of the same order as the areas per tin atom in various planes of the tin dioxide lattice:

(1,1,1) plane	31.0 Å^2
(1,1,0) plane	10.7 Å^2
(1,0,1) or (0,1,1) plane	13.5 Å^2
(1,0,0) or (0,1,0) plane	15.1 Å^2

It can be concluded therefore that the $MoO_2(OH)_2$ molecules are bound as a more or less continuous layer of $MoO_2(OH)_2$ units (or, in case water is released, of MoO_3 units) to the SnO_2 crystal faces (which may differ in $MoO_2(OH)_2$-binding capacity).

That nothing else happens but this coverage with molybdenum appears from the fact that X-ray diffraction diagrams and electron micrographs did not reveal any difference between loaded and unloaded SnO_2-A and SnO_2-B.

The sorption of $MoO_2(OH)_2$ to the SnO_2 surface is confirmed by the results of the diffusion experiments. The highest molybdenum content achieved equaled that reached in the experiments with an $MoO_2(OH)_2$-containing gas flow; the value found for the diffusion coefficient of $MoO_2(OH)_2$ is quite reasonable.

The two desorption experiments show that the molybdenum oxide bound to the SnO_2 surface can for the greater part be desorbed [no doubt as $MoO_2(OH)_2$] by feeding a flow of $MoO_2(OH)_2$-free water vapor to a bed of SnO_2 covered with molybdenum oxide. The variation of the $MoO_2(OH)_2$ concentration in the issuing gas with time (first experiment), as well as the variation in molybdenum content through the bed after the treatment with water vapor (second experiment), indicate that the adsorption isotherm is convex ($d^2q/dc^2 < 0$). The fact that, unlike a Langmuir isotherm (dq/dc tends towards an upper boundary value with decreasing q), a Freundlich isotherm (dq/dc increases without limitation with decreasing q) is in good agreement with the data obtained from the first experiment, suggests that a portion of the molybdenum is bonded rather strongly.

Some of the combinations of SnO_2 and MoO_3 used in the catalytic experiments consisted of SnO_2 treated with an $MoO_2(OH)_2$-carrying gas flow (preparations I and II), the others being mixtures of granular SnO_2 with crystalline or granular MoO_3. Before the tests a weak flow of water vapor was passed through these mixtures for one night at 475°C; so, there was sufficient opportunity for the transport of $MoO_2(OH)_2$—by convection and diffusion—to the SnO_2 surface.

As can be seen in Table 1, MoO_3, SnO_2, and SnO_2 combined with MoO_3, differ strongly as regards their catalytic behavior towards the oxidation of propylene in the presence of water vapor. This manifests itself in the first place in the reaction rates, the orders of magnitude of which are as follows: SnO_2, 0.1 mmole of propylene per hr and per m^2 at 370°C; MoO_3, 0.1 mmole/hr m^2 at a much higher temperature, i.e., at 500°C; SnO_2/MoO_3, 0.5 mmole/hr m^2 at 370°C.

Secondly, there is large difference between MoO_3 and SnO_2, on the one hand, and SnO_2/MoO_3, on the other, as regards the distribution of products obtained from the oxidation of propylene. With SnO_2 and MoO_3 half or more of the propylene is in most cases completely broken down and acrolein is formed as the main organic product. (MoO_3-C seems to be an exception.) With combinations of SnO_2 and MoO_3, however, only a relatively small part of the reacting propylene is broken down (approx. 15%) and acetic acid and acetone collectively constitute a large proportion of the reaction products.

Before the mixtures of SnO_2-A and SnO_2-C with crystalline MoO_3 or with MoO_3-C were treated with water vapor, we determined the rate of acid formation during the passage of the customary reaction mixture at 372°C. The rates (expressed as percent of the rate after the treatment with water vapor) are given below:

SnO_2-A + MoO_3 (cryst.)	Average over the first 15 min, 5% After 4 hr, 30%

SnO_2-A + MoO_3-C	Average over the first 15 min, 15% After 3 hr, 35%
SnO_2-C + MoO_3 (cryst.)	Average over the first 30 min, 55% Average over the second 30 min, 70%

This shows that the acid production was smaller, if not much smaller, than after the treatment with water vapor, and increased with time. It can be concluded, therefore, that the mere presence of MoO_3 crystals, or of MoO_3 with a surface area of 1 m^2/g, beside SnO_2, does not suffice; the presence of molybdenum on the SnO_2 surface is an essential requirement. The transport of molybdenum to the SnO_2 surface started already during the passage of the reaction mixture through the bed (not treated with water vapor) at 370°C because the reaction mixture contained water vapor. A slight amount of molybdenum already has a considerable effect; for, if the SnO_2 is first covered with molybdenum and then largely freed of it (I-des), the activity is still appreciable, as appears from the last two tests in Table 1. [It should be pointed out, that in the last test (at 397°C) the collective yield of acrolein and acrylic acid was remarkably high, viz. 45%.]

What has been said above can be summarized as follows. *SnO_2 is capable of sorbing $MoO_2(OH)_2$ to its surface (possibly, with simultaneous release of H_2O); the sorption of molybdenum strongly increases the catalytic activity of this surface with respect to the oxidation of propylene in the presence of water vapor, and causes the oxidation to go mainly to acetic acid and acetone.*

This is a case of a catalytic activity that is not due to a bulk compound, but must be ascribed to a surface compound of two oxides. We are inclined to believe that the surface compound of SnO_2 and MoO_3 (in which also OH groups may be involved) has a heteropolyacid character; an ammonium molybdostannate is mentioned already in the older literature (*18*).

As long as some 20 years ago, Russell and Stokes (*19*) dealt with a catalyst which, like ours, owes its activity to the presence of molybdenum oxide on its surface. These investigators used Al_2O_3, impregnated with an ammonium molybdate solution and subsequently heated, for the dehydrocyclization of *n*-heptane. The activity of this catalyst proved to be maximum when the amount of molybdenum oxide was large enough for forming a monolayer. They ascribed the distribution of the molybdenum on the surface to the volatility of the MoO_3 itself, but noted the favorable influence of water.

Some additional conclusions following from the catalytic experiments are given below.

(1) In two experiments (Nos. 19 and 27) with the combination SnO_2/MoO_3, no water vapor was supplied; as a result, the partial pressures of propylene and oxygen rose by a factor of 1.5. In these cases air had previously been passed through the catalyst bed for one night at 403° and 446°C, respectively, to remove surface hydroxyl groups in the form of water. The omission of water proved to lower the reaction rate of the propylene, notwithstanding the increase in the partial pressures of propylene and oxygen. The selectivities also changed: relatively, there was more total breakdown and formation of more acrolein and maleic acid, but of much less acetic acid and acetone, than in the presence of water vapor.

(2) In the application of SnO_2/MoO_3 catalysts, low temperatures are conducive to the formation of acetone, but have an adverse effect on the formation of acrolein. This clearly appears from experiment No. 20, which was carried out at a particularly low temperature (272°C).

(3) The coverage of the SnO_2 surface with MoO_3, although lowering the selectivity for the acrolein formation, considerably increases the absolute production of acrolein.

(4) Whereas the reactions on SnO_2 alone yield more CO_2 than CO, application of an SnO_2/MoO_3 catalyst gives more, often much more, CO than CO_2 (test No. 20 is an exception).

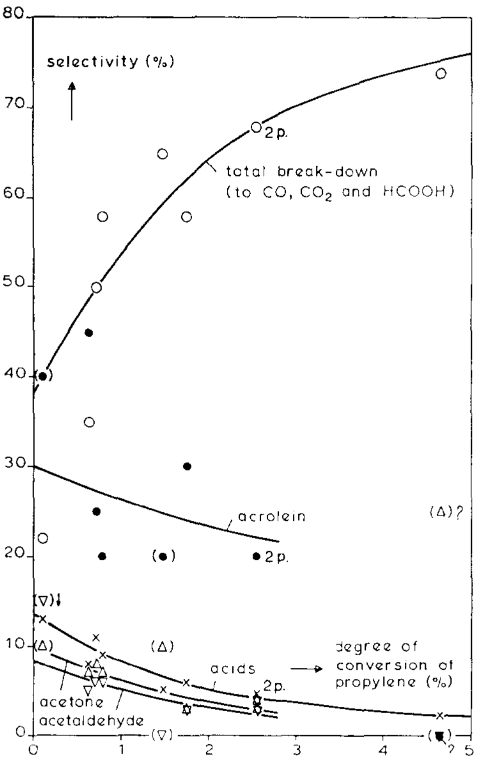

FIG. 3. Selectivities versus degree of conversion of propylene (SnO_2, tests Nos. 7–15): ○, total breakdown (to CO, CO_2, and HCOOH); ●, acrolein; ×, acids (acetic, acrylic and maleic); △, acetone; ▽, acetaldehyde.

(5) Figure 3, which relates to experiments with SnO_2, shows a plot of the selectivities versus the degree of propylene conversion. It is seen that the percentage of total breakdown increases with the degree of conversion: at 5% conversion it is already higher than 70%. As regards the formation of acid, acetone, and acetaldehyde, the selectivity decreases with increasing degree of conversion. It is not clear whether this also holds for acrolein. The trend of the selectivities suggests that SnO_2, in principle, has some capacity to oxidize propylene to acetone, acetic acid, and acetaldehyde, which compounds, however, are readily broken down on this oxide.

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