

TO THE OXIDATION OF PROPYLENE AND ACROLEINE ON BISMUTH-MOLYBDENUM CATALYST

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Small amounts of propylene and acroleine were oxidized on Bi-Mo-O catalyst in a static apparatus at low pressures. Composition of the gaseous phase was continuously followed by means of mass spectrometry. The effect of the catalyst in oxidized and partially reduced state was found to be different, similarly to the earlier studied selective oxidation of methanol on MoO₃. The effect of temperature on the composition of reaction products was also established.

Mixed bismuth-molybdenum oxide catalyst is being currently used in selective oxidation of propylene to acroleine. Most of the authors¹ concerned with the mechanism of this reaction agree in that it is a "redox" type of reaction. Oxidation takes place under consumption of catalyst oxygen which, in turn, is compensated from the gaseous phase. In his recent extensive paper, Peacock²⁻⁵ presumes that the selective oxidation of propylene and acroleine on Bi-Mo-O catalyst is effected by Mo⁶⁺ ion whose valence is stabilized at higher temperatures by the bismuth ion.

We were led to a similar conclusion as to the role of Mo⁶⁺ ion in the selective oxidation of methanol to formaldehyde when studying this reaction on a mixed Fe-Mo-O catalyst and on its components in oxidized and reduced state^{6,7}. For this reason we were interested in the study of the oxidation of propylene and acroleine on Bi-Mo-O catalyst in a similar manner, as it was described in the preceding paper⁶ dealing with methanol oxidation.

EXPERIMENTAL

The experiments were carried out on a technical Bi-Mo-O catalyst supported by silica gel; atomic ratio Bi : Mo was about 1, surface area 93 m²/g. The sample (0.1 g) was always heated *in vacuo* for 18 h at 500°C. Final pressure values were of the order 10⁻⁵ Torr. During this treatment the originally yellowish-green sample gradually lost water, carbon dioxide and carbon monoxide in amounts, corresponding to the combustion of one dose of propylene (*i.e.* roughly to the consumption of 40 μmol of the catalyst oxygen). The sample treated in this way was grey and in further measurements was referred to as "reduced" one. The reduction evidently proceeded under the participation of residual organic substances adsorbed on the catalyst surface during its production. Since the further behaviour of the catalyst was influenced by the above described reduction in the same way as by the reduction of propylene, we employed this procedure for the sake of simplification of the experiments. The "reduced" sample, oxidized by 20 Torr of oxygen

for 2 h at 500°C, served as "oxidized" catalyst. After a similar oxygen treatment of the mixed Bi-Mo-O catalyst, Mo=O vibrations corresponding to a bond in MoO₃ were found by infrared spectroscopy⁸. Samples were sealed off *in vacuo*, connected to a reservoir (volume 500 cm³, vapour pressure mostly 0.25 Torr) containing propylene or acroleine and directly joined to the leak of a mass spectrometer (MCh 1302, production USSR). Propylene, taken from a pressure flask and acroleine (p.a., Lachema) were frozen several times with subsequent evacuation. Oxygen was prepared by decomposition of KMnO₄. The amount of admixtures, determined mass spectrometrically up to molecular masses 80, did not exceed 1%. More detailed description of the measurement is presented in preceding publications^{6,7}.

RESULTS

Oxidation of Propylene and Acroleine at 500°C

Time course of propylene oxidation on both "oxidized" and "reduced" catalysts in the absence of oxygen in the gaseous phase is shown in Fig. 1a,b. The decrease of the pressure of propylene is slower on the "reduced" sample in comparison with

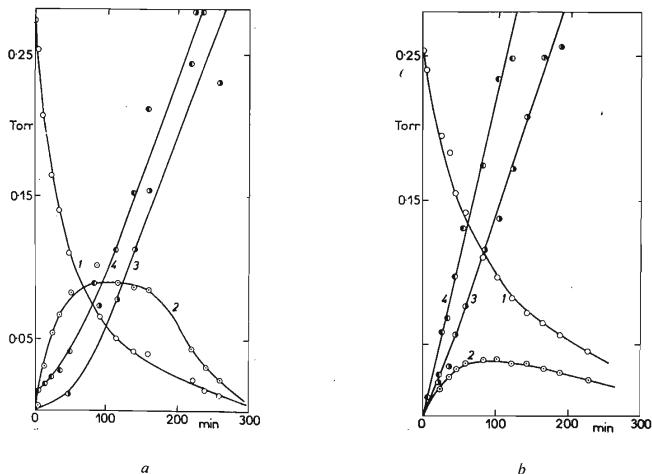


FIG. 1
Time Course of the Oxidation of Propylene on *a* "Oxidized" and *b* "Reduced" Bi-Mo-O Catalyst at 500°C

1 Propylene, 2 acroleine, 3 CO, 4 CO₂.

the "oxidized" one, the maximum of acroleine is lower and carbon dioxide and carbon monoxide are produced from the start of the reaction, showing no induction period. Further experiments were performed with oxygen-propylene mixtures with 1 : 1 and 1 : 2 ratio. The characteristic shape of the curves did not change, only the amount of the carbon dioxide formed was increased at the expense of carbon monoxide.

Oxidation of acroleine on both "oxidized" and "reduced" catalysts is given in Fig. 2a,b. The decrease of acroleine pressure is, contrary to propylene oxidation, faster with the "reduced" sample than with the "oxidized" one. The slower course of acroleine oxidation on the oxidized catalyst is in accordance with the results of Peacock⁵.

Whereas on the "oxidized" sample the decrease of the pressure of propylene and acroleine (the latter to a smaller extent) in the reaction course is greater than the increase in the pressure of the gaseous products, both values are practically equal with the reduced sample. The formation of water vapour could not be followed quantitatively, owing to the fact that water was partially sorbed on the carrier and partially because the analysis was distorted by excess water in the mass spectrometer background. In spite of this it can be stated that greater amounts of water were released on "reduced" samples than on "oxidized" samples.

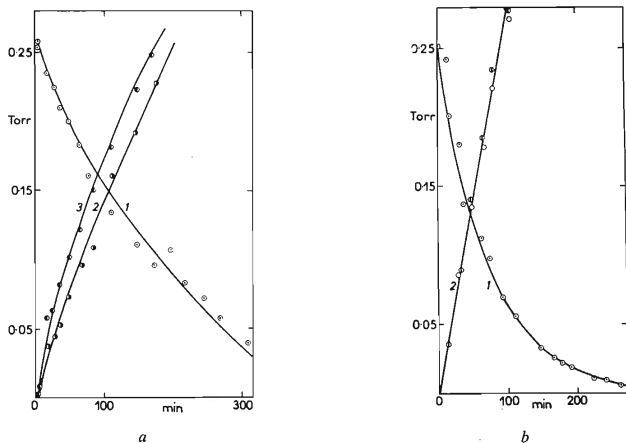


FIG. 2

Oxidation of Acroleine on a "Oxidized" and b "Reduced" Bi-Mo-O Catalyst at 500°C
1 Acroleine, 2 CO, 3 CO₂.

Oxidation of Propylene and Acroleine at 400°C and at Lower Temperatures

Oxidation of propylene and acroleine at 400°C shows a different course than that at 500°C. Propylene oxidation on an oxidized sample is very slow (Fig. 3a) with the maximum of acroleine pressure not exceeding 0.02 Torr even after 25 h, although the pressure of carbon dioxide reaches the value of 0.1 Torr. Thus, the composition of the gaseous phase indicates that the reaction is less selective at 400°C than it is at 500°C. Oxidation of propylene on a "reduced" sample (Fig. 3b) is essentially faster at 400°C than with an oxidized sample at the same temperature (differently from 500°C). The maximum of acroleine pressure is, however, practically the same as with the oxidized sample. Oxidation of acroleine both on oxidized and reduced samples is substantially faster than that of propylene (Fig. 4a,b). The decrease of propylene and acroleine pressure during the reaction at 400°C is greater than the pressure increase of the products, this difference being higher with the "oxidized" sample than the "reduced" one and simultaneously higher with propylene than with acroleine.

A few experiments were also performed at 170°C. The reaction was very slow and only traces of acroleine appeared in the gaseous phase together with small

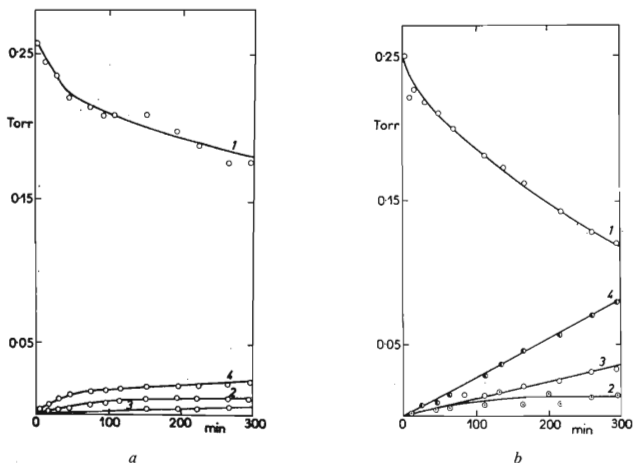


FIG. 3

Oxidation of Propylene on a "Oxidized" and b "Reduced" Bi-Mo-O Catalyst at 400°C
 1 Propylene, 2 acroleine, 3 CO, 4 CO₂.

amounts of carbon dioxide. With increasing temperature only carbon dioxide was produced. In the oxidation of propylene at 300°C on the "oxidized" sample the reaction was very slow too, and after a steep increase of temperature to 500°C the pressure of the acroleine formed was the same as it was at 500°C on the "reduced" sample, whereas at the same time the pressures of carbon dioxide and carbon monoxide exceeded by far the pressure of acroleine.

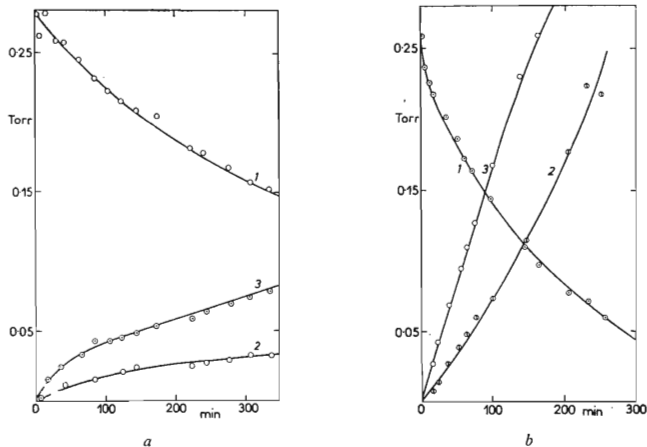


FIG. 4

Oxidation of Acroleine on *a* "Oxidized" and *b* "Reduced" Bi-Mo-O Catalyst at 400°C
1 Acroleine, 2 CO, 3 CO₂.

DISCUSSION

Identical courses of propylene oxidation at 500°C in the absence of oxygen and with a one- to two-fold excess of oxygen suggest a redox mechanism of this reaction, as it was after all supposed in most of the hitherto published papers¹. The formation of carbon dioxide and monoxide, taking place on the oxidized form of catalyst is, at least partly, a consecutive reaction, as can be seen from the induction period of their release (Fig. 1).

Although it is likely again a "redox" reaction that proceeds on a partly reduced catalyst surface (the reaction proceeds in the same way even in the absence of oxygen

in the gaseous phase) the way of interaction of both propylene and acroleine seems to be different. Probably, a deeper oxidation of propylene takes place already at the start of the reaction, parallel to the formation of acroleine. Peacock⁵ assumes that the oxidation of acroleine on partly reduced surface of the catalyst is slower than the oxidation of propylene, and for that reason acroleine is obtained during the oxidation of propylene. Our results disprove this assumption.

We have found the same decrease in selectivity with partial reduction of the surface in the oxidation of methanol to formaldehyde on molybdenum oxide which forms the substantial part of the mixed Fe-Mo-O catalyst⁶. No oxidation of formaldehyde was found to take place on the non-reduced MoO₃ surface, whereas with the partly reduced sample both methanol and formaldehyde were decomposed to CO and hydrogen and partly also oxidized to carbon dioxide. The formation of lower cation (probably Mo) valence in the reduced Bi-Mi-O catalyst also supports the deep oxidation of propylene and acroleine. Egashira and coworkers⁹ found by means of diffraction analysis in the reduction of Bi-Mo-O catalyst by propylene that reduction of Mo⁶⁺ to Mo⁴⁺ and of Bi³⁺ to metallic bismuth takes place during the reaction. According to Egashira reduction of molybdenum is connected with the formation of acroleine. Peacock⁵ obtained similar pathways for the oxidation of propylene on mixed Bi-Mo-O catalyst and pure MoO₃ oxide.

Non-stoichiometric conditions during propylene oxidation, particularly on an oxidized sample, may be explained by assuming a slow desorption of products, *i.e.* probably of acroleine. After sufficiently long time (20–25 h) the amounts of carbon dioxide and carbon monoxide correspond to the consumption of propylene. Very small amounts of high-molecular weight admixtures were also produced during the oxidation.

With decreasing temperature a change occurs in the oxidation products of propylene on Bi-Mo-O catalyst. Less acroleine is formed in favour of carbon dioxide. This experimental result may be explained in several ways; *e.g.* two of them are: 1. According to Peacock the stabilization effect of bismuth in preserving higher valence of molybdenum becomes effective only at higher temperatures. Peacock found that the ESR signal of Mo⁵⁺ ion in the oxidation of propylene is lower at higher temperatures. 2. According to Křivánek¹⁰ who found by calorimetric measurements that the reduction of the Bi-Mo-O catalyst surface by propylene occurs already at 170°C and that the amount of consumed oxygen from the catalyst corresponds to the amount of acroleine formed. The fact that acroleine could be determined only in traces in the gaseous phase is due, according to Křivánek, to immediate polymerisation of the formed acroleine.

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