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Contribution to the Study of Methanol Oxidation on MoO_3

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The oxidation of methanol on molybdenum trioxide (with its lattice oxygen only) was investigated. The composition of the gaseous phase analyzed by means of a mass spectrometer changed after the reduction of the oxygen surface layer. A change of the oxidation mechanism due to the lowering of the valency of Mo^{6+} to Mo^{4+} is suggested.

MoO_3 is contained in the Fe^{3+}–Mo^{6+}–O mixed catalysts which are widely used for the selective oxidation of methanol to formaldehyde (*1–8*). The mechanism of methanol oxidation on these mixed catalysts has not yet been quite explained; for that reason we have studied separately the behavior of both cations in the form of their oxides. The methanol oxidation on Fe_2O_3 will be dealt with in another publication.

Oxidizing methanol on MoO_3 in the presence of oxygen in the gaseous phase, Boreskov (*9*) found formaldehyde to be the main product of this reaction; the formation of carbon monoxide was explained as a result of a consecutive reaction. Boreskov found neither carbon dioxide nor hydrogen in the gaseous product; the latter experimental fact was explained by the nonexistence of a dehydrogenation step in the catalytic oxidation of methanol over several oxides, including MoO_3.

The composition of gaseous products of methanol oxidation (CH_2O, CO, and H_2O) is the same on molybdenum trioxide with oxygen in gaseous phase and on mixed Fe–Mo–O catalysts, the difference being in the rather low temperature of oxidation on Fe–Mo–O catalysts.

EXPERIMENTAL METHODS

The MoO_3 used was of analytical grade from Merck, its surface area being 2.6 m^2 (by adsorption of Ar at 78°K, where for the area of Ar molecule 16.6 A^2 was taken). Methanol used was the same as in Ref. (*6*), formaldehyde was obtained by evaporating solid paraformaldehyde of analytical grade from Lachema, carbon monoxide was prepared by decomposition of magnesium oxalate with freezing of sideproducts.

One g of MoO_3 was heat-treated *in vacuo* (10^{-5} Torr) for 15 hr at 400°C. Then the sample was joined with a reservoir of 500 cm^3 and the gaseous mixture (with a pressure about 0.5 Torr) was analyzed with a mass spectrometer MCH 1302 (USSR) directly linked to the reservoir with the sample. The changes of the composition of the gaseous mixture were followed continuously with time at constant temperature (generally $320 \pm 2°C$); in case of no changes observed the temperature was elevated up to 400°C.

The amount of methanol or another gas used in one dose was chosen in such a way that the number of gaseous molecules was approximatively the same as the number of oxygen atoms in the surface layer of MoO_3 (i.e., about 10^{19}). Therefore, we may suppose that the reaction proceeds—in a prevailing manner—in the surface of molybdenum trioxide. In order to show the differences in the behavior of the deeper layers of oxygen in solid MoO_3, the procedure was in some cases repeated after the evacuation of the sample.

RESULTS

The time-course of the methanol concentrations and of its oxidation products is plotted in Fig. 1a. After this experiment, MoO_3 was evacuated at the same temperature (320°C) for 1 hr and then was joined with another reservoir with methanol. The oxidation of this methanol sample is shown in Fig. 1b. A large difference in the character of concentration changes can be seen from these two plots. The rate of methanol oxidation does not substantially differ in both cases, being even a little larger in case b. The maximum of the formaldehyde concentration is, in case a, much higher and appears later than after the second dose of methanol (case b). The more complete oxidation (to CO and CO_2) proceeds in case b from the beginning of the methanol oxidation. Also the amount of liberated hydrogen in case b is much larger than in case a, where hydrogen started to appear after the maximum in formaldehyde concentration was attained.

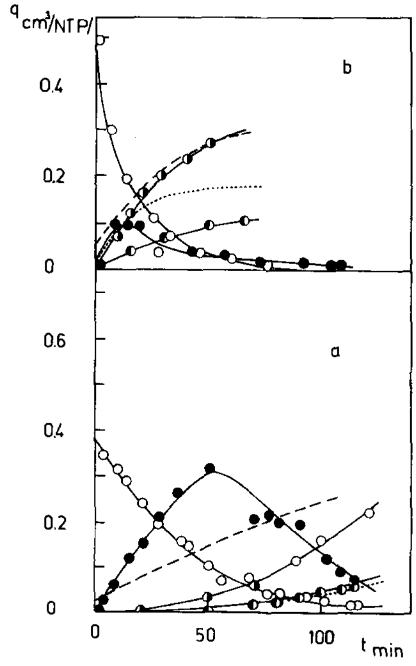


FIG. 1. The time-course of concentrations in the oxidation of methanol on molybdenum trioxide at 320°C: (a) the first dose of methanol; (b) the second dose of methanol after the evacuation of the sample. CH_3OH (○); CH_2O (●); CO (◑); CO_2 (◐); H_2O (---); and H_2 (....).

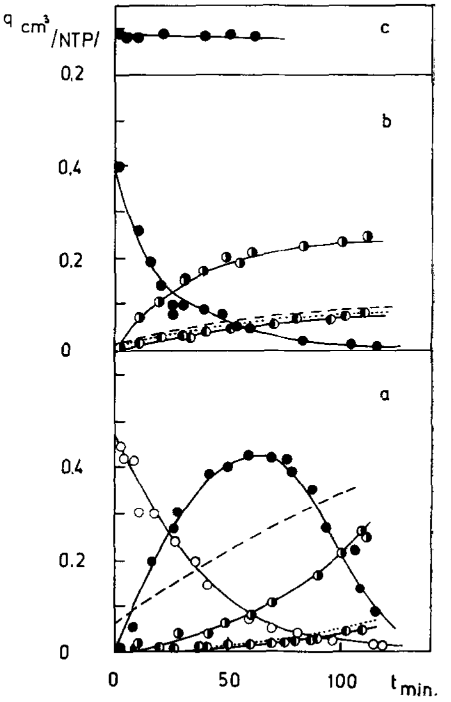


FIG. 2. The time-course of concentrations in the oxidation of formaldehyde and methanol at 320°C: (c) the first dose of formaldehyde; (a) the first dose of methanol; (b) the dose of formaldehyde after the evacuation of the sample. CH_3OH (○); CH_2O (●); CO (◑); CO_2(◐); H_2O (---); and H_2 (....).

With regard to these results it was interesting to follow the oxidation of formaldehyde on MoO_3 in the same way as the oxidation of methanol. The results of formaldehyde oxidations on MoO_3 are demonstrated in Fig. 2. In case c, formaldehyde was in contact with MoO_3 for 1 hr at 320° without any change in its composition; no oxidation proceeded when the temperature was elevated up to 400°C. Therefore, we have first oxidized methanol on another sample of MoO_3—the typical course of this oxidation is shown in Fig. 2a; then this sample was evacuated for 1 hr at 320°C and was joined to a new reservoir filled with formaldehyde. The time-course of formaldehyde concentration is plotted in Fig. 2b, its oxidation products being CO, CO_2, H_2O, and H_2.

The oxidation of carbon monoxide was followed in the same way. It proceeds neither on a fresh sample of MoO_3, nor on a sample previously reduced during the oxidation of methanol. The negative result with regard to the CO oxidation was the same when the temperature was elevated up to 400°C.

Discussion

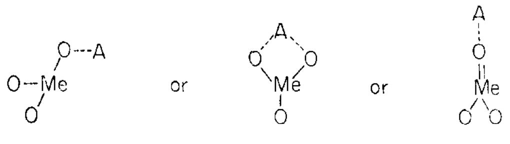
The results of the study of the interaction of CH_3OH, HCHO, and CO with MoO_3 at 320°C—without oxygen in the gaseous phase—can be summarized as follows: (a) MoO_3 oxidized CH_3OH to HCHO only under participation of a small part of its oxygen atoms, which is limited approximately to the surface oxygen. HCHO and CO were not oxidized on this unreduced MoO_3 at all. (b) A partly reduced MoO_3 was an agent for the deep oxidation of CH_3OH and HCHO, the products of oxidation being mainly CO, H_2, H_2O, and partly CO_2. CO was not oxidized at all.

The release of water into the gaseous phase is suggested to be proof for the participation of oxygen atoms from the solid phase in the oxidation reactions on MoO_3; together with the prevailing selective function of this catalyst in presence of oxygen in gaseous phase, this fact might be explained as a function of some "redox" mechanism. For this reason it might be useful to correlate the reactivity of lattice oxygen and the catalytic activity of MoO_3 as oxidation catalyst according to the ideas published already on the strength of the lattice oxygen bond (*10–13*). Recently, a parallelism has been found in oxidation catalysis between the catalytic selectivity and the differential increase of the enthalpy of oxygen release from the catalyst with an increasing degree of its reduction (*14*). Those catalysts, where the removal of oxygen from the surface is easy, possess high activity for deep oxidation. On the contrary, those catalysts, where the removal of more oxygen atoms from the solid at the same site requires more energy, act as selective catalysts.

When we apply this idea to the behavior of molybdenum trioxide in methanol oxidation, we are obliged to suppose that the remaining oxygen atoms are more active than those from the surface. Such an effect, which is not thermodynamically probable (*13*), could be found out by the method of oxygen exchange between gaseous labeled oxygen and oxygen atoms of MoO_3; this exchange, however, was measured by others (*15*) without similar effects. It is worth noting, that there are some other conditions between the experiments with the isotopic exchange of gaseous oxygen and the measurements of the oxygen pressure above the oxides, the main difference being in the substantially higher pressure of oxygen in the case of the exchange than that of the measurements of oxygen pressure. However, a simbatic relation for deep oxidation and an antibatic relation for selective oxidation has been found by Boreskov (*13*) between the catalytic activity on one side and the ability of oxygen exchange and oxygen release on the other side. Any direct relation among the degree of reduction of the oxide and the isotopic exchange has not been published; it seems, that the value of diffusion coefficient of lattice oxygen might be suitable for such a correlation.

The various functions of one oxidation catalyst in different oxidation reactions (deep, selective, or no catalytic action) cannot be explained only on the basis of differential increase of enthalpy of the oxygen removal from the catalyst too.

The idea about the prevailing role of the enthalpy of the release of lattice oxygen in deep and selective oxidation catalysis seems to be valid in the case when the oxidation of a substance A proceeds via the formation of surface complexes of the type, (a)

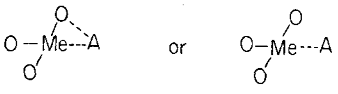


(a)

where A is in some manner bound to the

lattice oxygen O, Me being a cation of the oxide.

When A is bound to the surface via a complex (b) similar

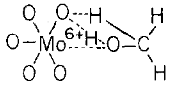


(b)

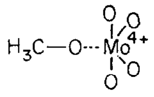
the function of oxygen release might be overlapped by the bonding Me---A. The existence and the strength of the Me---A bonding would probably be a complicated function of the degree of the catalyst reduction, the type and the valency of Me cation playing an important role.

The existence of various species of chemisorption of substance A in "redox" reactions seems therefore to be an explanation for the selective and deep oxidation functions of the catalyst, which is more probable than that based on mobility only.

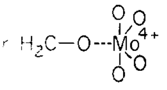
In our case—oxidation of methanol on MoO_3—the existence of a complex of type (b) may be used for the explanation of experimental data: e.g., CH_3OH might be bounded to Mo^{6+} by e.g., an alcoholate bonding:



which decomposes under formation of formaldehyde and water, one H atom from the methanol molecule being bond to a surface oxygen. On molybdenum of lower valency—probably Mo^{4+}—methanol and formaldehyde are decarbonylized and CO with H_2 appears in gaseous phase. Only a small part of bound



or



could for sterical reasons be oxidized to CO_2, the oxidation of H to H_2O being also sterically hindered.

Our results do not seem to be in agreement with the conclusions of Boreskov's paper: the formation of CO in methanol oxidation on MoO_3 is probably not a simple consecutive reaction, but is caused by the reduction of the MoO_3 surface (see a, b on Fig. 1). The absence of H_2 molecules in the gaseous phase is not necessarily the evidence for the nonexistence of the dehydrogenation step in oxidation; hydrogen atoms of methanol are probably bound with oxygen from the MoO_3 surface in case it has not yet been reduced. This phenomenon cannot be observed by measuring the oxidation of methanol in presence of oxygen in gaseous phase. In this case the oxidation probably proceeds only in the surface layer of MoO_3 which is immediately resaturated with oxygen.

It can be concluded that the selective oxidation of methanol on MoO_3 is joined with its unreduced surface. The function of the Fe^{3+} cation in mixed Fe–Mo–O catalyst may help (together with other functions) to maintain the higher value of molybdenum valency.

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