

Mn-Mo-O CATALYSTS FOR METHANOL OXIDATION.**II. OXIDATION OF METHANOL**Krasimir IVANOV^a, Penka LITCHEVA^a and Dimitar KLISSURSKI^b^a Department of Chemistry,

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The catalytic properties of MnMoO₄-based catalysts toward methanol oxidation are investigated. The effect of temperature, flow rate, and gas mixture composition on the catalytic activity is established. The highest activity and selectivity (comparable with those of industrial catalysts) of the samples obtained by precipitation in the presence of a small excess of MoO₃ was found. The oxidation of methanol on MnMoO₄-based catalyst is proposed to be a two-step process. The first step includes methanol interaction with Mo(VI) and reduction of Mo(VI) to Mo(V) (Mo(IV)). The second step consists in direct oxidation of the reduced molybdenum by oxygen from the alcohol-air mixture.

Modern production of formaldehyde is largely based on selective oxidation of methanol. Oxide catalysts such as Fe₂(MoO₄)₃-MoO₃ are used most often after promotion with various additives^{1,2}. The disadvantage of iron-molybdenum catalysts is their rapid deactivation as a result of the loss of MoO₃ and a partial reduction of the active Fe₂(MoO₄)₃ to the less active FeMoO₄. That is why new active and selective catalysts should be looked for. Catalysts based on the Mn-Mo-O system and containing the more stable MnMoO₄ seem to be promising in this respect.

Jírů et al.³ and Kolovertnov⁴ have established that pure MnMoO₄ is less active and selective than the molybdates of a series of di- and trivalent metals. Bliznakov and Klissurski^{5,6} have studied the catalytic properties of the MnO₂-MnO₃ system and determined the dependence of oxidation rate degree on methanol concentration in the gas mixture as well as on the MnO₂/MnO₃ ratio. It has been shown that the samples with the lowest MnO₂ content possess the highest selectivity during methanol oxidation. A high activity and selectivity of MnMoO₄ is also reported by Mann and Hahn⁷.

Our studies on MnO₂-MoO₃ catalysts prepared by calcination of a mixture of manganese nitrate and ammonium paramolybdate have shown the maximum activity

and selectivity for samples with a small excess of MoO_3 with respect to stoichiometric MnMoO_4 (ref.⁸). Samples with the same composition obtained by impregnation of MnMoO_4 with an ammonium paramolybdate solution have exhibited activities and selectivities close to those of industrial iron-molybdenum catalysts^{9,10}. These promising results were the reason for performing a more systematic study of this type of catalysts.

EXPERIMENTAL

The catalyst samples were prepared by precipitation as described in part I of the present paper (Method *A*). For comparison, data on samples obtained by calcination of a MnO_2 - MoO_3 mixture (Method *B*) and by impregnation of MnMoO_4 with a solution of ammonium paramolybdate (Method *C*) are also presented. The methods of preparation and some important properties of the catalysts under investigation are summarized in Table I.

The catalytic properties of the samples have been investigated in a flow apparatus at flow rates of 200 to 1 000 h^{-1} , methanol concentration in the alcohol-air mixture ranging from 1 – 7 vol.% and temperatures of 200 – 400 °C. In all cases the amount of the catalyst was 2 cm^3 and its particle size was 0.3 – 0.6 mm. The formaldehyde content in the reaction products was determined by the bisulfite method. The amounts of CO_2 , CO , H_2 , hydrocarbons and unreacted methanol were analysed by a gas-chromatograph.

TABLE I
Methods of preparation and main characteristics of catalysts

No.	Method ^a	Content	Mo/Mn ratio	Calcination °C/h	Surface area m^2/g
1	<i>A</i>	MnMoO_4	1.0	500/2	5.4
2	<i>B</i>	MnMoO_4	1.0	500/4	4.5
3	<i>A</i>	MnMoO_4 - MoO_3	1.1	450/4	5.8
4	<i>A</i>	MnMoO_4 - MoO_3	1.1	500/4	5.5
5	<i>A</i>	MnMoO_4 - MoO_3	1.1	550/4	5.1
6	<i>A</i>	MnMoO_4 - MoO_3	1.3	500/4	6.2
7	<i>C</i>	MnMoO_4 - MoO_3	1.1	550/4	3.5
8	<i>C</i>	MnMoO_4 - MoO_3	1.3	550/4	2.5
9	<i>B</i>	MnMoO_4 - MoO_3	1.1	550/4	3
10	<i>B</i>	MnMoO_4 - MoO_3	1.3	550/4	1.5

^a For designation see Part I.

RESULTS AND DISCUSSION

Effect of Temperature

The results presented in Table II show the activity and selectivity of the catalysts at 250 and 350 °C. X is the conversion of CH_3OH to CH_2O , CO , CO_2 , and total conversion in per cent, S is the selectivity of the oxidation to formaldehyde. The major oxidation product is formaldehyde, the catalyst selectivity being in all cases above 94%. However, there are large differences between the activities of the samples. The lowest activity is observed with the samples obtained by thermal dissociation of the salts, while the highest corresponds to precipitated samples. Figure 1 shows the temperature de-

TABLE II
Dependence of the rate of methanol oxidation to CH_2O , CO , CO_2 and the selectivity on the catalyst composition and method of preparation

No. ^a	Reaction temperature °C	Conversion X to				S^b
		CH_2O	CO	CO_2	total	
1	250	13.4	-	-	13.4	100.0
	350	67.5	2.0	-	69.5	97.1
2	250	3.9	-	-	3.9	100.0
	350	38.5	2.2	-	40.7	94.6
3	250	17.6	-	-	17.6	100.0
	350	63.9	2.0	2.1	68.0	94.0
4	250	20.6	-	-	20.6	100.0
	350	76.1	4.4	-	80.5	94.9
5	250	25.3	-	-	25.3	100.0
	350	79.3	2.2	2.2	83.7	94.7
6	250	38.9	-	-	38.9	100.0
	350	90.1	4.3	1.0	95.4	94.4
7	250	12.1	-	-	12.1	100.0
	350	83.5	1.2	-	84.7	98.6
8	250	14.3	-	-	14.3	100.0
	350	77.2	2.2	-	79.4	97.2
9	250	2.8	-	-	2.8	100.0
	350	38.3	1.8	-	40.1	95.5
10	250	3.1	-	-	3.1	100.0
	350	28.8	2.2	-	31.0	92.9

^a See Table I. ^b Selectivity to formaldehyde formation.

pendence of the activity and selectivity of sample 6 (Table II in Part I) which has the best catalytic properties.

At low temperatures, the oxidation rate is slow and the process takes place with 100% selectivity. The rise of temperature above 225 °C leads to a quick increase in the reaction rate, "enflamation" of the catalyst and a diffusion control of the process. To work in a kinetic region at 225 – 300 °C, very low methanol concentrations in the alcohol–air mixture (1.5 – 2 vol.%) should be used (Fig. 1). At temperatures above 300 °C, the oxidation rate depends on temperature, but very little, i.e. the process passes from kinetic- to diffusion-controlled region. The maximum conversion degree of methanol to formaldehyde under these conditions is found at temperatures of 325 – 350 °C. At the higher temperatures, the amount of formaldehyde drops due to its additional oxidation to CO. Formation of CO₂ begins at 325 °C, the amount of the product increasing slowly with temperature.

Figure 2 illustrates the temperature dependence of the oxidation rate of methanol on MnMoO₄ (sample 1) as well as on a sample containing MnMoO₄ and MoO₃ (Mo/Mn = 1.3, sample 6). The activation energies found for these and the remaining samples are given in Table III.

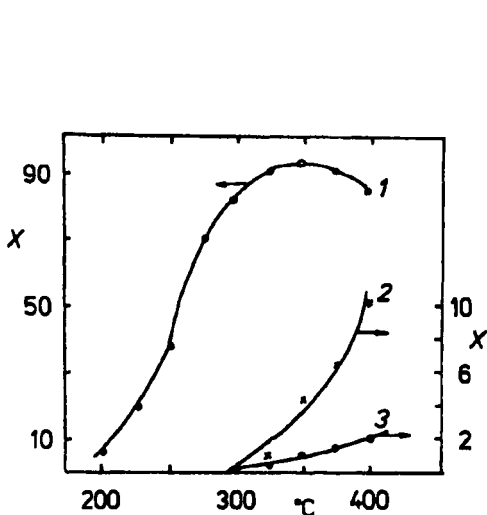


FIG. 1
Temperature dependence of the catalytic activity and selectivity of a MnMoO₄-MoO₃ catalyst with Mn/Mo at ratio of 1.33. 1 CH₂O, 2 CO, 3 CO₂. X (%) is conversion to the given product

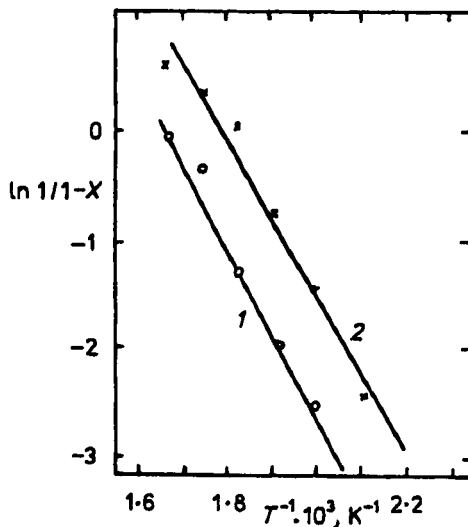


FIG. 2
Temperature dependence of the oxidation rate on 1 MnMoO₄ (sample 1) and 2 on a sample with Mo/Mn at ratio of 1.33 (sample 6). X is a methanol conversion to formaldehyde

Effect of the Concentrations of Oxygen and Methanol

Figure 3 shows the dependence of the process rate over $\text{MnMoO}_4\text{-MoO}_3$ (sample 6) on the methanol concentration at 225 °C. The data obtained indicate a linear dependence of the oxidation rate on the concentration of methanol in the alcohol-air mixture. Analogous correlations are found for the remaining catalyst samples. The first-order rate reaction with respect to methanol (n) is established in all cases (Table III). The investigations have shown that with oxygen concentrations above 5 vol.%, the process rate remains constant, i.e. the reaction order with respect to oxygen is equal to zero under these conditions.

Effect of Flow Rate

The effect of flow rate of the gas mixture on the rate of formation of the reaction products is shown in Fig. 4 for a temperature of 300 °C and methanol concentration of 4 vol.%. At this temperature, the rate of formation of the main product (formaldehyde) increases linearly with an increase of the flow rate, whereas the negligible amount of CO remains practically constant. The results obtained lead to an assumption that the oxidation of methanol on molybdates proceeds by a parallel mechanism at low temperatures, i.e. the reaction products are obtained by a direct oxidation of methanol. At high temperatures, successive processes are also observed, which results in an additional oxidation of some of the products obtained. This conclusion is also confirmed by

TABLE III
Dependence of activation energy E_a (kJ/mol) and of the reaction order n on catalyst composition and on method of catalyst preparation

No. ^a	Temperature interval, °C	Products	n	E_a
1	250 - 325	CH ₂ O	1.0	57.8
2	225 - 350	CH ₂ O, CO	1.0	66.8
3	250 - 325	CH ₂ O	1.0	54.3
4	200 - 300	CH ₂ O	1.0	50.6
5	200 - 300	CH ₂ O	1.0	63.2
6	200 - 300	CH ₂ O	1.0	48.4
7	250 - 325	CH ₂ O	1.0	78.9
8	225 - 325	CH ₂ O, CO	1.0	69.9
9	225 - 350	CH ₂ O, CO	1.0	81.4
10	225 - 350	CH ₂ O, CO	1.0	67.6

^a For numbering of the samples see Table I.

the temperature dependence presented in Fig. 1. On the basis of the data obtained it is difficult to draw an explicit conclusion on the way of formation of carbon dioxide due to its negligible amount.

Probable Mechanism of the Process

There is a large number of publications¹¹ dealing with the mechanism of methanol oxidation on $\text{Fe}_2(\text{MoO}_4)_3$ and on the molybdates of other trivalent metals. Methanol oxidation is usually assumed to be a three-step redox reaction process with participation of the oxygen from the crystal lattice of the catalyst. During the first step, methanol is oxidized by Mo(VI). During the second step, a redox process takes place in the crystal lattice between the reduced Mo(V) from an Fe(III). The last (third) step, consists of the oxidation of Fe(II) by oxygen from the gas mixture. The successive redox reactions can be presented by the following scheme:

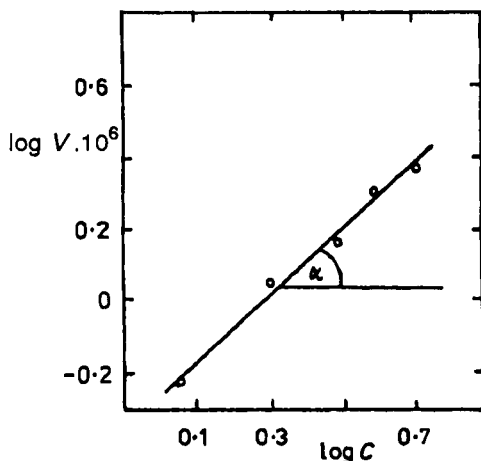
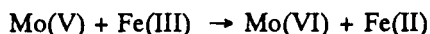
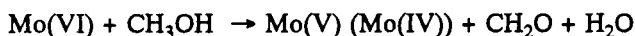


FIG. 3

Dependence of the rate of methanol oxidation (V , $\text{mol s}^{-1} \text{cm}^{-3}$) to formaldehyde on its concentration ($\log C$) in the alcohol-air mixture at 225 °C

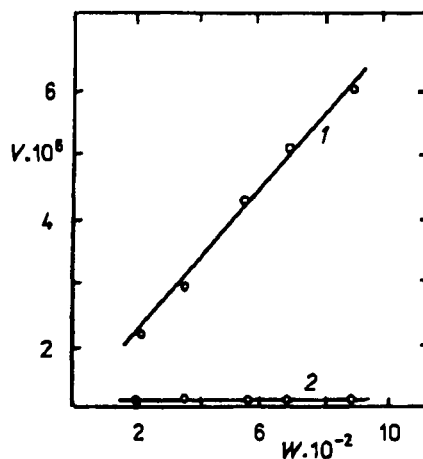
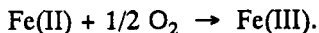
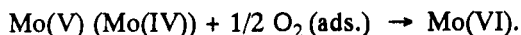


FIG. 4

Dependence of the rate of methanol oxidation (V , $\text{mol s}^{-1} \text{cm}^{-3}$) to CH_2O (1) and CO (2) at 300 °C on the flow rate W (h^{-1})



The two-center mechanism of methanol and oxygen interaction with the catalyst cannot be accepted in the case of $\text{MnMoO}_4\text{-MoO}_3$ catalysts because Mn(II) is in its lowest valency state and cannot oxidize the reduced Mo(V) or Mo(IV) . We suggest a two-step reaction between methanol and oxygen on the same catalyst center (as already stated by Trifiro et al.^{12,13} for hydrocarbon oxidation), i.e. the Mo reduced during the interaction with methanol is supposed to be oxidized directly by oxygen in the gas mixture. This process can be illustrated as follows:



In order to confirm the mechanism proposed, studies have been performed in the absence of oxygen. Figure 5 shows the results obtained after passing a mixture of $\text{CH}_3\text{OH-N}_2$ with a methanol concentration of 4 vol.% over MnMoO_4 at 350°C . Immediately after raising the temperature, the reaction products contain CH_2O , CO , and CO_2 . The amount of these products decreases with time and methane formation is established after several minutes. As evident from the plot, even after 100 min the gases leaving the apparatus contain small amounts of CH_2O , CO , and CO_2 . This is in agreement with the assumption about participation of the oxygen from the crystal lattice in the oxidation process. X-Ray studies have shown no change in the phase composition of the catalyst. However, changes in the catalyst surface are obvious: several minutes suffice for the

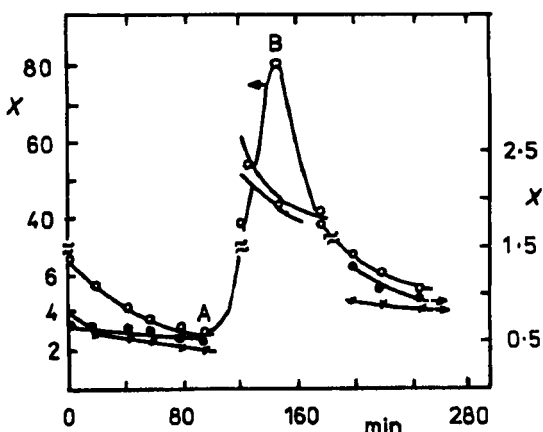


FIG. 5
Dependence of methanol conversion X , % to CH_2O (O), CO (●), CO_2 (x) on the time of passing a nitrogen-methanol mixture over MnMoO_4 at 350°C . At point A air was finely inserted, B air supply was stopped

white colour of the surface to become grey, with tendency to the increasing intensity with time. The introduction of air into the apparatus leads in several minutes to a complete regeneration of the initial catalyst properties and colour.

An analogous experiment was performed with a gas mixture containing formaldehyde and nitrogen at the same temperature. The gases coming out of the apparatus contained CO and CO₂, while the catalyst colour changed as described above. This result confirms that at temperatures above 300 °C the additional oxidation of the formaldehyde obtained is possible.

It was also attempted to elucidate the origin of the CO₂ formed, although in small amounts, at a high temperature. When a mixture of air and CO is passed over MnMoO₄ at 350 °C, the reaction products do not obtain CO₂. An analogous results was also reported by Trifiro et al.¹³. Passing the same mixture over a reduced catalyst leads to the appearance of a considerable amount of CO₂. After regeneration of the catalyst surface, CO₂ is absent in the outlet gases. This result explains the low conversion degree of methanol to CO₂ over metal molybdates.

Analogous investigations in the absence of air were carried out on MoO₃ and MnMoO₄-MoO₃ catalysts. MoO₃ exhibited a quite different behaviour. Fifteen minutes after the increase of temperature up to 350 °C, the presence of a MoO₃ + MoO₂ mixture was established by X-ray analysis, but the lines of MoO₃ disappeared after 30 min. The catalytic activity and the distribution of the reaction products also displayed substantial differences. The major product in this case was CH₄, the reaction rate being 10 times higher.

The EPR studies indicated no change in the valency state of the manganese present in the catalysts used both with and without air. This shows that manganese ions do not participate in redox processes during the catalytic oxidation of methanol.

CONCLUSIONS

1) The properties of MnMoO₄-based catalysts largely depend on the method of their preparation. The highest activity and selectivity (comparable with those of industrial catalysts) belong to the samples obtained by precipitation in the presence of a small excess of MoO₃ (Mo/Mn atomic ratio 1.1 – 1.3).

2) Under the conditions of selective oxidation of methanol, MnMoO₄-MoO₃ catalysts do not change their chemical composition. This presupposes a larger period of exploitation, i.e. the catalysts are promising as far as their application in practise is concerned.

3) The oxidation of methanol on MnMoO₄ is a two-step process. The first step includes methanol interaction with Mo(VI) and the reduction of Mo(VI) to Mo(V) (Mo(IV)). The second step consists of the direct oxidation of the reduced molybdenum by oxygen from the alcohol-air mixture.

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