

Mn-Mo-O CATALYSTS FOR METHANOL OXIDATION.**I. PREPARATION AND CHARACTERIZATION OF THE CATALYSTS**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.

Mn-Mo-O catalysts with a different Mo/Mn ratio have been prepared by precipitation. The precipitate composition as a function of solution concentration and pH was studied by X-ray, IR, thermal and chemical methods. Formation of manganese molybdates with $\text{MnMoO}_4 \cdot 1.5 \text{H}_2\text{O}$, $\text{Mn}_3\text{Mo}_3\text{O}_{12} \cdot 2.5 \text{H}_2\text{O}$, and $\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot 4 \text{H}_2\text{O}$ composition has been supposed. It is concluded that pure MnMoO_4 may be obtained in both acid and alkaline media, the pH values depending on the concentration of the initial solutions. The maximum Mo/Mn ratio in the precipitates is 1.33. The formation of pure $\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot 4 \text{H}_2\text{O}$ is possible in weakly acidic media. This process is favoured by increasing the concentration of initial solutions.

Manganese(II) molybdate can be prepared by solid phase interaction between MnO_2 and MoO_3 as well as by precipitation¹⁻⁴. All precipitation methods⁵⁻¹⁰ concern the preparation of stoichiometric MnMoO_4 . To the best of our knowledge there are no data on the preparation of a specimen with an excess of MoO_3 by precipitation. On the other hand, it is known that the samples with a Mo/Mn ratio of 1.1 to 1.3 possess high activity and selectivity in the oxidation of methanol and in other oxidation processes^{11,12}. Ozkan et al.¹³ impregnated MoO_3 catalysts with MnMoO_4 and reported that they were active for the partial oxidation of hydrocarbons to maleic anhydride. The purpose of the present study was to find the conditions for precipitation of Mn-Mo-O catalysts with a prefixed composition. The results from such investigation will throw additional light on the possibility of precipitation of manganese polymolybdates and on the determination of their composition.

EXPERIMENTAL

Aqueous solutions of $\text{Mn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ (p.a.) with concentrations of 5 to 40 wt.% were used for the experiments. Precipitation was carried out by slow adding, with continuous

stirring, of an aqueous solution of manganese nitrate to an aqueous solution of ammonium paramolybdate with a prefixed pH and pre-heated to 60 °C. The Mn and Mo concentrations were controlled by chemical analyses and by atomic absorption spectrometry. The precipitates were characterized using X-ray, IR spectrometry, DTA, TG and DTG analyses.

RESULTS AND DISCUSSION

Table I shows the dependence of the composition of the precipitates obtained (the Mo/Mn ratio) on the pH of the precipitation. In all cases the concentration of the initial solutions was 5 wt.%, and the Mo/Mn ratio 1.5.

It should be pointed out that the precipitation conditions only weakly influence the Mo/Mn ratio in the precipitates obtained. The only exceptions are samples 3, 4, and 5, for which this ratio is much larger than 1. It is worth noting that with these samples the amount of the precipitate is much larger. With decreasing pH below 5, this amount abruptly drops. The conductance of the filtrates decreases from the alkali to acid region despite of the fact that the amount of free ions is nearly the same. This can be ascribed to the formation of polymolybdate ions.

The state of molybdate ions in aqueous solution of the molybdates is not elucidated. According to an earlier report¹⁴, composition of the ions in aqueous solutions depends on the pH value of the medium according to the Eq. (A).

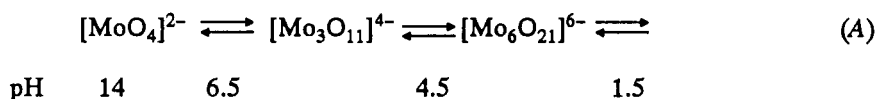
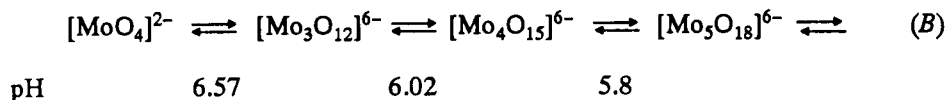


TABLE I
Dependence of composition of precipitates on pH of precipitation

No. ^a	pH ₁	pH ₂	S	G	ΔG	Mo/Mn ratio
1	6.65	5.60	28.0	8.1	6.5	1.01
2	6.71	5.80	28.0	8.8	6.8	1.03
3	8.10	6.00	28.5	9.4	8.0	1.10
4	8.50	6.20	30.5	10.5	8.1	1.19
5	8.80	6.35	30.7	9.3	10.1	1.08
6	9.05	6.50	31.0	9.1	11.1	1.00
7	9.15	7.65	31.8	9.0	12.0	1.00
8	9.30	8.20	31.9	8.7	11.5	0.98
9	9.50	8.65	31.5	8.8	11.0	0.95

^a pH₁ is pH of ammonium paramolybdate in the beginning of precipitation, obtained by adding a 10% aqueous solution of ammonia, pH₂ is pH at the end of precipitation, G is mass of precipitates dried for 4 h at 110 °C in g, ΔG is change of the mass of precipitates after a 4 h calcination at 500 °C in %, S is conductance of filtrates (mS).

This equilibrium is also affected by the concentration and temperature of the solutions as well as by the presence of other components. Karagyozyova¹⁵ has established the existence of a homologous series of different polymolybdate ions depending on pH and concentration of the solutions used (Eq. (B)).



Assuming the existence of this homologous series for the molybdate ions, we supposed formation of polymolybdate ions according to Eq. (B). The excess of molybdenum in samples 3, 4, and 5 can be assumed to be due to the formation of a mixture of polymolybdate with the compositions $\text{Mn}_3\text{Mo}_3\text{O}_{12}$ and $\text{Mn}_3\text{Mo}_4\text{O}_{15}$ while the Mo/Mn ratio of 1 for sample 1 should be a result of the higher solubility of $\text{Mn}_3\text{Mo}_4\text{O}_{15}$ at a lower pH value. The small excess of manganese in samples 8 and 9 can be attributed to the formation of $\text{Mn}(\text{OH})_2$. The water content in the precipitates varies from 6 to 12%. On the basis of the results in Table I it can be concluded that molybdenum-enriched precipitates can be obtained at pH of about 6.2.

Table II presents the dependence of the composition of the precipitates obtained (Mo/Mn-2 atomic ratio) on the concentration of initial solutions for a constant final pH of 6.2. In most cases the atomic ratio in the initial solutions (Mo/Mn-1) was 1.5 while their concentration (*C*) varied from 5 to 40 wt.%. The results in Table II show that the concentration of the initial solutions essentially affects the equilibria in Eq. (B), the rise of concentration leading to more complex ions. Samples 1 – 3 are probably mixtures of $\text{Mn}_3\text{Mo}_3\text{O}_{12}$ and $\text{Mn}_3\text{Mo}_4\text{O}_{15}$, the amount of $\text{Mn}_3\text{Mo}_4\text{O}_{15}$ increasing from 1 to 3,

TABLE II
Dependence of composition of precipitates of the initial solution concentration at a constant pH

No. ^a	Mo/Mn-1 ratio	<i>C</i>	<i>G</i>	ΔG	Mo/Mn-2 ratio
1	1.5	5	10.5	8.1	1.19
2	1.5	10	20.8	8.3	1.22
3	1.5	20	40.5	8.5	1.26
4	1.5	30	68.5	8.5	1.32
5	1.5	40	88.9	8.5	1.33
6	1.3	30	68.0	8.5	1.33
7	1.0	30	51.0	8.5	1.33

^a *C* Initial solution concentration (wt.%), Mo/Mn-1 atomic ratio before precipitation, Mo/Mn-2 atomic ratio in the precipitate, *G* mass of precipitates dried at 110 °C in g, ΔG mass loss after a 4 h calcination of precipitates at 500 °C in %.

whereas samples 4 – 6 correspond to the chemical composition of $\text{Mn}_3\text{Mo}_4\text{O}_{15}$. Mo/Mn ratio in the initial solutions has no substantial effect on the precipitate composition. In this case, the precipitates obtained contain a considerable amount of water, too.

From the X-ray structure analysis of all precipitates it is seen that some of them (samples 1 and 7 from Table I and sample 6 from Table II) are manganese molybdates with different composition, isolated at definite conditions. The others are different-ratio mixtures of these molybdates.

The data from the X-ray analysis of sample 7 from Table I and of sample 6 from Table II are given in Table III. The X-ray patterns of sample 1 from Table I differs from that of the others, but its reflections are less expressed.

Combining the results in Table I with the chemical analysis data we can propose the probable composition of the molybdates isolated. Sample 6 is precipitated at a pH value of 6.5 and has a Mo/Mn ratio of 1. Since, according to data from the literature, under these conditions the equilibrium in concentrated solutions is shifted to MoO_4^{2-} . Sample 6 could be crystalhydrate of manganese molybdate with a composition $\text{MnMoO}_4 \cdot x \text{H}_2\text{O}$. Sample 6 in Table II also is, according to the data presented in Table III, manganese polymolybdate with Mo/Mn = 1.33. We assume that, when pH is 6.2 and the initial solutions have high concentrations, the equilibrium can be shifted to the polymolybdate ions $\text{Mo}_4\text{O}_{15}^{6-}$, and the composition of the precipitate obtained can be described by the formula $\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot y \text{H}_2\text{O}$. Sample 1, which is prepared at low pH values and has a relatively low crystallization degree, is characterized by a Mo/Mn atomic ratio of 1 and a crystalline structure differing from that of the above samples. The same X-ray data are also found for the manganese molybdate obtained by Trifiro et al.¹⁰, Sinhamahapatra et al.¹⁶ and by us⁷. In our opinion, this precipitate has the composition which can be described by the formula $\text{Mn}_3\text{Mo}_3\text{O}_{12} \cdot z \text{H}_2\text{O}$. The absence of the proposed $\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot y \text{H}_2\text{O}$ in this sample may be ascribed to its higher solubility in acid media and its passing into the filtrate. Samples 1, 2, and 3 in Table II are mixtures of the proposed $\text{Mn}_3\text{Mo}_3\text{O}_{12} \cdot x \text{H}_2\text{O}$ and $\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot y \text{H}_2\text{O}$, while sample 6 in Table I can be considered as a mixture of MnMoO_4 and $\text{Mn}_3\text{Mo}_3\text{O}_{12} \cdot z \text{H}_2\text{O}$.

The above assumptions are supported in a great extent by the X-ray patterns of samples calcined at 500 °C. The thermal treatment of samples 1 and 7 in Table I leads to the formation of well shaped crystals of stoichiometric $\alpha\text{-MnMoO}_4$ according to Abrahams and Reddy¹⁷. Heating of sample 4 in Table I and samples 2 and 6 in Table II results in crystallization of MnMoO_4 and MoO_3 , the lines characteristic of molybdenum trioxide being most intense with sample 6 in Table II.

Figure 1 shows the IR spectra of samples 1 and 7 from Table 1 and sample 6 from Table II, and Fig. 2 the IR spectra of the same samples heated for 4 h at 500 °C.

The comparison of IR spectra of samples obtained after precipitation and dried at 110 °C leads to the conclusion that the precipitates obtained are complexes with different composition, in which the initial substances used for their production are not found

in a free state. The absorption bands, typical for the manganese molybdate and molybdenum trioxide, are not observed, either. The absorption bands at 1 620 – 1 610 and 3 500 – 3 400 cm^{-1} , found in all spectra, confirm the presence of crystallization water in all four samples. The absorption bands at 1 385 and 1 402 cm^{-1} and the bands in the region of 3 250 – 1 270 cm^{-1} can be ascribed to the presence of NH_4^+ ion. The intensity of these bands shows a sharp decrease with the rise of temperature, which is indicative of a crystalhydrate destruction and the formation of new phases. This process is accompanied by substantial changes of the positions and intensities of

TABLE III
X-Ray patterns of manganese molybdate precipitates in aqueous media

Sample 7 (Table I)		Sample 6 (Table II)	
<i>d</i> , Å	<i>I/I</i> ₀ , %	<i>d</i> , Å	<i>I/I</i> ₀ , %
7.1823	11	9.6122	59
5.3654	100	7.9330	76
4.9729	11	7.1958	28
3.8363	29	6.3942	45
3.6639	50	4.6558	60
3.5857	7	4.4857	27
3.4260	62	4.4645	15
3.3794	19	4.3880	54
3.1862	40	4.3571	28
3.0579	17	3.7290	42
2.9325	38	3.5893	20
2.7606	48	3.5130	10
2.7390	13	3.3750	77
2.6716	13	3.2851	77
2.4560	9	3.2038	57
2.3251	12	3.1863	51
2.2439	4	3.0818	100
1.9920	7	3.0690	43
1.8721	6	2.9473	13
1.8533	13	2.8679	14
1.8483	10	2.7738	29
1.8119	15	2.7510	22
		2.5688	11
		2.5388	15
		2.5066	10
		2.1463	17

absorption bands in the range $700 - 1\,000\text{ cm}^{-1}$, as seen from the spectra of calcination at $500\text{ }^{\circ}\text{C}$ shown in Fig. 2.

It is interesting that in the spectra of samples 1 and 7 from Table I, absorption bands at $721, 799, 865, 926,$ and 948 cm^{-1} are observed that are specific only for pure MnMoO_4 and are described in detail by other authors¹⁰. This supports the suggestion that samples of the more complex composition ($\text{Mn}_3\text{Mo}_3\text{O}_{12} \cdot z\text{ H}_2\text{O}$ and $\text{MnMoO}_4 \cdot x\text{ H}_2\text{O}$) are obtained on precipitation, and their calcination at $500\text{ }^{\circ}\text{C}$ leads to their destruction and the formation of MnMoO_4 . In the spectra of the calcined sample 6 from Table II besides the bands specific for MnMoO_4 , absorption bands are also observed at 996 and 616 cm^{-1} , the appearance of which can be explained by formation of a free MoO_3 . This result is in agreement with the suggestion that sample 6 from Table II represents a manganese polymolybdate ($\text{Mn}_3\text{Mo}_4\text{O}_{15} \cdot y\text{ H}_2\text{O}$).

The X-ray and IR data have shown that the molybdates obtained by precipitation substantially change after thermal treatment. Additional information on these changes at $20 - 1\,000\text{ }^{\circ}\text{C}$ was obtained by DTA, TG, and DTG studies. Figure 3 presents the DTA, DTG and TG curves of sample 7 in Table I.

The DTA curve of sample 7 shows a distinct endothermic effect at $210\text{ }^{\circ}\text{C}$ and also a distinct exothermic effect at $330\text{ }^{\circ}\text{C}$. The initial effect is considered as a result of the decomposition of the precipitated crystallohydrate and the removal of crystallization

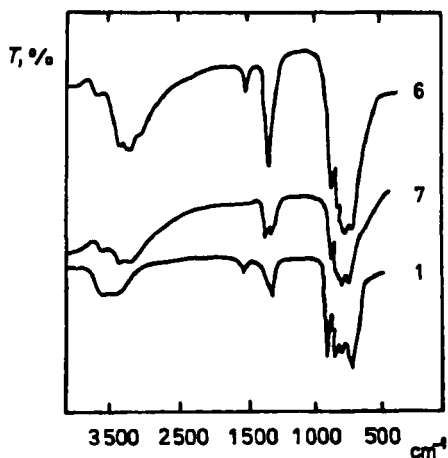


FIG. 1
IR spectra of samples 1 and 7 from Table I and of sample 6 from Table II, dried at $110\text{ }^{\circ}\text{C}$

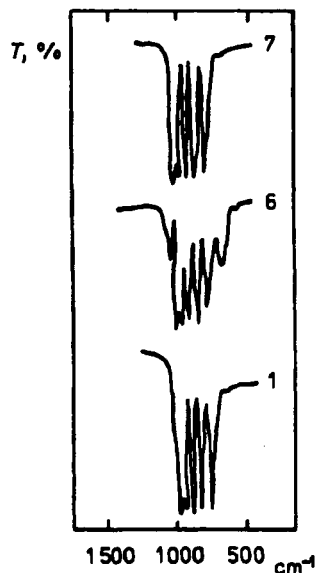


FIG. 2
IR spectra of samples 1 and 7 (Table I) and of sample 6 (Table II) calcined at $500\text{ }^{\circ}\text{C}$

water, while the latter is associated with the crystallization of manganese molybdate. The TG curve of this sample indicates that crystallization water is eliminated in two stages, to which two pronounced minima in the DTG curve (at 210 and 330 °C) correspond. The amount of this water is 12% of the total weight of the sample and its elimination can be presented by the following equations ((C), (D)).

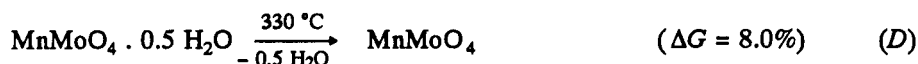
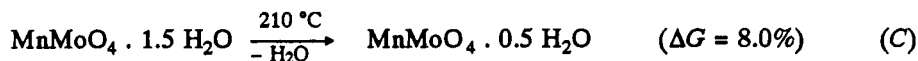


Figure 4 shows the DTA, DTG, and TG curves of sample 6 in Table II. The DTA curve of sample 6 is characterized by a pronounced endothermic effect at 300 °C followed by a broad indistinct exothermic peak with a maximum at about 400 °C and a second endothermic effect at 690 °C. The first endothermic effect is associated with the elimination of crystallization water. Here again the process is two-stage one. The TG curve indicates a slow weight loss up to 295 °C, after which the rate of the process quickly increases and passes through a maximum at 300 °C. At 690 °C, there is a decrease in weight again, which is associated with the removal of the excess of MoO₃. The above processes can be described by the following sequence:

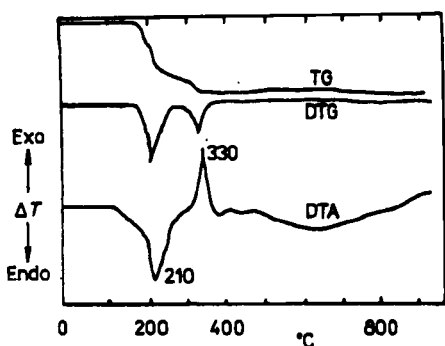


FIG. 3
TG, DTG, and DTA curves of sample 7 (Table I)

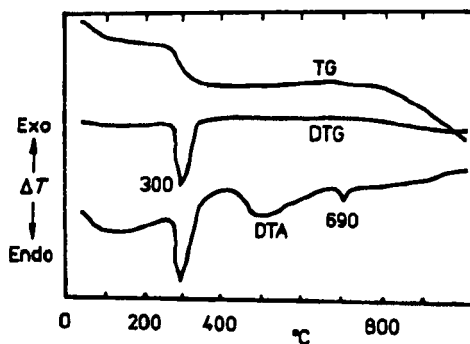
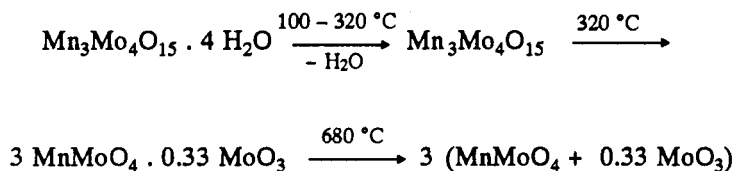


FIG. 4
TG, DTG, and DTA curves of sample 6 (Table II)



The total weight loss at 1 000 °C is 16.5%, of which 8.5% are due to the crystallization water, the remaining 8% can be ascribed to MoO₃.

In contrast to sample 7, a weak heating effect is observed in this case during crystallization of MnMoO₄. This effect is due to the fact that decomposition of the polymolybdate proposed occurs according to the above scheme simultaneously with its crystallization. The decomposition process requires a considerable amount of heat and compensates for the heating effect of crystallization. The endothermal effect at 690 °C has been ascribed to the eutectics formed between MnMoO₄ and MoO₃ (ref.¹⁸).

Figure 5 shows the results from a derivatographic investigation of sample 1 in Table I. The DTA curve of this sample exhibits no noticeable heating effect excepting a very weak endothermal effect at 690 °C due to the melting of the proposed eutecticum of MnMoO₄ and MoO₃. The shape of the DTA curve can be explained by complete compensation of the heating effect produced by the crystallization of MnMoO₄ and the decomposition of the polymolybdate proposed. The TG curve shows a smooth decrease in weight of the sample by 6.5% as a result of the removal of water and an additional decrease by 1.5% at temperatures above 700 °C. This shows that the precipitate contains, in addition to Mn₃Mo₃O₁₂, also a small amount of Mn₃Mo₄O₁₅, whose decomposition leads to the stoichiometric amount. The DTA, TG, and DTG curves of the remaining samples represent combinations of the DTA, TG and DTG curves in Figs 3, 4, and 5.

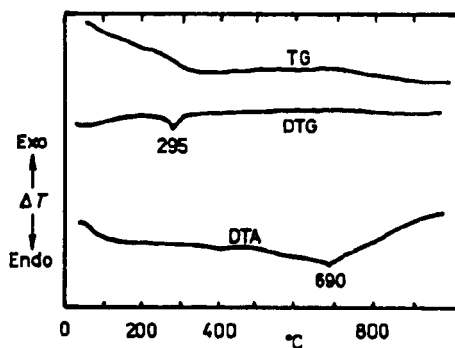


FIG. 5
TG, DTG, and DTA curves of sample 1 (Table I)

The results from the analyses allow determination of the exact composition of both the pure molybdates isolated and the mixtures obtained under different conditions.

Table IV presents data on the composition of the most interesting samples. The amounts of Mn, Mo and H₂O are found experimentally by direct methods, while the oxygen is determined indirectly as the residue to 100%.

Finally, it was established that the composition of the Mn-Mo-O catalysts obtained by precipitation largely depends on the precipitation conditions and the concentrations of the solutions used. Pure MnMoO₄ can be obtained in both acid and alkali media, the pH values depending on the concentration of the initial solutions. Strongly acid media are unfavourable because under these conditions the solubility of the polymolybdates is significant and the amount of the precipitate formed is small. The maximum Mo/Mn ratio in the precipitates is 1.33. The existence of Mn₃Mo₄O₁₅ · 4 H₂O is assumed as possible in a weakly acid media only. This process should be favoured by the rise of concentration of the initial solutions. Varying the precipitation conditions, it is possible to control the preparation of catalyst samples with a Mo/Mn atomic ratio of 1.0 – 1.33. At pH values above 8, Mn(OH)₂ may be formed, which is decomposed with rising temperature and strongly decreases the selectivity of catalysts in oxidation processes.

TABLE IV
Composition of the most interesting samples

Sample No.	Content (wt. %) of				Composition
	Mn	Mo	O	H ₂ O	
1 ^a	23.9	41.8	27.8	6.5	Mn ₃ Mo ₃ O ₁₂ · 2.5 H ₂ O
7 ^a	22.5	39.8	25.7	12.0	MnMoO ₄ · 1.5 H ₂ O
6 ^b	19.2	44.5	27.8	8.5	Mn ₃ Mo ₄ O ₁₅ · 4 H ₂ O

^a Table I; ^b Table II.

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