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THERMAL STABILITY OF $MnMoO_4$-MoO_3 CATALYSTS FOR METHANOL OXIDATION

*K. Ivanov, P. Litcheva, P. Klissurski** and *T. Popov*

DEPARTMENT OF CHEMISTRY, VSI 'V. KOLAROV', 4000 PLOVDIV, BULGARIA
*INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, BULGARIA ACADEMY OF SCIENCES, 1040 SOFIA, BULGARIA

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The thermal stability of $MnMoO_4$-MoO_3 catalysts for methanol oxidation has been studied. Formation of eutectic composition of 33 wt.% $MnMoO_4$ and 67 wt% MoO_3 and a melting point of 969-973K was observed. An attempt has been made to plot a state diagram of the $MnMoO_4$-MoO_3 system.

The thermal stabilities of the Mn-Mo-O and commercial Fe-Mo-O catalysts have been compared. It has been concluded that manganese(II) molybdate catalysts are stable up to 973 K and are of a definite interest in view of their application in practice.

The most widely used catalysts for selective oxidation of methanol to formaldehyde represent mixtures of ferrimolybdate and molybdenum trioxide which are sometimes promoted by various additives [1, 2]. Their main disadvantage is the short lifetime [8-18 months]. The rapid deactivation of iron-molybdenum catalysts is mainly due to [3-5]

(1) partial reduction of the active component $Fe_2(MoO_4)_3$ to $FeMoO_4$, and

(2) an increase in resistance of the reactor because of condensation of the molybdenum trioxide coming from the "hot spot" to the lower catalyst layers.

For these reasons, new active and high-selectivity catalysts for methanol oxidation characterized by a longer lifetime should be looked for. Promising results in this respect were obtained in studies of $MnMoO_4$-based oxide catalysts. Our investigations on the manganese(II) molybdate-molybdenum trioxide system showed the samples with a molybdenum/manganese ratio of 1.1 - 1.5 to be not inferior to industrial catalysts with respect to their catalytic properties. However, there are no investigations published on the

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Akadémiai Kiadó, Budapest*

thermal stability of this system. In the present paper we try to fill this gap by presenting some results on these promising catalysts for mild oxidation of methanol.

Experimental

Catalyst samples with various MoO_3 contents were prepared in two ways reported earlier: (i) by thermal decomposition of a mixture of ammonium paramolybdate and manganese nitrate [6] and (ii) by precipitation from aqueous solutions of the same salts [7].

The thermal studies were performed with a derivatograph within a temperature range of 293-1273 K. The phase composition was determined with a DRON-1 apparatus using CoK_α radiation and by atomic absorption and chemical analyses for Mn, Mo, and Fe.

Results and discussion

The results from the derivatographic studies of a precipitated sample with a Mo/Mn atomic ratio of 1.2 are presented in Fig. 1. The DTA curve is characterized by two endothermal peaks at 573 K and 969 K and an exothermal effect at about 673 K. The first endothermal effect is accompanied by a decrease in weight of the sample and it can be ascribed to the removal of the water of crystallization. The immediately following exothermal effect can be attributed to the transition of the system to a crystalline state. The second endothermal effect at 969 K is of special interest. It can be associated neither with the melting of MoO_3 nor with the decomposition of manganese(II) molybdate which is stable at this temperature. A satisfactory explanation of the effect observed can only be the assumption that $MnMoO_4$ and MoO_3 form eutectic mixture with a melting point of about 969 K. This assumption is supported by the fact that a microscope observation of the sample reveals partial melting.

The TG curve in Fig. 1 shows that at temperatures above 973 K the sample weight decreases. The X-ray and chemical analyses indicated this to be due to a loss of MoO_3. After prolonged heating of the sample at 1173 K, only pure $MnMoO_4$ was found in the residue.

Ziolkovski and Courtine [8] investigated the solid-phase interaction between Mn_2O_3 and MoO_3 and established a substantial decrease of the melting point of MoO_3 under the effect of the $MnMoO_4$ obtained. They are of

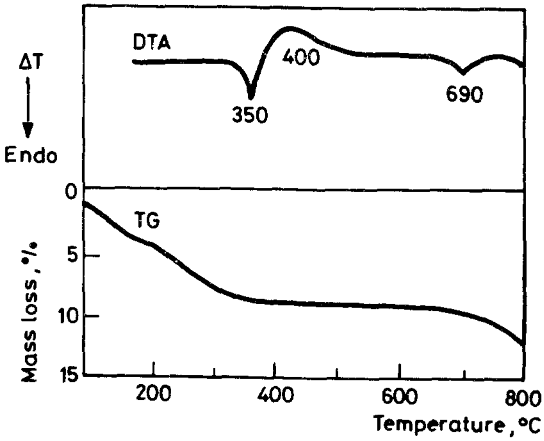

Fig. 1 DTA and TG curves of a precipitated sample with a Mo/Mn atomic ratio of 1.2

the opinion that this is due to the formation of eutectic composition of 33 wt.% $MnMoO_4$ and 67 wt.% MoO_3 with a melting point of 928 K, i.e. considerably lower than the endothermal effect observed by us at 969 K.

To elucidate the reasons for the differences observed, we investigated a large number of samples with different ratios of the two components. Prior to the thermal analyses, the mixtures of $MnMoO_4$ and MoO_3 were homogenized and calcined for 4h at 773 K. The results from derivatographic analyses are presented in Fig. 2a. The DTA curve of pure $MnMoO_4$ exhibits no thermal effects. No change in sample weight is indicated either, which confirms the absence of changes over the temperature interval investigated. In the case of MoO_3 there is an endothermal effect at 1073 K due to the melting of the sample at this temperature. Samples richer in $MnMoO_4$ show only one endothermal effect within the temperature range of 969-973 K. The signal intensity increases with the MoO_3 content and reaches a maximum with a sample consisting of 31% $MnMoO_4$ and 68% MoO_3. The further increase of the amount of MoO_3 is associated with the appearance of a second endothermal effect in the DTA curves as a result of the melting of MoO_3 not participating in the eutectic compound. The intensity and temperature of the second signal increases with the MoO_3 content (Fig. 2b). The rise of temperature above 973 K with compositions close to the eutectic is accompanied by intense evaporation and an abrupt drop in weight down to 60-65% at 1273 K. This does not allow to obtain correct data on the diagram of state to the left of the eutectic composition where a melt of L_2 and solid $MnMoO_4$ are present.

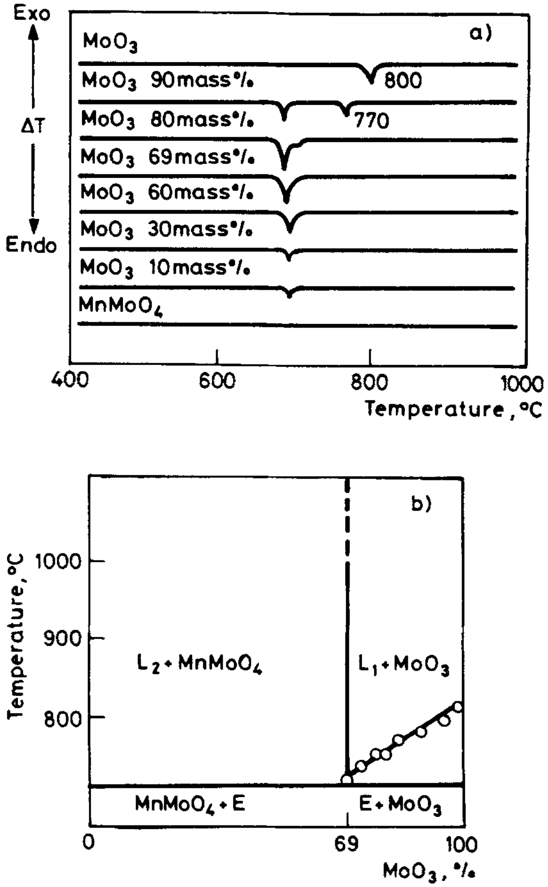

Fig. 2 a) DTA curves of $MnMoO_4$ and different $MnMoO_4$-MoO_3 samples
b) State diagram of the $MnMoO_4$-MoO_3 system: E - eutecticum, L_1 - melt, containing excess of MoO_3 with respect to E, L_2 - melt, containing excess of $MnMoO_4$ with respect to E

The small difference between our eutectic composition and that obtained by Ziolkovski and Courtine [8] can be explained in two ways: the $MnMoO_4$ obtained by precipitation usually contains 1-3% MoO_3 depending on the conditions of precipitation [7], which can lead to an error in the calculations; the fast increase of temperature (15°/min in ref. [8]) can produce a change in sample composition at temperatures close to the melting point of the eutectic composition due to the evaporation of small amounts of molybdenum trioxide. The pronounced difference between the melting points of the eutectic mixtures is more difficult to explain. To obtain more reliable results, we studied several samples with eutectic composition at slowly (5 deg/min) increasing/decreasing temperatures near the melting point. A signal at 971 + 2 K was observed in all cases.

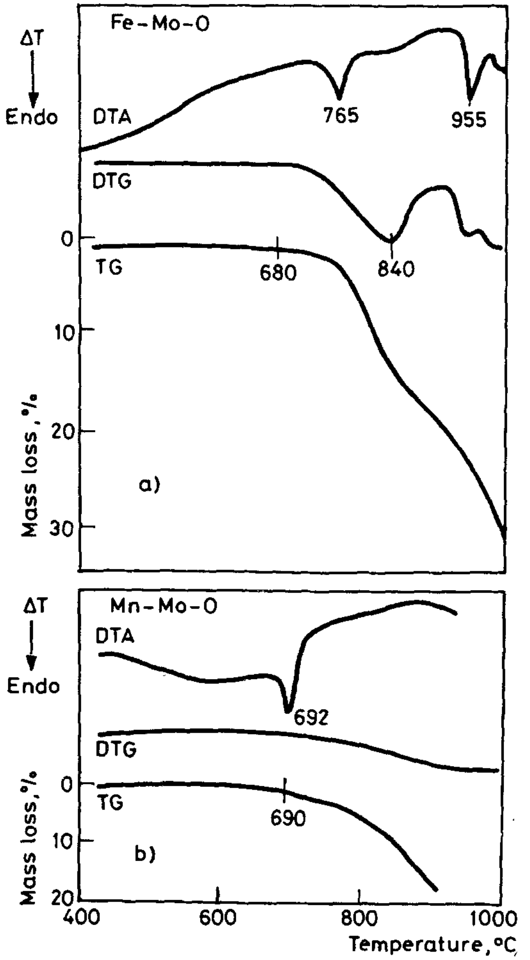

Fig. 3 DTA, DTG and TG curves of a commercial Fe-Mo-O catalyst a) and $MnMoO_4$-MoO_3 catalyst, containing 20 wt.% MoO_3 b)

As was pointed out, one of the main reasons for the deactivation of industrial catalysts is that MoO_3 evolves from the "hot spot" and deposits in the lower catalyst layers. It is interesting to determine the temperature range of exhaustion of Mn-Mo-O catalysts and to compare it with that for industrial iron-molybdenum samples. Figure 3 presents the results of thermal investigations of an industrial (upper part of the figure) and a Mn-Mo-O catalyst with 20 wt.% MoO_3 (Lower part of the figure). The DTA curve of the industrial sample is characterized by two endothermal effects at 1042 and 1268 K, which is in agreement with results published by other authors [9]. The TG curve shows that MoO_3 evolves gradually. The first step concerns excess MoO_3, and the second, that included in $Fe_2(MoO_4)_3$. This is confirmed by the presence of two distinct minima in the DTG curve.

The DTA curve of the $MnMoO_4$ and MoO_3 - containing sample shows only one endothermal effect at 969 K due to the above reasons. From the TG curve it is obvious that in this case again the evolution of MoO_3 begins at about 973 K. However, the lack of a minimum in the DTG curve indicates that the rate of MoO_3 evolution is in this case significantly lower. This is confirmed by the dependence of the weight change on the calcination time of the same catalysts at 973 K (Fig. 4).

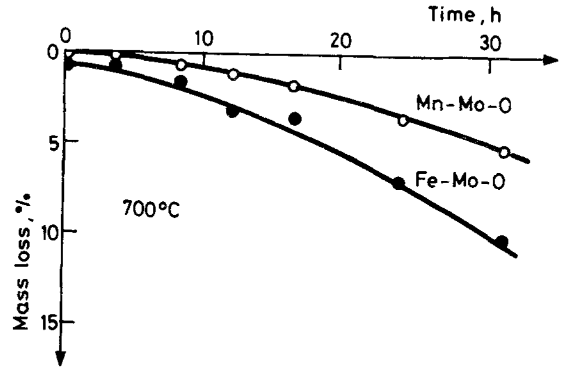

Fig. 4 Dependence of the weight change of the Fe-Mo-O and Mn-Mo-O catalysts on the calcination time at 700°C

The results obtained by derivatographic analyses on the thermal stability of Mn-Mo-O catalysts were confirmed by X-ray studies and chemical analyses. Figure 5 shows X-ray patterns of precipitated catalyst with Mo/Mn = 1.2, calcined at different temperatures. It is evident that the intensity of the reflections characteristic of MoO_3 increases at temperatures up to 973 K due to a higher degree of crystallinity of the compound. After that the signal intensities noticeably decrease due to its evolution at higher temperatures. The chemical analyses show that up to 973 K the Mo/Mn ratio remains constant and then begins to decrease.

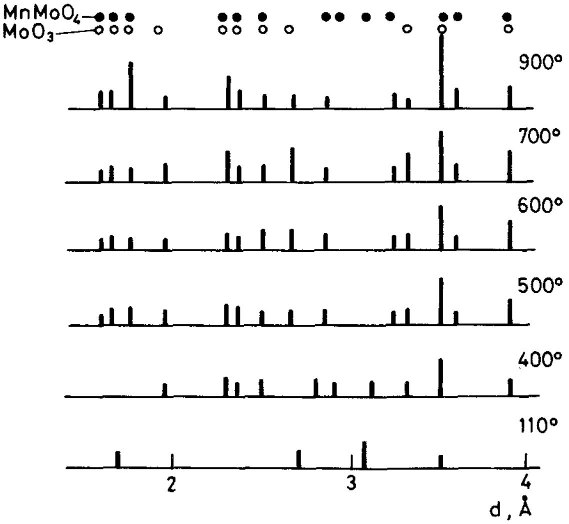

Fig. 5 X-ray diffraction patterns of a precipitated catalyst (Mo/Mn = 1.2), calcined at different temperatures

The investigations on the thermal stability of the system $MnMoO_4$-MoO_3 lead to some conclusions on the possibility of preparation of active and highly-selective catalysts for methanol oxidation which would have a longer lifetime than that of the catalysts used at present. As was already pointed out, the main reasons for the deactivation of industrial iron-molybdenum catalysts are the change in their chemical composition and the condensation of MoO_3. The active component of Mn-Mo-O catalysts is $MnMoO_4$ [7], which is a stable compound showing no substantial changes under the conditions of the process. The evolution of MoO_3 begins at the same temperature as with industrial catalysts, but proceeds at a lower rate. This allows assuming that the Mn-Mo-O catalysts proposed by us are of a definite interest in view of their application in practice.

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Zusammenfassung — Es wurde die thermische Stabilität von $MnMoO_4$-MoO_3-Katalysatoren für die Methanoloxidation untersucht. Es wurde die Bildung eines Eutektikum mit der Zusammensetzung von 33m% $MnMoO_4$ und 67m% MoO_3 und dem Schmelzpunkt von 969-973 K beobachtet sowie versucht, daß Zustandsdiagramm für das $MnMoO_4$-MoO_3-System zu erstellen.

Weiterhin wurde die thermische Stabilität von Mn-Mo-O-Katalysatoren mit der von handelsüblichen Fe-Mo-O-Katalysatoren verglichen. Es wurde festgestellt, daß Mangan(II)-molybdatkatalysatoren bis zu 973 K hitzebeständig und im Hinblick auf ihre praktische Anwendung von eindeutig großer Bedeutung sind.