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HIGH TEMPERATURE REACTIONS IN THE MoO_3–Ag_2O SYSTEM

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Abstract

High-temperature reactions were investigated in the MoO_3–Ag_2O system by means of X-ray, DTA and scanning microscopy methods, and a model was proposed according to which first an $Ag_2Mo_4O_{13}$ phase was formed at the MoO_3 and Ag_2O (or metallic Ag) interface. Subsequently, at the $Ag_2Mo_4O_{13}$–Ag_2O contact area a layer of $Ag_2Mo_2O_7$ appeared. If the amount of silver oxide is sufficiently high, a layer of Ag_2MoO_4 is formed between the Ag_2O and $Ag_2Mo_2O_7$ phases.

Keywords: Ag_2MoO_4, $Ag_2Mo_2O_7$, $Ag_2Mo_4O_{13}$, Ag_2O, DTA, MoO_3, phase diagram

Introduction

Vanadia-molybdena catalysts containing silver oxide additives have been used for the oxidation of various hydrocarbons [1–3]. In the case of benzene oxidation, an appreciable increase in the selectivity to maleic anhydride could be obtained with silver additives [4]. However, in certain cases, depending on the Ag_2O content, catalysts were either non-selective or non-active. This led to the conclusion that a more thorough knowledge of the V_2O_5–MoO_3–Ag_2O ternary system is necessary. In [5–7] the binary systems V_2O_5–MoO_3, V_2O_5–Ag_2O and MoO_3–Ag_2O, respectively, were studied. The relatively low temperature of decomposition of Ag_2O as well as the sublimation of MoO_3 in the course of the heating created numerous experimental difficulties which were the most pronounced in the study of the MoO_3–Ag_2O system. In addition, the equilibration of these systems at temperatures below eutectic melting points was slow and the phase compositions of the samples prepared from the mixtures of MoO_3 and Ag_2O depended on the heating procedure. In fact, within a certain concentration range of Ag_2O (20–80 mol%) the sequence of appearance of new phases was independent of the initial sample composition. This was evidently due to the diffusional limitations of the reaction kinetics. The aim of the present research was to investigate in more detail the processes occurring in the MoO_3–Ag_2O system

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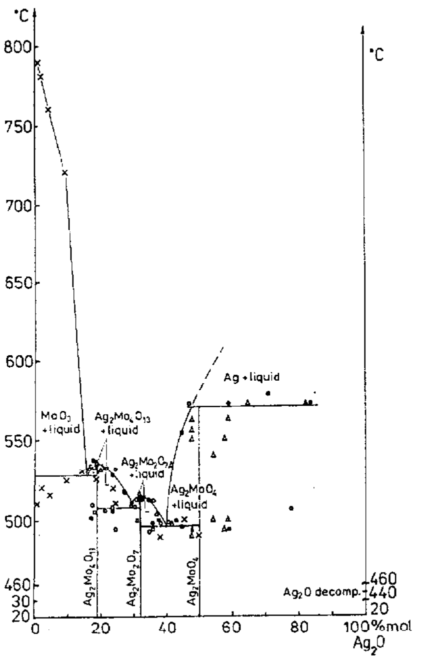

Fig. 1 Phase diagram of the MoO_3–Ag_2O system

(Fig. 1). In this system, besides the MoO_3 and Ag_2O (or Ag above 713 K), the following phases appear [7, 8]:

$Ag_2Mo_4O_{13}$ (*m.p.* 809 K)
$Ag_2Mo_2O_7$ (*m.p.* 789 K)
β-Ag_2MoO_4 (*m.p.* 849 K)

Three eutectics appear below an Ag_2O content of 50 mol% in the system:

MoO_3/$Ag_2Mo_4O_{13}$ (characteristic melting temperature 801 K)
$Ag_2Mo_4O_{13}$/$Ag_2Mo_2O_7$ (781 K)
$Ag_2Mo_2O_7$/Ag_2MoO_4 (769 K)

Experimental

MoO_3 p.a. (Analar, England) and Ag_2O p.a. (POCh, Poland) and metallic Ag (obtained by the decomposition of Ag_2O) were used for the investigations. The powdered substrates were mixed in the ratios corresponding to the compounds detected in the MoO_3–Ag_2O system: $Ag_2Mo_4O_{13}$, $Ag_2Mo_2O_7$ and Ag_2MoO_4 i.e. they contained 20, 33 and 50 mol% Ag_2O, respectively.

The changes in the phase composition in the course of heating of the samples were studied by using an X-ray heating camera (CuK_α radiation, heating rate

6°C h^{-1}). The samples were heated in air from room temperature to the temperature just below the melting points. The technique used allowed to state the positions and the number of diffraction lines but only qualitatively determine their intensities. Differential thermal and gravimetric analyses were carried out using a Mettler TA-2 Thermoanalyser and Al_2O_3 as reference material. The flow of air over the sample was 4 l h^{-1}. Initially the heating rate was 5°C min^{-1}. However, in such conditions the thermal effects were not distinct enough.

Besides, sublimation of MoO_3 took place and at higher temperature silver crept out of the crucible. Therefore a heating rate of 10°C min^{-1} was chosen. Because of the above mentioned facts, programmed-temperature cooling was not applied and the reversibility of thermal effects was not verified. The samples were heated from room temperature to about 923 K and exceptionally to 1273 K.

Microanalysis was carried out using a Jeol X-ray Microanalysis.

Results and discussion

X-ray analysis

MoO_3–Ag_2O mixtures with molar ratios of 4:1, 2:1, 1:1 prepared six months before the experiments, were heated and cooled down in the X-ray heating camera in the course of 4–5 days. X-ray diffraction spectra were registered; the results are shown in Figs 2–4.

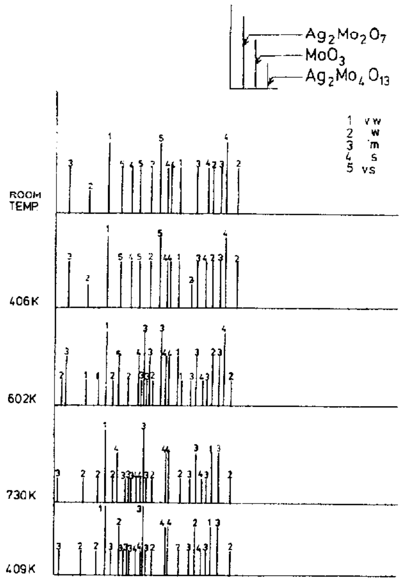

Fig. 2 X-ray diagram of a MoO_3–Ag_2O mixture with a molar ratio of 4:1

It is interesting to observe that small amounts of disilver 13-oxotetramolybdate ($Ag_2Mo_4O_{13}$) and disilver-hepta-oxo-dimolybdate ($Ag_2Mo_2O_7$) were detected in the samples which were kept for a longer period of time at room temperature without any heating, which indicates that solid state reactions could be initiated already under these conditions. It is seen from Fig. 2 (MoO_3/Ag_2O=4:1) that while the temperature was slowly rising, the amount of $Ag_2Mo_4O_{13}$ increased but MoO_3 did not disappear completely. This indicated that further formation of $Ag_2Mo_4O_{13}$ was in some way blocked. After cooling down to 409 K the composition of the sample remained unchanged.

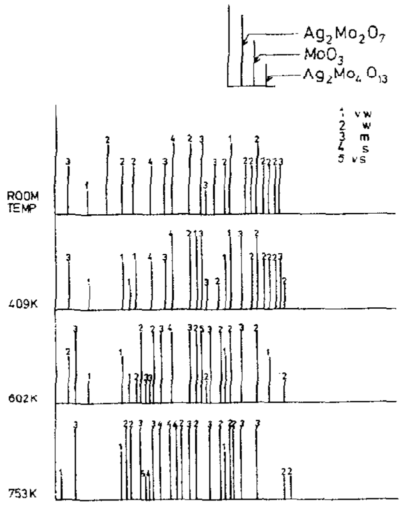

Fig. 3 X-ray diagram of a MoO_3–Ag_2O mixture with a molar ratio of 2:1

The MoO_3–Ag_2O mixture of a molar ratio of 2:1 corresponding to $Ag_2Mo_2O_7$ heated up to 753 K (Fig. 3) revealed the presence of $Ag_2Mo_2O_7$ as the predominant phase but $Ag_2Mo_4O_{13}$ and MoO_3 were still present. In a 1:1 mixture (Fig. 4) the phase of β-Ag_2MoO_4 was registered for the first time at 495 K and on further heating it became predominant, but $Ag_2Mo_2O_7$ as well as MoO_3 were still visible.

In all samples, independently of the temperature, MoO_3 was always present. It was not consumed completely even after the 1:1 mixture was heated just below its melting point for two weeks. X-ray analysis made in normal camera revealed the same diffraction patterns as in Fig. 4. All these results justify the conclusion that independently of sample composition, the first product which appears at the contacts of Ag_2O and MoO_3 grains is $Ag_2Mo_4O_{13}$ – the phase the richest in MoO_3. In the case of a MoO_3/Ag_2O ratio of 4:1 it became the predominant phase. However, in the case of 2:1 ratio it was transformed into $Ag_2Mo_2O_7$. The same sequence was observed also for samples with 1:1 ratio, but $Ag_2Mo_2O_7$ turned finally into Ag_2MoO_4.

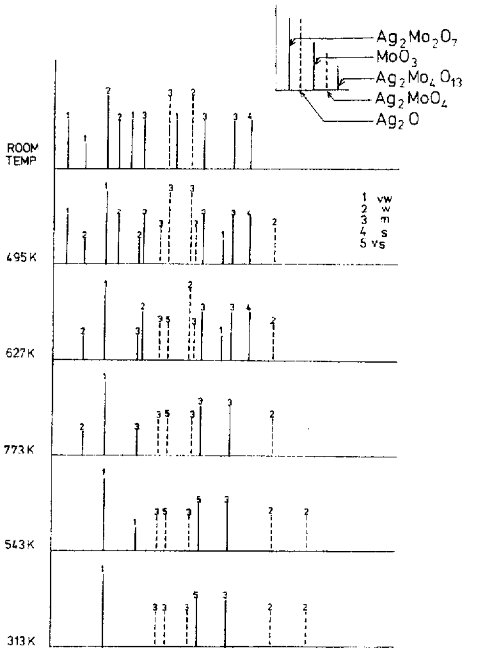

Fig. 4 X-ray diagram of a MoO_3–Ag_2O mixture with a molar ratio of 1:1

Thermal analysis

Further information concerning the solid-state reactions in the MoO_3–Ag_2O system was supplied by differential thermal and thermogravimetric analyses. Two sets of experiments were carried out: a) heating the mixtures of MoO_3 and Ag_2O of proper ratios, b) heating the mixtures of MoO_3 and metallic silver of the same ratios. The results denoted as a and b respectively, are shown in Figs 5–7.

Figure 5a represents the DTA and TG curves obtained during the heating of a 4:1 MoO_3–Ag_2O mixture from room temperature to 923 K. The first endothermic effect observed at 713 K and simultaneous loss of mass were evidently due to the decomposition of silver oxide

$$Ag_2O \rightarrow 2Ag + 1/2O_2 \qquad (1)$$

However, the decrease in mass was smaller than it could be expected considering the amount of silver oxide contained in the sample. It means that before decomposition, Ag_2O partly reacted with MoO_3 according to the equation:

$$Ag_2O + 4MoO_3 \rightarrow Ag_2Mo_4O_{13} \qquad (2)$$

which is in accordance with the results of X-ray analysis shown in Fig. 2. A subsequent increase in mass indicates that the next reaction taking place was connected with the absorption of oxygen as e.g.:

$$2Ag + 4MoO_3 + 1/2O_2 \rightarrow Ag_2Mo_4O_{13} \qquad (3)$$

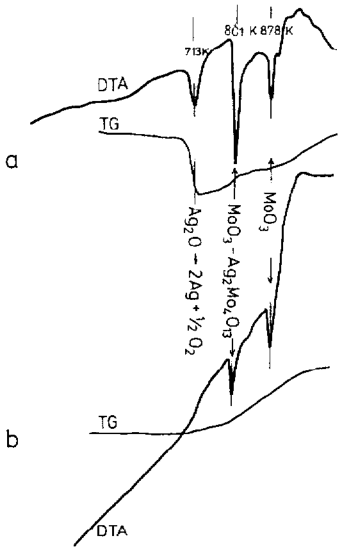

Fig. 5 DTA and TG curves of: a) MoO_3–Ag_2O mixture and b) MoO_3–Ag mixture corresponding to the composition of $Ag_2Mo_4O_{13}$

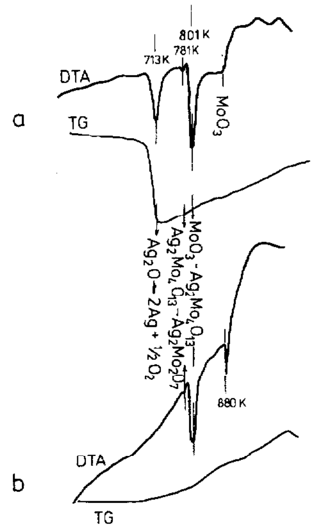

Fig. 6 DTA and TG curves of a) MoO_3–Ag_2O mixture and b) MoO_3–Ag mixture corresponding to the composition of $Ag_2Mo_2O_7$

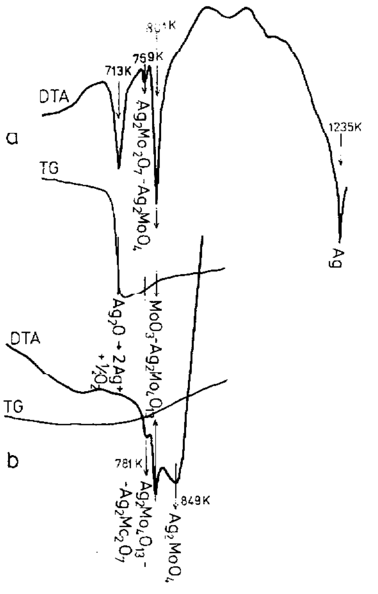

Fig. 7 DTA and TG curves of a) MoO_3–Ag_2O mixture and b) MoO_3–Ag mixture corresponding to the composition of Ag_2MoO_4

The endothermic effect at 801 K corresponds to the melting point of the eutectic MoO_3–$Ag_2Mo_4O_{13}$. Further increase in mass pointed out that reaction (3) was not complete before all the sample was melted. Heating the sample up to the melting point of silver was deliberately avoided as the liquid metal crept out of the crucible and attacked the thermocouple.

The course of DTA and TG curves (5b) for a MoO_3–Ag mixture corresponding to the composition $Ag_2Mo_4O_{13}$ was essentially the same as in the case of mixed oxides except for the effect of decomposition of Ag_2O. The increase in mass at about 823 K shows the beginning of reaction (3).

The sets of DTA and TG curves presented in Fig. 6a and 6b were obtained for 2:1 MoO_3–Ag_2O (a) and MoO_3–Ag (b) mixtures corresponding to the composition $Ag_2Mo_2O_7$. Comparing Figs 5 and 6 one can see that they are quite similar except for a very small peak at 781 K which corresponds to the melting of the eutectic $Ag_2Mo_4O_{13}$–$Ag_2Mo_2O_7$. This is an indication that under conditions of fast heating both phases, $Ag_2Mo_4O_{13}$ and $Ag_2Mo_2O_7$, were present at this temperature. It can be suggested that the primary product $Ag_2Mo_4O_{13}$ was transformed into $Ag_2Mo_2O_7$ in one of the following reactions:

$$Ag_2O + Ag_2Mo_4O_{13} \rightarrow 2Ag_2Mo_2O_7 \qquad (4)$$

$$2Ag + Ag_2Mo_4O_{13} + 1/2O_2 \rightarrow 2Ag_2Mo_2O_7 \qquad (5)$$

However, there is no endothermic effect due to the melting of $Ag_2Mo_2O_7$.

The course of sintering of 1:1 mixtures of oxides corresponding to a composition of Ag_2MoO_4 is shown in Fig. 7a and 7b. A number of phases were formed during the heating of the mixtures, the presence of which was signalled by the DTA peaks corresponding to the eutectic melting points:

801 K	MoO_3–$Ag_2Mo_4O_{13}$
781 K	$Ag_2Mo_4O_{13}$–$Ag_2Mo_2O_7$
769 K	$Ag_2Mo_2O_7$–β-Ag_2MoO_4

Only β-Ag_2MoO_4 (849 K in Fig. 7b) and Ag (1235 K in Fig. 7a) melted as separate phases.

Among all the registered endothermic effects (Figs 5–7) the strongest was that at 801 K due to the melting of the eutectic MoO_3–$Ag_2Mo_4O_{13}$. This was evidently due to the fact that $Ag_2Mo_4O_{13}$ was the primary and the most rapidly formed product at the contact of the grains of the oxides MoO_3 and Ag_2O (or Ag).

Considering the observed sequence in which particular phases appear in the course of heating, the model of solid state processes in the MoO_3–Ag_2O system shown in Fig. 8 may be proposed.

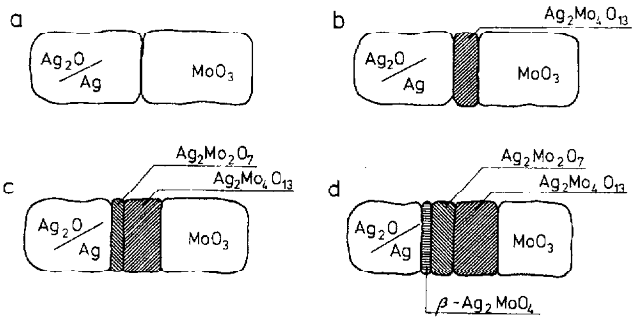

Fig. 8 Hypothetical model of the solid state processes in the MoO_3–Ag_2O system

At the contacts of MoO_3 and Ag_2O (or Ag) a thin layer of $Ag_2Mo_4O_{13}$ is formed due to reaction (2) or (3) which can be initiated even at room temperature (Fig. 8b). When the thickness of this layer increases, the initially relatively fast diffusion becomes difficult and the process becomes slow even at higher temperatures. At this stage at the contacts of $Ag_2Mo_4O_{13}$ and Ag or Ag_2O phases, reaction (4) or (5) starts and proceeds until the diffusion across the $Ag_2Mo_2O_7$ layer becomes very slow (Fig. 8c). At the $Ag_2Mo_2O_7$/Ag_2O (or Ag) contacts the next reaction begins (8d):

$$Ag_2O + Ag_2Mo_2O_7 \rightarrow 2\beta\text{-}Ag_2MoO_4 \quad (6)$$

or

$$Ag + Ag_2Mo_2O_7 + 1/2O_2 \rightarrow 2\beta\text{-}Ag_2MoO_4 \quad (7)$$

During thermal and thermogravimetric analyses not only reactions between the solids but also solid/oxygen reactions occur at atmospheric pressure. The effects observed by these methods are connected with: 1) the loss of oxygen of Ag_2O or/and 2) the fixation of oxygen on the mixtures MoO_3–Ag to form various molybdates.

So, the observed reactions are probably depending on the rate of the fixation of oxygen on the different molybdates, which may not be the same for the three investigated molybdates.

The additional evidence which confirmes the above described model was obtained from the following experiments. Two pellets: one containing pure Ag_2O and the other – MoO_3 were pressed together and heated at 623 K for 24 h. Ag_2O partly decomposed to metallic silver but the pellet was not destroyed.

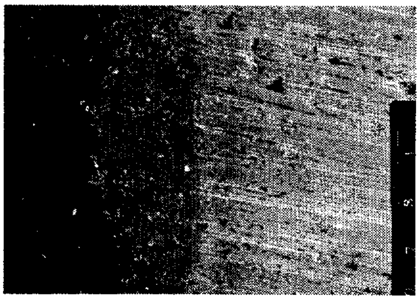

Fig. 9 Electron micrograph of the crosscut of MoO_3 and Ag sintered pellets. Between the MoO_3 pellet (light colour) and the Ag pellet (black colour) a new phase formed during the heating of pressed pellets is distinctly visible

Subsequently the pressed pellets were immersed in hardening resin and cut perpendicularly to their contact surface. On the photograph of the crosscut (Fig. 9), between the molybdenum trioxide and the silver layers, a new phase is distinctly visible. The relative amounts of silver and molybdenum atoms within

Fig. 10 Changes in the concentration of silver and molybdenum atoms within the area of phase at the interface of MoO_3 and Ag pellets

the new phase as registered by X-ray microprobe analysis is shown in Fig. 10. Their concentrations change mutually. It means that more than one compound is formed at the Ag/MoO_3 interface. Before sintering, the pressed MoO_3–Ag_2O pellets do not reveal the evidence of such layers.

* * *

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