Journal of Thermal Analysis, Vol. 52 (1998) 587-594

THERMAL STUDY OF THE Cr–Mo–O SYSTEM IN AIR

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(Received January 10, 1997; in revised form July 1, 1997)

Abstract

The phase diagram of the ternary system Cr–Mo–O in air was established from the results of thermal analysis of mixtures with different initial CrO_3 to MoO_3 ratios. It was found that MoO_3 did not take any chromium oxide into solid solution. The presence of Cr_2O_3 destabilized MoO_3 causing it to decompose to MoO_2 in the temperature range 723–958 K depending on the initial Cr/Mo ratio. The decomposition of pure MoO_3 MoO_2 did not occur in air at any temperature. However, this decomposition took place through the formation of the compound $Cr_2O_3{\cdot}3MoO_3(ss)$ and its decomposition to $Cr_2O_3{\cdot}3MoO_2(ss)$. The latter compound has never been reported before and the X-ray data for this compound are given. The previously reported catalytic activity of $Cr_2O_3{\cdot}3MoO_3(ss)$, at high temperatures, is presumably due to its reduction to $Cr_2O_3{\cdot}3MoO_2(ss)$.

Keywords: catalytic activity, Cr Mo O system

Introduction

The Cr–Mo–O system has an importance in iron and steel industries. Chromium gives hardness and toughness to steels while molybdenum improves forging, machining and strength [1]. Various chromium molybdenum oxides are described in the literature such as Cr_2MoO_6, $CrMoO_4$, $Cr_xMo_{1-x}O_2$ (with x ranging from 0 up to 1, $Cr_2(MoO_4)_3$, $Cr_2Mo_3O_{12}$, $Cr_{0.33}Mo_{0.67}O_2$, $Cr_{0.22}Mo_{0.78}O_2$ and $Cr_{0.19}Mo_{0.81}O_2$. The crystalline structure, lattice parameters and preparation conditions are also reported [2]. The binary system Mo–O was was investigated, the phase relations were determined between 873 and 1973 K, and the phase diagram was established by Chang and Philips [3]. The binary system Cr–O was investigated by Abadir *et al.* [4], and two intermediate nonstoichiometric compounds were reported. The MoO_3–M_2O_3 system is of very complex nature. However, this system is not dealt with in this paper since we are only concerned with the MoO_3–Cr_2O_3 system and the compounds encountered in it. $Cr_2Mo_3O_{12}$ is one of these compounds in which the catalytic activity may be attributed to the devia-

1418–2874/98/ $ 5.00
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tion from stoichiometry. $CrMoO_4$ is a molybdate (V) which has distorted rutile structure, the 6-coordination of $Mo^{(+V)}$ is made possible by the fact that the 4d electrons are stabilized by the formation of Mo–Mo pairs. The solid solution system $Cr_xMo_{1-x}O_2$, with $x \leq 0.5$, was investigated by Shimony and Ben-Dor [5]. Four different rutile related phases were investigated in this system, tetragonal rutile structure for $0.96 \leq x \leq 1.0$ and $0.12 \leq x \leq 0.36$, monoclinic distorted rutile for $0.36 \leq x \leq 0.5$ ($CrMoO_4$ type), MoO_2 type for $0 \leq x < 0.12$ and trirutile structure for $x=0.66$. These results were a good evidence for the existence of trivalent chromium ions rather than tetravalent as proposed by Sundholm *et al.* [6]. The study of oxidation-reduction reactions of chromium molybdenum oxides and their equilibrium relationships is of great importance for understanding the mechanisms of oxidation of containing chromium and molybdenum. The chromium molybdate mixed oxide is an important catalyst which finds many industrial applications especially in the oxidation of deuterium to deuterium oxide [7].

Experimental

The starting materials were chromium trioxide A.R. grade 99.7% purity, imported from Mallinchrodt Chemical Works, St. Louis, USA and the molybdenum trioxide was prepared by heating ammonium paramolybdate of 99.8% purity, (imported from Kemika, Zagreb, Croatia), up to 968 K for 10 h [8]. The mixtures were prepared by weighing the appropriate amounts of the dry oxides according to their purity, and mixed in an agate mortar before hanging in the thermobalance [9]. The composition to be investigated was put in a high alumina crucible suspended by a platinum wire from one of the balance arms and passed centrally through a furnace which was heated electrically. The temperature was measured by using a Pt/PtRh 10% thermocouple and controlled by an on-off controller. For low temperatures the accuracy was ±3 K and above 1273 K the limit increased up to ±6 K. The samples used for X-ray investigations were heated to the prespecified temperature, air quenched and ground in an agate mortar [10]. The X-ray diffraction pattern was obtained using the powder technique and a Ni filter.

Results and discussion

Mixtures of CrO_3 and MoO_3 of molar ratios 1:4, 1:3, 2:3, 2:1 and 4:1 were prepared as described previously and heated in the thermobalance at various temperatures till equilibrium was attained. The results were plotted to obtain the dissociation curves in which O/(Mo+Cr) is shown as a function of temperature. The dissociation curves of the previously mentioned mixtures in air were found to fall into two categories. These categories correspond to compositions initially containing $Cr/Mo \geq 1/3$ and $Cr/Mo < 1/3$. The mixtures containing initially less than or equal to 75 mol% MoO_3 are represented by the curve corresponding to 20 mol%

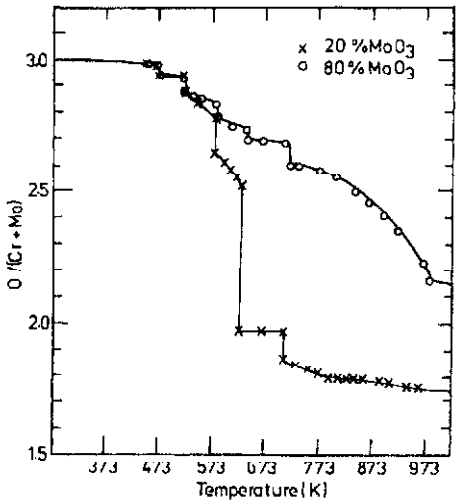

Fig. 1 Dissociation curves of the mixtures CrO_3:MoO_3=4:1 and 1:4 in air, based on molar basis

MoO_3, as it is shown in Fig. 1, while those corresponding to more than 75 mol% MoO_3 are represented by the curve corresponding to 80 mol% MoO_3 in the same figure. The vertical steps on these curves represent composition changes associated with monovariant situations which, at constant oxygen pressure will proceed to completion at constant temperatures. In such transitions, three condensed phases coexist with the gas phase. Curves on these figures represent a change in which a maximum of two condensed phases will coexist in equilibrium with the gas phase.

In Fig. 1, considering the mixture with a Cr/Mo molar ratio of 4/1 which represents the category Cr/Mo≥1/3, i.e. 20 mol% MoO_3, the following interpretation of the dissociation curve can be given.

The O/(Cr+Mo) ratio remains almost constant up to about 473 K where a slight isothermal step occurs due to the melting of CrO_3 and a slight loss of oxygen. From 473 to 521 K the oxygen to metal ratio remains constant. At 521 K an isothermal step occurs due to the reaction:

$$CrO_3(l) = CrO_x(s) + (3-x)/2O_2(g) \quad (1)$$

From this equation it is clear that four components coexist in equilibrium: $CrO_3(l)$, $CrO_x(s)$, $MoO_3(s)$ and $O_2(g)$. From 521 to 583 K oxygen is lost progressively, implying that two condensed phases are in equilibrium; these phases are $CrO_x(s)$ and $MoO_3(s)$. At 583 K an isothermal step occurs indicating the coexistence of $CrO_x(s)$, $CrO_y(s)$ and $MoO_3(s)$. $CrO_x(s)$ is converted to $CrO_y(s)$ according to the reaction:

$$CrO_x(s) = CrO_y(s) + (x-y)/2O_2(g) \quad (2)$$

At the end of this step oxygen is lost progressively due to the coexistence of $CrO_y(s)$, $MoO_3(s)$ and $O_2(g)$ in equilibrium with them. At 640 K a fourth isothermal step occurs due to the reaction:

$$2CrO_y(s) = Cr_2O_3(s) + (2y-3)/2O_2(g) \quad (3)$$

At 640 K four phases coexist in equilibrium. These are: $CrO_y(s)$, $MoO_3(s)$, $Cr_2O_3(s)$ and $O_2(g)$. It is to be noted that the temperatures at which reactions (1), (2) and (3) occur are practically the same in the absence of MoO_3 [4]. From 640 up to 723 K the weight is almost constant, and at 723 K an isothermal step occurs. This step is due to the formation of the reduced compound $Cr_2O_3 \cdot 3MoO_2(ss)$ which has not been reported previously. The results obtained from different dissociation curves indicate that this compound is nonstoichiometric, i.e. it exists over a range of composition. This is evidenced by the gradual loss in weight in all mixtures having Cr/Mo≥1/3, above 723 K. The tie triangle at 723 K connects the three condensed phases $Cr_2O_3(s)$, $MoO_3(s)$ and $Cr_2O_3 \cdot 3MoO_2(ss)$, Fig. 2. It seems therefore that the presence of Cr_2O_3 has destabilized $Mo^{(+VI)}$ causing it to decompose to $Mo^{(+IV)}$ at temperatures ranging from 450 to 958 K depending on the Cr/Mo molar ratio. The formation of $Cr_2O_3 \cdot 3MoO_3(ss)$ in the temperature range 640–723 K, previously reported by Trunov *et al.* [11], was evidenced by the X-ray pattern of a sample prepared at 723 K. The peaks of this compound were identified. Therefore at 723 K a peritectoid reaction occurs as follows:

$$Cr_2O_3 \cdot 3MoO_3(s) = Cr_2O_3 \cdot 3MoO_2(s) + 3/2O_2(g) \quad (4)$$

Mixtures containing initially Cr/Mo<1/3, on the high molybdenum side, are represented by the mixture which corresponds to a Cr/Mo ratio of 1/4 (80 mol%

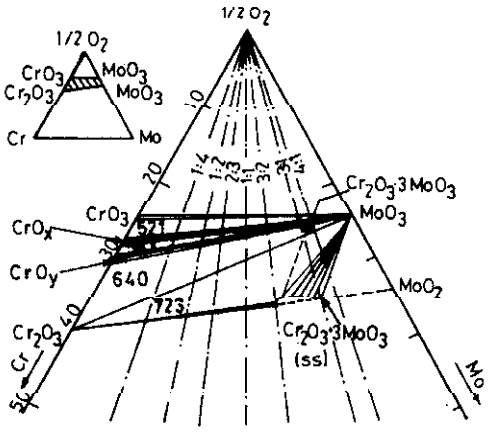

Fig. 2 Isobaric section of the ternary system Cr–Mo–O in air, (molar basis)

MoO_3), Fig. 1. From the dissociation curve of the latter mixture and the ternary isobaric diagram (Fig. 2) the behaviour of such mixtures is almost identical to those with Cr/Mo≥1/3 since reactions 1, 2, 3 and 4 occur at the same temperatures. However, the O/(Cr+Mo) ratio at 723 K does not allow the composition to lie on the Cr_2O_3–MoO_2 tie line as it is seen in Fig. 2. Above 723 K an appreciable gradual oxygen loss is observed and the final composition lies on the MoO_3–$Cr_2O_3{\cdot}3MoO_2(ss)$ edge. This means that on the Mo rich side there exists an equilibrium between MoO_3 and $Cr_2O_3{\cdot}3MoO_2(ss)$ as it is clear from the ternary diagram.

To confirm the possibility of formation of the compound $Cr_2O_3{\cdot}3MoO_2(ss)$, a mixture containing originally Cr_2O_3 and MoO_3 in a molar ratio of 1:3 was heated up to 953 K, quenched rapidly down to room temperature and the X-rayed. According to the proposed scheme of decomposition, (Fig. 2), at that temperature the product would be MoO_3 and the proposed compound $Cr_2O_3{\cdot}3MoO_2(ss)$. The X-ray results are given in Table 1. All the lines obtained are classified as MoO_3 and (X), which is the proposed compound $Cr_2O_3{\cdot}3MoO_2(ss)$. No evidence for Cr_2O_3 was obtained which indicates that the mechanism of decomposition of $Cr_2O_3{\cdot}3MoO_3(ss)$ is not as proposed by Hassanein and Youssef [12], probably due to the difference between the experimental conditions in the two works. Further evidence for the proposed scheme of dissociation was obtained by visual inspection of the colours of the products from different mixtures heated to temperatures up to 973 K. The colour of the mixture Cr/Mo=1:3 is brick red, which indicates the formation of a compound that ruled out the presence of Cr_2O_3, which is green.

The ternary isobaric section Cr–Mo–O, obtained on plotting the beginnings and ends of each vertical step in the dissociation curves, is shown in Fig. 2. The

Table 1 X-ray results

I/I_0	dA	Compound identified	I/I_0	dA	Compound identified
69	7.07	MoO_3	9	6.41	X
13	5.82	X	15	4.36	X
20	4.09	X	48	3.86	MoO_3
8	3.75	X	15	3.56	X
100	3.49	MoO_3	15	3.29	X
21	3.24	MoO_3	11	3.21	X
14	2.96	MoO_3	10	2.84	X
15	2.62	MoO_3	70	2.32	MoO_3
14	2.27	MoO_3	8	1.73	MoO_3
8	1.71	MoO_3	7	1.43	MoO_3
11	1.38	MoO_3			

tie triangles shown represent invariant situations where three condensed phases and a non-condensed phase, oxygen in this case, coexist in equilibrium with each other. Ignoring the triangle corresponding to CrO_3 melting due to its narrowness, four other triangles are shown. These triangles are:

1. at 521 K, in which $CrO_3(l)$, $MoO_3(s)$, $CrO_x(s)$ and $O_2(g)$ are in equilibrium.
2. at 583 K, in which $CrO_x(s)$, $CrO_y(s)$, $MoO_3(s)$ and $O_2(g)$ are in equilibrium.
3. at 640 K, in which $CrO_y(s)$, $Cr_2O_3(s)$, $MoO_3(s)$ and $O_2(g)$ are in equilibrium.
4. at 723 K, in which $Cr_2O_3(s)$, $Cr_2O_3{\cdot}3MoO_2(s)$, $MoO_3(s)$ and $O_2(g)$ are in equilibrium.

A fifth tie triangle should exist joining the compositions of $MoO_3(s)$, CrO_3 $3MoO_3(ss)$ and $Cr_2O_3{\cdot}3MoO_2(ss)$. However, it seems that the temperature at which these phases coexist in equilibrium with O_2 is very close to 723 K since it could not be differentiated practically. This is shown dotted in Fig. 2 and the temperature tentatively taken is 728 K.

Monovariant situations appear in the diagram as tie lines joining two condensed phases in equilibrium. They are associated with a gradual change in temperature and composition. There are four such situations:

1) $CrO_x(s)$ and $MoO_3(s)$ coexist in equilibrium with $O_2(g)$ at temperatures ranging from 521 to 583 K.
2) $CrO_y(s)$ and $MoO_3(s)$ coexist in equilibrium with $O_2(g)$ at temperatures ranging from 583 to 640 K.
3) $Cr_2O_3{\cdot}3MoO_2(ss)$ and $Cr_2O_3(s)$ coexist with $O_2(g)$ in equilibrium at temperatures ranging from 723 to 973 K. However, the composition change in this case is very small.
4) $Cr_2O_3{\cdot}3MoO_2(ss)$ and $MoO_3(s)$ coexist with $O_2(g)$ in equilibrium at temperatures ranging also from 723 to 973 K. However, the change in composition along the tie lines in this case is appreciable.

Two intermediate ternary compounds are formed, namely:

1) $Cr_2O_3{\cdot}3MoO_3$ which is formed at a temperature around 673 K and decomposes at 723 K to $Cr_2O_3{\cdot}3MoO_2(ss)$.
2) $Cr_2O_3{\cdot}3MoO_2(ss)$ which is nonstoichiometric and in which the valency of Mo is (+VI).

It is worth noting that MoO_3 is not readily decomposable to MoO_2 by heating i air at any temperature. However, the formation of $Cr_2O_3{\cdot}3MoO_3(ss)$ and its subsequent decomposition at 723 K reduced the valency of Mo from (+VI) to (+IV). This is why the joint between $Cr_2O_3{\cdot}3MoO_2(ss)$ and MoO_2 has been shown dotted in the diagram.

A quasi-binary section in air is constructed by projecting lines of constant composition from the ternary isobaric section onto a binary diagram (Fig. 3), to facilitate following up to phase changes that take place in the system Cr–Mo–O.

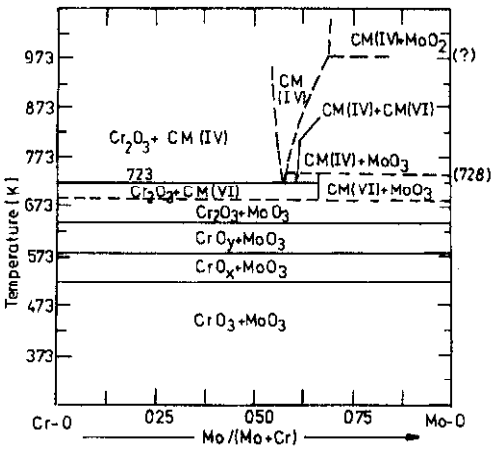

Fig. 3 Isobaric quasi binary temperature/composition diagram for the Cr–Mo–O system in air, (molar basis)

The main feature appearing in the diagram is the nonstoichiometry of the compound $Cr_2O_3{\cdot}3MoO_2(ss)$. Also the decomposition of $Cr_2O_3{\cdot}3MoO_3(ss)$ to $Cr_2O_3{\cdot}3MoO_2(ss)$ yields excess MoO_3. It is to be noted that the phase rule can not be applied to this type of diagram.

Conclusions

From the results and discussion given above, the following conclusions can be drawn:

1. MoO_3 did not take any of the chromium oxides into solid solution.
2. The presence of Cr_2O_3 destabilizes the MoO_3 causing it to decompose to MoO_2 in the temperature range 723–958 K depending on the Cr/Mo molar ratio initially present.
3. The decomposition of MoO_3 to MoO_2 and oxygen does not occur in air at any temperature. However, reduction of MoO_3 occurred through the formation of $Cr_2O_3{\cdot}3MoO_3(ss)$ and its decomposition to $Cr_2O_3{\cdot}3MoO_2(ss)$.
4. The catalytic behaviour of $Cr_2O_3{\cdot}3MoO_3(ss)$ when used at high temperatures is attributed to its reduction to $Cr_2O_3{\cdot}3MoO_2(ss)$ and the nonstoichiometry of the latter compound which leads to the creation of oxygen vacancies that assist absorption and diffusion processes, which in turn are the main factors enhancing catalysis.

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