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THERMAL ANALYSIS OF THE REACTION OF MOLYBDENUM TRIOXIDE WITH VARIOUS METALS*

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ABSTRACT

The solid state reaction between various metal powders (Ti, Zr, V and Fe) and molybdenum trioxide were investigated by means of differential thermal analysis and X-ray diffraction analysis. The reaction between these metals and MoO_3 are all multistage reactions in which the MoO_3 is first reduced to MoO_2 and then to elemental Mo. The Ti–MoO_3 and Zr–MoO_3 mixtures produce well defined exotherms and are capable of self sustained combustion while the V–MoO_3 and Fe–MoO_3 mixtures produced poorly defined exotherms and are not capable of self sustained combustion. Enthalpic values can explain the differences in combustion behavior but to explain the shape of the heating curves, multistage reactions which occur simultaneously and in sequence must be invoked. The reaction sequence follows the order of increasing oxidation state of the metal and is most clearly observed with Ti in which TiO, Ti_2O_3, and TiO_2 were observed and with Fe in which FeO, Fe_3O_4, and Fe_2O_3 were observed. The temperature at which reaction begins appears to be independent of the nature of the metal and is 465 ±35°C. It is therefore concluded that MoO_3 is activated at this temperature and reacts in a bimolecular process with metal to form the monoxide.

INTRODUCTION

The reduction of molybdenum trioxide by hydrogen[1] or carbon[2] occurs over the temperature range 450–800°C and has been shown to be a two stage process, the MoO_3 being first reduced to MoO_2 and then to Mo. The reduction of MoO_3 in a thermite-type reaction is less well understood although its reduction by Al[3] and Mg[4] have been used extensively in extractive metallurgy. Schwalb[5] studied the kinetics of the reaction of Ge with MoO_3 over the temperature range 440–475°C and showed that reaction occurs in the solid state and is diffusion controlled. Evidence was presented indicating that oxygen produced in the dissociation of MoO_3 is the diffusing substance. However, MoO_3 has been observed[6] to be stable to 630°C, which indicates

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that the oxidation of metals by MoO_3 cannot be simply explained by diffusion of oxygen alone to the metal surface. A study was therefore undertaken to investigate the reaction of MoO_3 with various metals, using DTA and X-ray analysis, with a view of resolving the reaction sequence and gaining insight into the identity of the diffusing species.

EXPERIMENTAL PROCEDURE

TG–DTA studies

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a Mettler thermoanalyzer. A 25–35-mg sample was placed in a platinum cup and heated at a rate of 15°/min in a helium atmosphere.

X-ray diffraction studies

Samples of the metal–molybdenum trioxide, in platinum crucibles, were heated in vacuo to desired temperatures as indicated by the exotherms of the DTA curves, kept at those temperatures for 15–30 min, quenched, and then analyzed by X-ray diffraction using a Siemens Crystalloflex II. In addition, DTA's were interrupted at different temperatures and samples taken for X-ray diffraction analysis.

Combustion studies

The combustion tests were done in the following manner: About 2 g of the metal–MoO_3 stoichiometric mixture was tamped into an aluminium tube and the mixture ignited using a hot wire or a black powder squib. Propagative combustion was observed by simply noting the appearance of light at the back end of the tube.

Materials

The metal powders (-100 to -325 mesh) used in these studies were 99+% pure and were used as received. The FeO was prepared by heating 99% ferrous oxalate in vacuo. The MoO_3 and other oxides used in these studies had a purity of 99+% and were used as received.

RESULTS

Simultaneous TG and DTA studies were made on titanium–molybdenum trioxide, zirconium–molybdenum trioxide, iron–molybdenum trioxide and vanadium–molybdenum trioxide mixtures. These systems showed multistage reactions with no change in weight. In all cases thermal activity started at 465 ± 35°C.

(*A*) *The Ti–MoO_3 system*

Differential thermal analysis showed that a 50 wt.% Ti–50 wt.% MoO_3 mixture, heated in helium produced at least 3 exotherms — one peaking at 640°C, another at 730°C and the third at 860°C as shown in Fig. 1. Samples of the 50:50

mixture, heated to points *a*, *b*, and *c* in Fig. 1, were analyzed by X-ray diffraction. Interpretation of the data obtained showed that the first reaction in the Ti–MoO_3 system is

$$Ti + MoO_3 \rightarrow TiO + MoO_2 \qquad \Delta H = -78 \text{ kcal} \qquad (1)$$

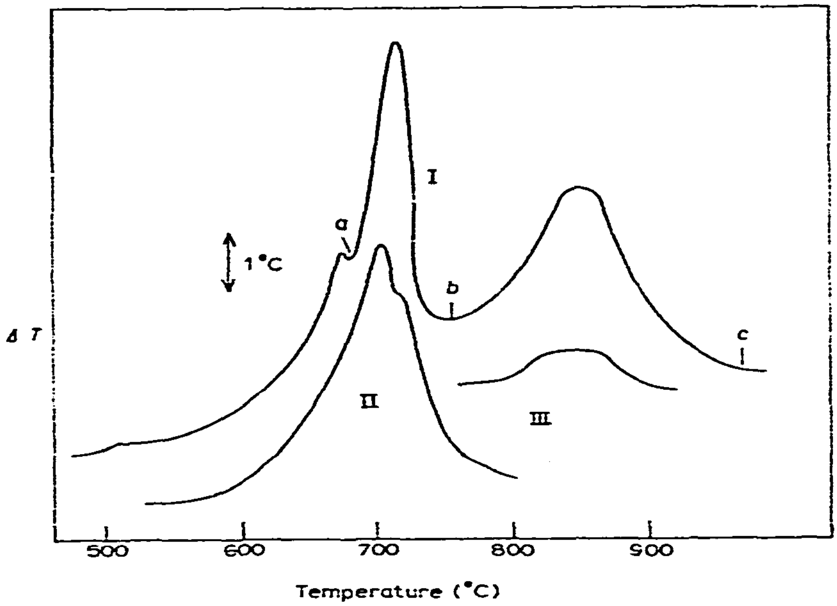

Fig. 1. DTA of (I) Ti–MoO_3, (II) TiO–MoO_3, (III) Ti_2O_3–MoO_2.

The X-ray diffraction analysis at point *b*, in Fig. 1 showed the presence of MoO_2, Ti_2O_3 and TiO_2. There are indications that Ti_3O_5 is also formed. This information coupled with X-ray data for point *a* indicate that the exotherm at 730°C is due to the reactions

$$2TiO + MoO_3 \rightarrow Ti_2O_3 + MoO_2 \qquad \Delta H = -83 \text{ kcal} \qquad (2)$$

and

$$TiO + MoO_3 \rightarrow TiO_2 + MoO_2 \qquad \Delta H = -66 \text{ kcal} \qquad (3)$$

A DTA (Fig. 1, curve II) of a TiO–MoO_3 mixture confirmed this conclusion. A well-defined exotherm with a maximum at 730°C was observed. Also, the exotherm showed a slight change in slope on the down curve indicating that at least two reactions are taking place.

The X-ray diffraction data obtained on the sample at point *c* indicate that the following reaction may be responsible for the third exotherm

$$2Ti_2O_3 + MoO_2 \rightarrow 4TiO_2 + Mo \qquad \Delta H = -51 \text{ kcal} \qquad (4)$$

A DTA of a mixture of Ti_2O_3 and MoO_2 (Fig. 1, curve III) showed that the above reaction is partially responsible for the third exotherm. The Ti_2O_3–MoO_2 mixture produced an exotherm at the same temperature as the third exotherm obtained with Ti–MoO_3. However, this exotherm is not as well defined as the third exotherm. The complexity of the X-ray data makes it difficult to further delineate other reactions which may be occurring simultaneously with reaction (4).

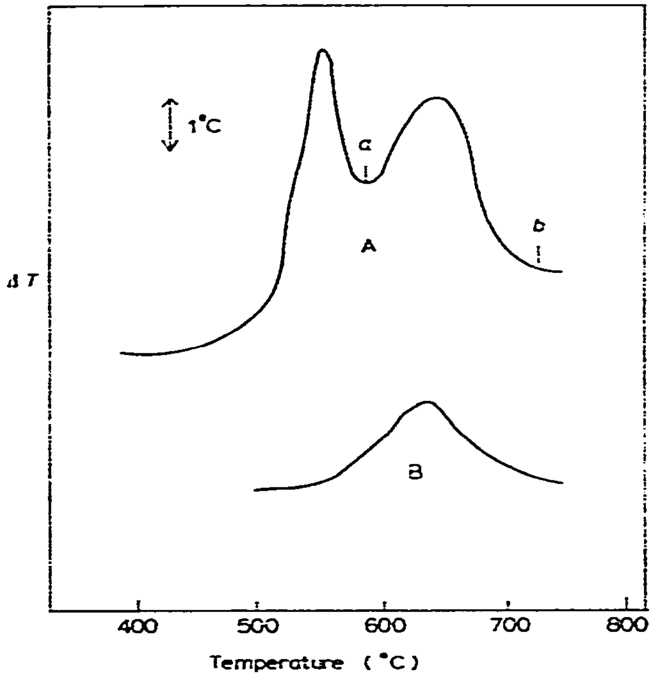

Fig. 2. DTA curves of (A) Zr–MoO_3, and (B) Zr–MoO_2.

(*B*) *The Zr–MoO_3 system*

The DTA curve obtained for a 70wt.% zirconium–30 wt.% molybdenum trioxide mixture is presented in Fig. 2, curve A. The curve shows two exotherms, the first peaks at 550°C and the second at 650°C indicating at least a two-stage reaction. The interpretation of the two-stage reaction was derived from X-ray diffraction analysis of the products after the first and second exotherms at points *a* and *b*. The results of X-ray diffraction analysis show that the reaction responsible for the first exotherm is

$$Zr + 2MoO_3 \rightarrow ZrO_2 + 2MoO_2 \qquad \Delta H = -163.5\ \text{kcal} \qquad (5)$$

The second exotherm is due to

$$Zr + 4MoO_2 \rightarrow ZrO_2 + 2Mo_2O_3 \qquad (6)$$

$$3Zr + 2Mo_2O_3 \rightarrow 3ZrO_2 + 4Mo \qquad (7)$$

There is some question[7] about the existence of Mo_2O_3. It is contended that the substance is a solid solution of Mo in MoO_2. However, the X-ray analysis corresponds to that reported[8] for Mo_2O_3. It is quite possible that the MoO_2 is reduced to Mo, which is retained in the crystal lattice of the dioxide. In that case, Eqns. (6) and (7) would be

$$Zr + MoO_2 \rightarrow ZrO_2 + Mo \qquad \Delta H = -130\ \text{kcal} \qquad (8)$$

To confirm this, a DTA was run on a zirconium-molybdenum dioxide mixture with the result shown in Fig. 2, curve B. The exotherm begins at 545°C and peaks at 625°C and corresponds closely with the second exotherm derived from the zirconium-molybdenum trioxide reaction.

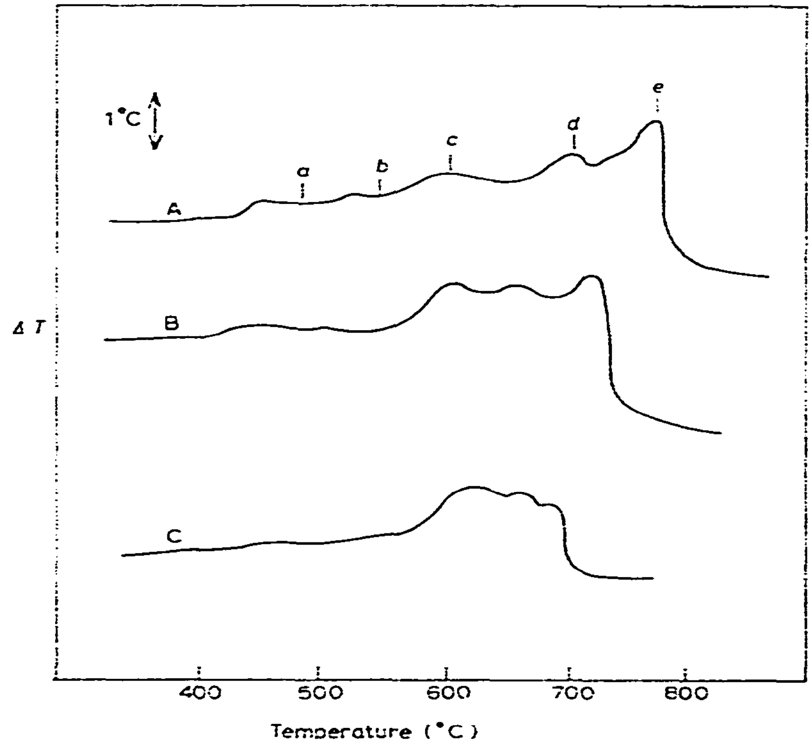

Fig. 3. DTA curves for V–MoO_3 of varying weight ratios; (A) 5:8, (B) 1:1, and (C) 2:1.

(C) *The V–MoO_3 system*

The DTA curve obtained when a 38 wt.% vanadium–62 wt.% molybdenum trioxide mixture is heated in helium to 900°C showed thermal activity from 425 to 800°C. Five exotherms were observed indicating that multistep reactions occur. The largest exotherm occurred at 785°C. Changing the vanadium:molybdenum trioxide ratio altered the DTA curve as shown in Fig. 3. Increasing the vanadium content from 38 wt.% to 67 wt.% (Fig. 3, curve B) reduced the temperature range of thermal activity from 430–800°C to 435–710°C. At the higher vanadium content (curve C) only 3 exotherms are obtained with the greatest activity occurring during the first exotherm which peaks at 610°C. The extensive overlap of the heating curves show the complexity of the V–MoO_3 reaction.

Samples of the 38 wt.% vanadium mixture, heated isothermally in vacuo at temperatures selected on the basis of the DTA curve, (points *a–e*) and quenched were analyzed by X-ray diffraction. The results obtained at point *a* showed the presence of V, V_2O_3, MoO_3 and MoO_2. This indicates that the initial reaction between vanadium and molybdenum trioxide is

$$2V+3MoO_3 \rightarrow V_2O_3+3MoO_2 \qquad \Delta H = -180 \text{ kcal} \qquad (9)$$

It is possible that VO is first formed at the elevated temperatures. However, VO, on cooling, is converted[9] to V_2O_3 and V.

The X-ray diffraction analysis of the products at points *b* and *c* showed the presence of V, V_2O_3, VO_2, MoO_2 and Mo_2O_3 or Mo since Mo_2O_3 is a solid solution of Mo and MoO_2. The amount of VO_2 present at point *c* was greater than at point *b*. No MoO_3 was present at point *c* while some was still present at point *b*. These results indicate that the exotherm with a maximum at 605°C is due to

$$2V_2O_3+MoO_2 \rightarrow 4VO_2+Mo \qquad \Delta H = -90 \text{ kcal} \qquad (10)$$

and/or

$$V+2MoO_3 \rightarrow VO_2+2MoO_2 \qquad \Delta H = -81 \text{ kcal} \qquad (11)$$

The X-ray diffraction data at point *d* shows that V is still present at 700–730°C, the amount of V_2O_3 increased at the expense of the VO_2 while the amounts of Mo, Mo_2O_3 and MoO_2 has not changed. This would indicate that the exotherm at 710°C may be due to

$$V+3VO_2 \rightarrow 2V_2O_3 \qquad \Delta H = -82 \text{ kcal} \qquad (12)$$

A V–MoO_3 mixture containing an excess of MoO_3 was heated in vacuo to 900°C, quenched, and analyzed by X-ray diffraction. The data obtained shows the presence of small amounts of V_2O_5 indicating that in the presence of excess MoO_3 the following reaction occurs

$$2VO_2+MoO_3 \rightarrow V_2O_5+MoO_2 \qquad (13)$$

The fact that V_2O_5, when heated above 600°C in vacuum[10], starts losing O_2 could account for the presence of only small amounts of V_2O_5. It was also observed that whenever an excess of V was used, the samples heated above 900°C did not contain V_2O_5 since

$$V+V_2O_5 \rightarrow V_2O_3+VO_2 \qquad \Delta H = -82 \text{ kcal} \qquad (14)$$

There is no conclusive evidence on the reaction responsible for the exotherm at 785°C in curve A. However, reaction (14) may contribute to this exotherm since V is found to be present at all temperatures below 800°C.

(*D*) *The Fe–MoO_3 system*

Differential thermal analysis showed that a 44 wt.% Fe–56 wt. % MoO_3 mixture heated in helium produced 2 exotherms — one peaking at 550°C (*b*) followed by a plateau between 600 and 630°C (*c*) as shown in Fig. 4. The reaction started at

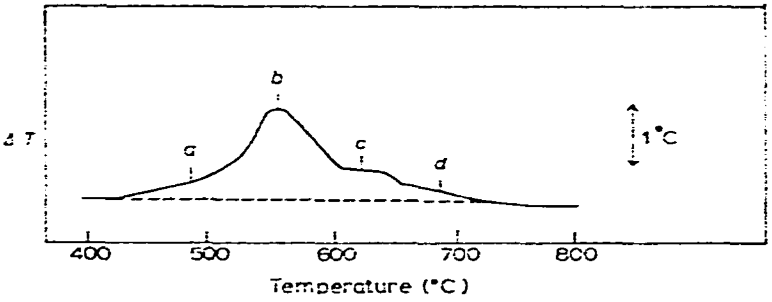

Fig. 4. DTA of Fe–MoO_3.

430 °C and ended at 725 °C. Samples of this mixture, heated isothermally in vacuo at temperatures selected on the base of the DTA curve (points *a–d*), and then quenched were analyzed by X-ray diffraction. The analyses of the products taken at point *a* show small amounts of FeO and MoO_2 in addition to the starting materials. Thus the initial reaction in the Fe–MoO_3 system is

$$Fe + MoO_3 \rightarrow FeO + MoO_2 \qquad \Delta H = -25\ \text{kcal} \qquad (15)$$

The reaction is slow initially at 473 °C but most likely accelerates at 550 °C when the exotherm peak is observed. The X-ray data, however, shows small amounts of FeO and large quantities of Fe_3O_4 at 550 °C in addition to small amounts of MoO_3 and large quantities of MoO_2. The presence of only small amounts of FeO can be explained by two possibilities. (*1*) The FeO is unstable and at temperatures above 400 °C[11] it dissociates exothermally into Fe_3O_4 and Fe. This would also explain the persistent presence of small amounts of Fe even at the high temperatures. (*2*) The FeO produced is further oxidized by MoO_3 at 550 °C according to the reaction

$$3FeO + MoO_3 \rightarrow Fe_3O_4 + Mo \qquad \Delta H = -35\ \text{kcal} \qquad (16)$$

Reaction (16) was confirmed by heating a stoichiometric mixture of FeO and MoO_3 in helium. The DTA curve showed an exotherm with a maximum at 550 °C. Analyses of the product showed Fe_3O_4 and MoO_2. When the mixture contained an excess of MoO_3, the exothermic shoulder at 600–630 °C was obtained in addition to the exotherm at 550 °C. Analysis of the product showed the presence of Fe_2O_3 in addition to Fe_3O_4 and MoO_2. Thus, the reaction responsable for the exothermic shoulder at 600–630 °C is

$$MoO_3 + 2Fe_3O_4 \rightarrow 3Fe_2O_3 + MoO_2 \qquad \Delta H = -16\ \text{kcal} \qquad (17)$$

It was observed in our experiments, that whenever an excess of Fe was used, the product at 675 °C was found to contain Fe_3O_4 and Mo in addition to MoO_2.

DISCUSSION

The reactivity of molybdenum trioxide with metal powders can be explained qualitatively on the basis of the enthalpy of the reaction in which the most stable oxide and molybdenum are produced. The enthalpic values (in cal/g) and a statement on the propagative combustion characteristics of the mixture are shown in Table I. It is noted that those reactions which are exoergic by more than 700 cal/g will propagate while those which are exoergic by less than 500 cal/g will not propagate. Undoubtedly, this phenomenon is also governed by other considerations such as thermal properties, reaction kinetics and reaction mechanism. A consequence of the high enthalpic values of the Zr–MoO_3 and Ti–MoO_3 is that the exothermic peaks in the heating curves are relatively well defined, while the exothermic peaks for the less energetic systems such as V–MoO_3 and Fe–MoO_3 are less sharp and there is considerable overlap. It is likely that this overlap is due to several reactions occurring simultaneously and indeed, the X-ray patterns of both these systems show the presence of the oxides in several oxidation states. One observation that emerges from the X-ray data is the presence of the monoxide of both titanium and iron in the early stages of the reaction. Both VO and ZrO are only stable at high temperatures and, under the conditions of the experiment, are not expected to be present.

TABLE I

GRAVIMETRIC ENTHALPIES AND PROPAGATIVE COMBUSTION REACTIONS OF METALS WITH MOLYBDENUM TRIOXIDE

$M + MoO_3 \rightarrow Mo + M_xO_y$

Metal	*M. p. of metal (°C)*	*ΔH_m (cal/g)*	*Propagative combustion*
Mg	650	−1158	Yes
Al	659	−1105	Yes
Ti	1667	−758	Yes
Zr	1855	−737	Yes
B	2027	−729	Yes
V	1917	−495	No
Mn	1244	−190	No
Fe	1536	−73	No
W	3377	−57	No
Ge	937	−47	No

However, CO is formed in the reaction[2] of C with MoO_3, and GeO forms in the early stages of the reaction of Ge with MoO_3. The latter finding was deduced from a simultaneous DTA–TG shown in Fig. 5. The weight loss beginning at 400°C is attributed to the GeO which is a volatile oxide. Since MoO_2 is always produced in the first stages as well, it is likely that the reaction

$$M + MoO_3 \rightarrow MO + MoO_2 \qquad (18)$$

is common to most metal–MoO_3 reactions. The MoO_3 does not dissociate[6] and therefore it is likely that reaction (18) occurs through an activated complex of the type $MoO_2 \cdots O{-}M$. For the activated complex to form it is necessary for the MoO_3

to become activated. This implies that activation of MoO_3 is the controlling factor in the initiation of the reaction. In fact, the temperature at which reaction is first observed is essentially constant (465 ±35°C) for the four metals studied. The small deviations can be explained by the differences in the protective quality and thickness of the oxide layer on the metal being oxidized.

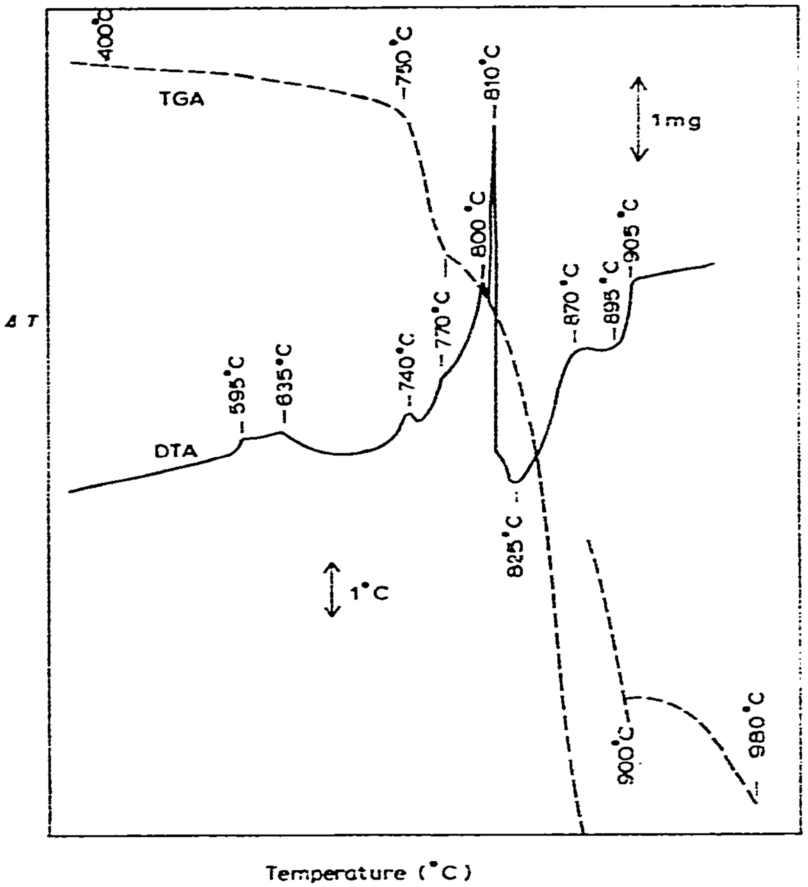

Fig. 5. DTA–TG of Ge–MoO_3

It has also been shown that the TiO and FeO react exothermally with MoO_3 and this reaction has been verified in DTA experiments. Its occurrence precludes the necessity of the MoO_3 to diffuse through the monoxide layer, at least in the Ti and Fe systems. In subsequent reactions, however, diffusion of some species must occur but the complexity of the reactions requires more elaborate studies for clarification.

It is of interest to note, that only TiO_2 is produced in the oxidation of titanium by oxygen or water vapor at temperatures below 800°C[12], while titanium oxides in their various oxidation states are formed in the oxidation of Ti by MoO_3. This means that the attacking oxygen in the Ti–MoO_3 system is different from molecular oxygen. A possible answer is that the oxygen in the activated MoO_3 reacts as O^{2-}. This explanation, while speculative, appears reasonable if a cationic vacancy diffusion mechanism is involved, as has been done for the oxidation of iron by oxygen[12].

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