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Note

Studies on the formation of zinc molybdate

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Molybdates of the type $AMoO_4$, where A denotes a divalent transition metal ion, are generally obtained by the solid state reaction of MoO_3 with oxides such as AO, AO_2, A_2O_3 or A_3O_4 by suitable reduction reactions. For example, oxides of manganese, namely, MnO_2, Mn_2O_3 or MnO (ref. 1) as well as cobalt oxide Co_3O_4 (ref. 2), react with MoO_3 to give rise to α-$MnMoO_4$ or α-$CoMoO_4$, respectively. Carlston[3] reported the formation of the molybdates of Mn, Ni, Co and Mg around 700°C from the interaction of MoO_3 and the respective divalent metal oxides while Mamykin and Batrakov[4] have obtained the molybdates of Mn, Fe, Co, Ni and Zn by sintering equimolar mixtures of the bivalent metal carbonates and MoO_3 in air in the temperature range 600–900°C. Most of these molybdates of composition $AMoO_4$ crystallise in either monoclinic or tetragonal form depending upon the size of the cation involved.

The study of the kinetics of formation of zinc molybdate is particularly interesting because, in this case, such a reduction reaction step is not possible and hence the present investigation has been undertaken with a view to gaining information on the mechanism of formation of zinc molybdate.

EXPERIMENTAL

MoO_3 was obtained by heating ammonium paramolybdate at 520°C for about 12 h. Zinc oxide, obtained from May and Baker, of purity greater than 99% was mixed with MoO_3 in 1 : 1 molar ratio. Known quantities of this mixture were heated under atmospheric conditions in silica crucibles at various selected temperatures ranging from 500 to 600°C for definite periods of time up to a maximum of 3 h. After heating for a known period of time, the samples were withdrawn from the furnace and the contents analysed for unreacted ZnO by titrating against standard EDTA solution using Eriochrome Black T indicator. The fraction of the reaction completed was calculated by material balance.

The differential thermal analysis (DTA) of the sample was carried out with a Netzsch Differential Thermal Analyser (Netzsch Gerätebau, GmbH, Selb, West Germany) in the temperature range 30–800°C.

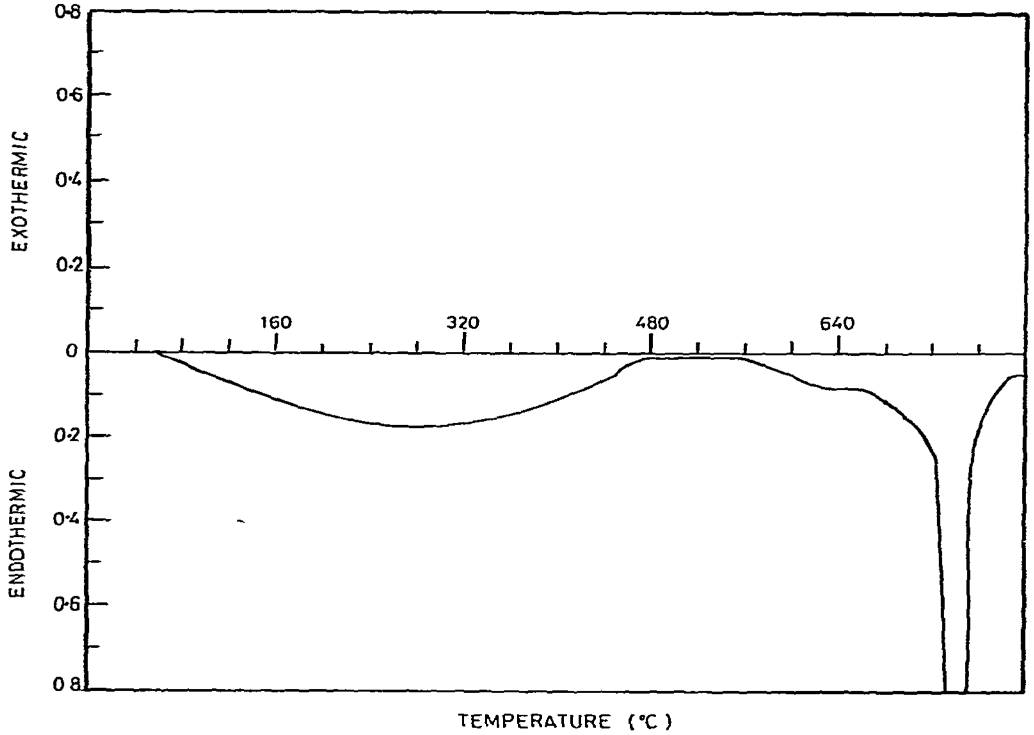

Fig. 1. DTA curve for the reaction between ZnO and MoO_3.

RESULTS AND DISCUSSION

The differential thermal analysis curve obtained for the 1 : 1 mixture showed two endothermic peaks (Fig. 1). The broad endotherm in the temperature range 100–500 °C results from the removal of adsorbed moisture as well as from the reaction between the constituent oxides. Both the dehydration as well as the solid state reaction overlap in this temperature range so that the temperature at which the reaction actually starts is not clearly discernible. The second endotherm around 750 °C is due to the polymorphic change of the molybdate formed on heating. Such a change has been reported in the literature[4] for $ZnMoO_4$ in the temperature range 650–750 °C.

The isothermal kinetic data on solid state reactions of the type

$$A(s) + B(s) \rightarrow C(s)$$

occurring in a mixture of fine powders are usually analysed through a number of expressions[5–8] which are essentially based upon the assumptions originally proposed by Jander[9]. The main assumption underlying these expressions is that the reaction is controlled by unidirectional bulk diffusion. According to Jander, the surface of one of the components, on which the reaction takes place, is continuously and completely covered with particles of the other component. According to Komatsu[10] and Schwab[11], the reaction can start at a few points of contact between the two components and the rate of the reaction is proportional to the number of contact points. On the basis of this model, Komatsu derived the expression

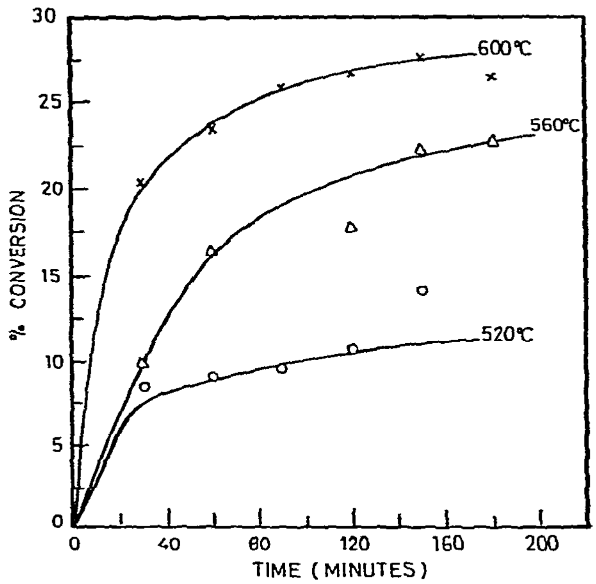

Fig. 2. Isothermal kinetic plots for the solid state reaction between ZnO and MoO_3.

$$1 - (1 - \alpha)^{1/3} = kt$$

where α is the fraction converted at time t and k is a constant. This equation has been demonstrated to be applicable to the kinetic data in the formation of a number of molybdates[2, 10, 12, 13].

The isothermal kinetic data obtained for the reaction between ZnO and MoO_3 are represented in Fig. 2 and the data have been systematically analysed through the various expressions applicable for solid state reactions. From the consistency of the values of k (Table 1), it is found that Jander's equation

$$kt = [1 - (1 - \alpha)^{1/3}]^2$$

is applicable to the kinetic data with an activation energy value of 30 kcal $mole^{-1}$.

Mechanistically, the reaction can be considered to occur as follows. Initially, MoO_3 covers the surface of ZnO by surface diffusion. Transport through the gas phase is less likely since the volatility of MoO_3 at the experimental temperatures is rather small. Once a layer of MoO_3 covers the ZnO grains, the reaction then proceeds by the diffusion through the layer of the product. In order to find out the nature of the diffusion process, an additional experiment was carried out. Two pellets, a large one of ZnO and a small one of MoO_3 were kept in contact with each other. After several hours of heating at 560°C, a bright white deposit was observed on the ZnO. This deposit was found to spread along the surface rather than towards the bulk of the pellet. The experiment showed the ease with which MoO_3 migrated over the ZnO surface, thus supporting the reaction mechanism proposed. This is in conformity with Jander's conclusion that the diffusing component is MoO_3 in the reaction between $CaCO_3$ and MoO_3.

In conclusion, it may be stated that, whichever model is appropriate for the

TABLE 1

RATE CONSTANT VALUES FOR THE FORMATION OF ZINC MOLYBDATE ACCORDING TO JANDER'S EQUATION

Time (min)	$k \times 10^5$		
	520°C	*560°C*	*600°C*
30	2.901	3.943	17.860
60	1.602	5.587	12.070
90	1.181		9.965
120	1.128	3.297	8.069
150	1.640	4.331	6.963
180		3.763	5.174

kinetics of the solid state reaction leading to the formation of molybdates, the mobile component is MoO_3 and the mechanism of the reaction involves the diffusion of the mobile component MoO_3 on ZnO and this diffusion step is rate-controlling for the overall process.

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