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STUDIES ON THE FORMATION OF MANGANESE MOLYBDATE

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ABSTRACT

The reaction of MoO_3 with various oxides of manganese (MnO, Mn_2O_3, Mn_3O_4 and MnO_2) and with $MnCO_3$ has been studied in air and nitrogen atmospheres employing DTA, TG and X-ray diffraction methods, with a view to elucidating the conditions for the formation of $MnMoO_4$. Thermal decomposition of $MnCO_3$ has also been studied in air and nitrogen atmospheres to help understand the mechanism of the reaction between $MnCO_3$ and MoO_3. The studies reveal that, whereas MnO, Mn_2O_3 and MnO_2 react smoothly with MoO_3 to form $MnMoO_4$, Mn_3O_4 does not react with MoO_3 in the temperature range investigated (480–600°C). An equimolar mixture of $MnCO_3$ and MoO_3 reacts in air to yield $MnMoO_4$, while only a mixture of Mn_3O_4 and MoO_3 remains as final product when the same reaction is carried out in nitrogen. Marker studies reveal that manganese ions are the main diffusing species in the reaction between MoO_3 and manganese oxides that result in $MnMoO_4$.

INTRODUCTION

Molybdates of transition metals ($AMoO_4$ where A denotes a divalent transition metal ion) offer an interesting class of materials with considerable potential applications. Studies of their structures[1], catalytic properties[2], infrared absorption[3] and magnetic susceptibility[4] have been reported in recent years. They are usually obtained by reacting MoO_3 with transition metal oxides AO, A_2O_3 or AO_2 at suitable temperatures[5,6]. Doyle *et al.*[7] have reported the formation of $MnMoO_4$ by heating mixtures of MoO_3 and MnO_2 or MoO_3 and Mn_2O_3 in the required mole proportion in air at 700°C, while Mamykin and Batrakov[8] have obtained it by heating an equimolar mixture of $MnCO_3$ and MoO_3 in air in the temperature range 600–930°C. That only $MnMoO_4$ (with Mn in $+2$ state) is obtained as the final product, irrespective of the oxidation state of manganese in the starting material, indicates that the reaction involves an oxidation–reduction mechanism. The present study concerns the mode of formation of $MnMoO_4$ by reacting MoO_3 with various oxides of manganese (MnO, Mn_2O_3, Mn_3O_4 and MnO_2) and with $MnCO_3$. Decomposition of $MnCO_3$ in air and in nitrogen has also been studied with a view to understanding the nature of $MnCO_3$–MoO_3 reaction.

EXPERIMENTAL

MoO_3 was prepared from ammonium paramolybdate (BDH, AnalaR) by the method given by Palmer[9]. The $MnCO_3$, MnO_2 and α-Mn_2O_3 used were reagents of certified purity. MnO was obtained by reducing α-Mn_2O_3 in a stream of hydrogen (60 ml/min) at 600°C for 12 h[10].

The differential thermal analysis (DTA) curves of the various solid samples were obtained with Netzsch apparatus (Netzsch Gerätebau, GmbH, Seib, West Germany) while the thermogravimetric (TG) studies were carried out with a Stanton Recording Thermobalance, Model HTSM (Stanton Redcroft Ltd., London). The heating rates for the DTA and TG studies were 10 and 6°C min^{-1}, respectively. For studies in inert atmosphere, cylinder nitrogen was used after passing the gas successively through activated charcoal, magnesium perchlorate, and hot copper gauze (350–400°C).

The solid products obtained at various stages of reaction were analysed by conventional analytical methods[11]. The total manganese content was determined by EDTA-titration at pH 10 using Eriochrome Black-T indicator, after reduction of manganese in the higher oxidation states to +2 state using hydroxylamine hydrochloride. Higher oxidation states of manganese (+3 and +4 states) were determined by sodium oxalate–potassium permanganate method. Molybdenum was determined gravimetrically by the oxinate method.

RESULTS AND DISCUSSION

The reaction, $MnCO_3 + MoO_3 \rightarrow MnMoO_4 + CO_2$, appears deceptively simple. Samples of $MnCO_3$ and MoO_3 heated in air at 400–600°C for 1–4 h have shown the presence of higher oxidation states of manganese, although prolonged heating gives only $MnMoO_4$. This observation suggests the possibility of an oxidation-reduction mechanism for the formation of $MnMoO_4$. It was thought that a study of the decomposition of $MnCO_3$ itself would provide a clue to the mechanism of $MnCO_3 + MoO_3$ reaction. The thermal behaviour of $MnCO_3$ was therefore studied in air and inert atmospheres by the methods of DTA and TG and the solid products characterised by chemical analysis and X-ray diffraction. The results (Fig. 1 and Table 1) reveal that $MnCO_3$ decomposes in air at 300–400°C to yield MnO_2 (endotherm centred around 400°C in DTA) which subsequently transforms to Mn_2O_3 around 550°C (endotherm in DTA). Thermogravimetric data show that the Mn_2O_3 formed undergoes further weight loss to yield Mn_3O_4 around 860°C. These findings on the decomposition of $MnCO_3$ in air are in agreement with those of Paulik and Paulik[12] and Dollimore and Tonge[13].

The decomposition in inert atmosphere (flowing nitrogen, ~200 ml/min) of $MnCO_3$ shows only one endothermic peak around 410°C in the DTA curve. Chemical analysis and X-ray diffraction of the product obtained at this temperature have shown it to be Mn_3O_4. The fact that only Mn_3O_4 is obtained directly from the decomposition of $MnCO_3$ in inert atmosphere is in conformity with the results of Westerdahl and Leader[14], who too have obtained only Mn_3O_4, and not MnO as claimed by others[13,15], by the decomposition of $MnCO_3$ in argon atmosphere.

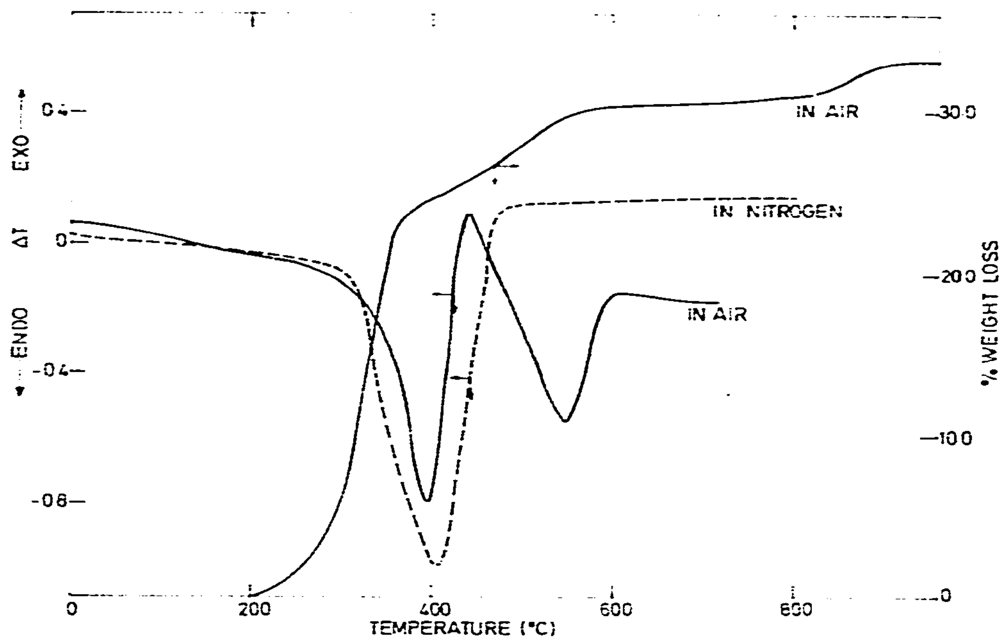

Fig. 1. DTA and TG curves of $MnCO_3$ in air and nitrogen.

TABLE 1

THERMAL DECOMPOSITION DATA OF $MnCO_3$

Atmosphere	*Temperature range (C)*	*Chemical analysis data*[a]	*XRD d spacings of the solid phase*[b]	*Product formed*	*% weight loss*	
					Obs.	*Calc.*
air	280–400	Mn^t 63.59% Mn^{IV} 63.87%	3.11 vs, 2.40 vs, 2.12 s, 1.63 vs, 1.55 s, 1.40 s.	α-MnO_2	24.30	24.37
	500–580	Mn^t 69.90% Mn^{III} 70.04%	3.78 w, 2.71 vs, 2.31 s, 2.00 m, 1.85 s, 1.66 vs, 1.44 w, 1.42 m, 1.38 w.	α-Mn_2O_3	30.70	31.33
	860–890	Mn^t 71.87%	4.90 w, 3.08 m, 2.87 s, 2.48 vs, 2.37 m, 2.21 s, 2.04 m, 1.79 w, 1.57 m, 1.44 w, 1.34 w, 1.28 w.	Mn_3O_4	33.20	33.65
nitrogen	320–440	Mn^t 71.34%	same as above	Mn_3O_4	33.50	33.65

[a] Mn^t refers to the total manganese in the solid phase. [b] X-ray diffraction *d* spacings have been obtained using MoK radiation. The observed *d* spacings compare very well with those reported for the respective compounds by Moore *et al.*[17]. The intensity of the lines is denoted as vs = very strong, s = strong, m = medium and w = weak.

Reaction of $MnCO_3$ and MoO_3

The DTA and TG results for the reaction between equimolar $MnCO_3$ and MoO_3 mixtures in air are given in Fig. 2 and Table 2. Chemical analyses and X-ray diffraction data for the intermediates and final products are also summarised in Table 2. The DTA results indicate that $MnCO_3$ decomposes around 360–400 °C to yield MnO_2 (endotherm I) which subsequently reacts around 520 °C with MoO_3 forming $MnMoO_4$ (endotherm II). The required weight losses are noted in the corresponding TG curve.

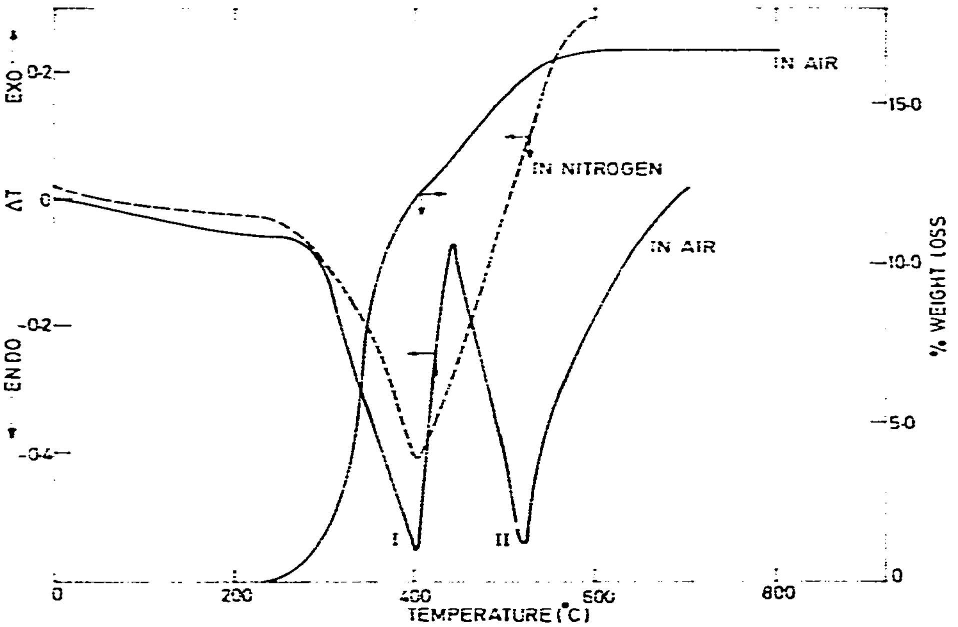

Fig. 2. DTA and TG curves of $MnCO_3$–MoO_3 mixture in air and nitrogen.

It is to be noted that the formation temperature of $MnMoO_4$ ($\sim$520 °C) falls within the range (450–580 °C) reported[13] for the conversion of MnO_2 to α-Mn_2O_3. This strongly suggests, though it cannot be taken as unequivocally proved, that Mn_2O_3 is the reactive intermediate in the reactions of $MnCO_3$ and of MnO_2 with MoO_3. This is further supported by the finding that mixtures of MnO_2 and MoO_3 and of Mn_2O_3 and MoO_3 in requisite proportions, both lead to the formation of pure $MnMoO_4$ when heated in air at around 520 °C.

The results of the reaction of $MnCO_3$ with MoO_3 in inert atmosphere (flowing N_2) stand in contrast with those obtained in air in that, only a mixture of Mn_3O_4 and MoO_3, *and not* $MnMoO_4$, is obtained as the final product when the reaction is carried out in the absence of oxygen. The DTA curve of the mixture (Fig. 2) shows, unlike the curve obtained in air, only one endotherm corresponding to the formation of Mn_3O_4. That there is no further reaction between Mn_3O_4 and MoO_3 is indicated by the absence of any other heat effects in the DTA curve even up to 700 °C.

TABLE 2

ANALYTICAL X-RAY DIFFRACTION AND THERMOGRAVIMETRIC RESULTS ON THE FORMATION OF $MnMoO_4$

Atmosphere	*System*	*Temperature range (°C)*	*Chemical analysis (%) for Mn and Mo in the product*[a]	*XRD d spacings of the product*	*Product formed*	*% weight loss*	
						Obs.	*Calc.*
air	$MnCO_3$–MoO_3 (1:1)	280–400	Mn^t 25.12 Mn^{IV} 20.03 Mo 44.72		$MnO_2 + MoO_3$	11.20	10.82
		480–600	Mn^t 25.34 Mn^{IV} 1.38 Mo 44.95	3.90 m, 3.58 m, 3.44 vs, 3.33 s, 3.21 m, 2.86 m, 2.71 m, 2.51 w, 2.37 w, 2.30 w, 1.99 m, 1.96 m.	$MnMoO_4$	16.70	17.00
	MnO_2–MoO_3 (1:1)	480–600	Mn^t 25.43 Mn^{IV} 1.24 Mo 44.28	same as above	$MnMoO_4$	7.12	6.93
	Mn_2O_3–MoO_3 (1:2)	500–600	Mn^t 25.12 Mn^{IV} 1.15 Mo 44.61	same as above	$MnMoO_4$	3.52	3.59
nitrogen	Mn_2O_3–MoO_3 (1:2)	500–600	Mn^t 25.34 Mn^{IV} 0.86 Mo 44.84	same as above	$MnMoO_4$	3.49	3.59
	MnO_2–MoO_3 (1:1)	480–600	Mn^t 25.72 Mn^{IV} 0.98 Mo 44.72	same as above	$MnMoO_4$	7.04	6.93
	$MnCO_3$–MoO_3 (1:1)	300–440	Mn^t 25.01 Mo 44.13		$Mn_3O_4 + MoO_3$	15.12	14.94

[a] Mn^t refers to the total manganese content in the solid product. [b] The observed *d* spacings agree well with those reported by Corbet and Eyraud[18]. The intensity of the lines is denoted as vs = very strong, s = strong, m = medium and w = weak.

The absence of any reaction between Mn_3O_4 and MoO_3 is further substantiated by heating separate mixtures of Mn_3O_4 and MoO_3 in air and flowing nitrogen at about 600 °C for 2–4 h. In the latter experiments, no formation of $MnMoO_4$ is detected, in contrast to the facile conversion of MnO_2+MoO_3 and $Mn_2O_3+MoO_3$ to $MnMoO_4$ under similar conditions. Thus, of the various manganese oxides, only Mn_3O_4 appears to be non-reactive towards MoO_3 at least up to 600 °C.

TABLE 3

COMPARATIVE RATES OF FORMATION OF $MnMoO_4$ FROM $MnCO_3+MoO_3$ AND MnO_2+MoO_3 MIXTURES

Temperature (°*C*)	*Time* (*sec*)	*Fraction of reaction completed*	
		$MnCO_3+MoO_3$	MnO_2+MoO_3
500	300	0.848	0.33
	400	0.97	0.73
520	300	0.96	0.74
	400	0.98	0.79
540	300	0.97	0.795

Isothermal experiments (Table 3)carried out by heating mixtures of oxides of manganese and MoO_3 and of $MnCO_3$ and MoO_3 in the temperature range 500–540 °C, show that $MnMoO_4$ is formed at a faster rate when the carbonate is used as the reactant than when manganese oxides are employed. Apparently the microscopic grain size and poor crystallinity of the freshly formed MnO_2 and Mn_2O_3 are conducive to the diffusion of Mn ions and hence the facile formation of $MnMoO_4$ from $MnCO_3$ and MoO_3 mixtures.

In order to identify the diffusion process that controls the formation of $MnMoO_4$, marker studies[16] were carried out. Pellets of MnO_2 and MoO_3 were pressed together with a thin gold wire marker in between and the composite pellet was heated at 650 °C for 30 h. The gold marker was found at the interface of Mn_2O_3 (formed from MnO_2) and $MnMoO_4$. The pellet gave way at the Mn_2O_3–$MnMoO_4$ interface while the MoO_3–$MnMoO_4$ interface remained intact. The results suggest that manganese ions are the main diffusing species during the formation of $MnMoO_4$.

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