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STUDIES ON THE REACTION BETWEEN MANGANIC OXIDE AND MOLYBDENUM TRIOXIDE

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ABSTRACT

The kinetics and mechanism of the reaction between manganic oxide (Mn_2O_3) and molybdenum trioxide (MoO_3) forming manganese molybdate in the solid state have been studied. The reactants were mixed in a stoichiometric ratio. The conversion data were recorded at four temperatures, viz. 460, 480, 500 and 520 °C, and were tested with various mathematical models of solid–solid reactions corresponding to different mechanisms. The reaction was found to belong to the diffusion-controlled reaction mechanism. Among these models, the Valensi–Carter model was found to be the most suitable. The activation energy was calculated to be 44.7 kcal g^{-1} mol^{-1} and the Arrhenius equation was given by $11.37 \times 10^9 \exp(-44700/RT)$.

Experiments to study the effect of a vacuum of 2×10^{-4} mm Hg on the conversion and kinetics of this reaction were also conducted. The conversion was found to increase under vacuum, with the same conditions of temperature and time, compared to that under atmospheric pressure. The activation energy was found to be 40.7 kcal g^{-1} mol^{-1} an the Arrhenius equation was given by $10.548 \times 10^8 \exp(-40700/RT)$.

INTRODUCTION

Solid-state reactions are of considerable industrial importance, particularly among oxides, carbonates, silicates and metals. Yet, there have been few studies yielding information about the effect of various factors on the kinetics and mechanism of solid–solid reactions. The solid-state reaction between manganic oxide (Mn_2O_3) and molybdenum trioxide (MoO_3) is examined here to gain a better understanding of solid-state reactions in general. The system finds application in the manufacture of manganese molybdate ($MnMoO_4$) (which is used as a catalyst for the oxidation of alkenes, and in ammonia synthesis) and in metal–ceramic joints.

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The reaction between Mn_2O_3 and MoO_3 takes place according to the equation

$$Mn_2O_3 + 2\ MoO_3 \rightarrow 2\ MnMoO_4 + 0.5\ O_2$$

The temperature range of the reaction is 450–600 °C. This is an addition type, elimination reaction.

This paper reports studies on the effect of reaction temperature, time and vacuum on the conversion of the solid-state reaction with a view to determining the kinetics and mechanism of the reaction.

MATHEMATICAL MODELS REPORTED IN THE LITERATURE

Mathematical models used to analyse the reaction-rate data of solid-state reactions correspond to reaction mechanisms of basically the following three different types.

Product growth controlled by difussion of reactants through the product layer

The equations in this category are as follows

Jander [1]: $K_E t = \left[1-(1-x)^{1/3}\right]^2$ (1)

Kroger–Ziegler [2]: $K_E \ln t = \left[1-(1-x)^{1/3}\right]^2$ (2)

Zhuravlev–Lesokhin–Tempelman [3]: $K_E t = \dfrac{1}{(1-x)^{1/3}} - 1$ (3)

Ginstling–Brounshtein [4]: $K_E t = 1 - \frac{2}{3}x - (1-x)^{2/3}$ (4)

Valensi–Carter [5,6]: $K_E t = \dfrac{Z - [1+(Z-1)x]^{2/3} - (Z-1)(1-x)^{2/3}}{(Z-1)}$ (5)

Dunwald–Wagner [7]: $K_E t = \dfrac{6}{\ln \pi^2(1-x)}$ (6)

Product growth controlled by nuclei growth [8]

$$\ln(1-x) = -(K_E t)^m \tag{7}$$

where m is a parameter which is a function of (a) reaction mechanism, (b) number of nuclei present, (c) composition of the parent and product phases, and (d) geometry of the nuclei.

Product growth controlled by phase boundary reactions [9]

For a sphere reacting from the surface inward

$$K_E t = 1 - (1 - x)^{1/3} \tag{8}$$

For a circular disk reacting from the edge inward, or for a cylinder

$$K_E t = 1 - (1 - x)^{1/2} \tag{9}$$

For any of the models to represent a reaction, the reaction rate constant (K_E) should be independent of the reaction time under isothermal conditions [8].

EXPERIMENTAL

Materials

Manganic oxide (Mn_2O_3)

Manganic oxide was prepared by heating manganese dioxide at 600 °C for 48 h. The manganic oxide thus prepared was tested for purity by X-ray diffraction and chemical analysis (sodium oxalate–potassium permanganate method).

Molybdenum trioxide (MoO_3)

The molybdenum trioxide used was from Loba Chemicals, and was reported to be 99.5% pure. It was also tested by X-ray diffraction and chemical analysis (oxinate method). It was heated at 550 °C for 6 h prior to use, to remove impurities such as ammonia. The properties of the materials used are presented in Table 1.

Manganic oxide and molybdenum trioxide were mixed in a stoichiometric ratio with a mortar and pestle. Mixing was carried out until the chemical analysis closely agreed with the known composition of the original mixture. The mixture was placed in alumina boats and subjected to reaction temperature in a tubular furnace. The furnace was of 5 cm in diameter and 1 m in length and capable of working up to 1000 °C. The furnace temperature could be controlled to within ±2 °C. A separate chromel–alumel thermocouple was placed near the sample to obtain an accurate sample temperature. After subjecting the samples to various reaction temperatures, they were cooled and ground. Two samples were taken at random from the ground powder of each sample for analysis.

To study the effect of vacuum on the conversions and kinetics, experiments were conducted with mixtures of manganic oxide and molybdenum trioxide (stoichiometric ratio) placing them in 10 mm ID, 8 cm long quartz tubes. The tubes were sealed under a vacuum of 2×10^{-4} mm Hg. These

TABLE 1

Properties of the materials

No.	Material	Molecular weight	Average particle size (μm)	Colour	Specific gravity
1	Manganic oxide (Mn_2O_3)	157.86	6	Black	4.81
2	Molybdenum trioxide (MoO_3)	143.85	6	Yellowish green	4.50
3	Manganese molybdate ($MnMoO_4$)	214.00	–	Reddish brown	4.02

experiments were conducted under the same conditions of temperature as those under atmospheric pressure.

The scope of the experimental data is presented in Table 2.

Chemical analysis

The analysis of the mixture of the three components (Mn_2O_3, MoO_3 and $MnMoO_4$) is based on the determination of unreacted Mn_2O_3 by sodium oxalate–potassium permanganate titration and that of total manganese by EDTA titration with Eriochrome Black-T as indicator.

RESULTS AND DISCUSSION

The conversion data at various temperatures under atmospheric pressure and under vacuum are shown in Figs. 1 and 2, respectively. A comparison of the data indicates that higher conversions are obtained for experiments conducted under vacuum for the same reaction temperature and time. This is in agreement with information in the literature [10], that the rate of formation of molybdates from the respective reactants increases under low surrounding pressure. The increased conversion for the present reaction under vacuum compared to that at atmospheric pressure under identical conditions

TABLE 2

Scope of experimental data

No.	Variable	Range
1	Temperature (°C)	460, 480, 500, 520
2	Time of reaction (min)	5, 10, 15, 20, 30, 40, 60, 80, 100, 120
3	Surrounding pressure	Atmospheric, 2×10^{-4} mm Hg

of temperature and time is expected, due to the absence of oxygen, thus providing an increased driving force for the evolution of oxygen in the reaction. After some time, however, oxygen accumulates in the tube, which should hinder the rate of reaction and thereby decrease the percentage conversion. Experimental observations indicate, however, that the percentage conversion is greater under vacuum, irrespective of time. This shows that the presence of oxygen enhances the rate of reaction. It is felt that further investigation is necessary to understand this aspect.

The experimental data were found to fit the diffusion-controlled reaction model (Valensi–Carter). Correlations of conversion data based on the Valensi–Carter model for atmospheric and vacuum conditions are shown in Figs. 3 and 4, respectively. The values of K_E obtained at different temperatures for both cases are presented in Table 3. The activation energies for the reaction of the system under vacuum and that under atmospheric pressure are found to be 40.7 and 44.7 kcal g^{-1} mol^{-1}, respectively. The Arrhenius

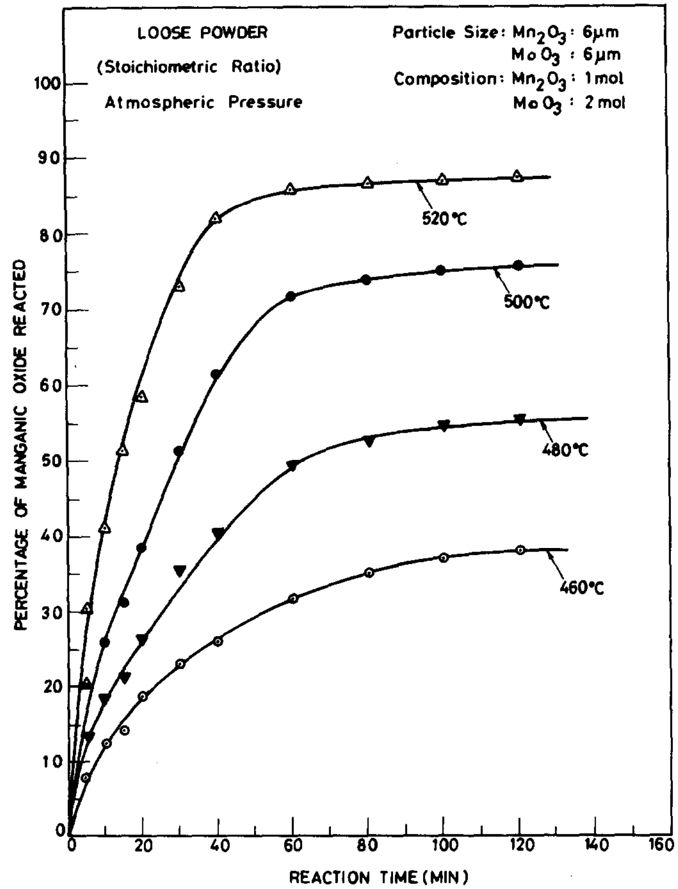

Fig. 1. Effect of temperature and time on conversion in the mixed powder system.

TABLE 3

Values of reaction rate constant (K_E)

No.	Temperature (°C)	K_E (min^{-1})
Surrounding pressure, atmospheric		
1	460	5.36×10^{-4}
2	480	12.06×10^{-4}
3	500	26.08×10^{-4}
4	520	54.43×10^{-4}
Surrounding pressure, vacuum of 2 × 10^{-4} mm Hg		
1	460	7.77×10^{-4}
2	480	16.24×10^{-4}
3	500	32.7×10^{-4}
4	520	64.1×10^{-4}

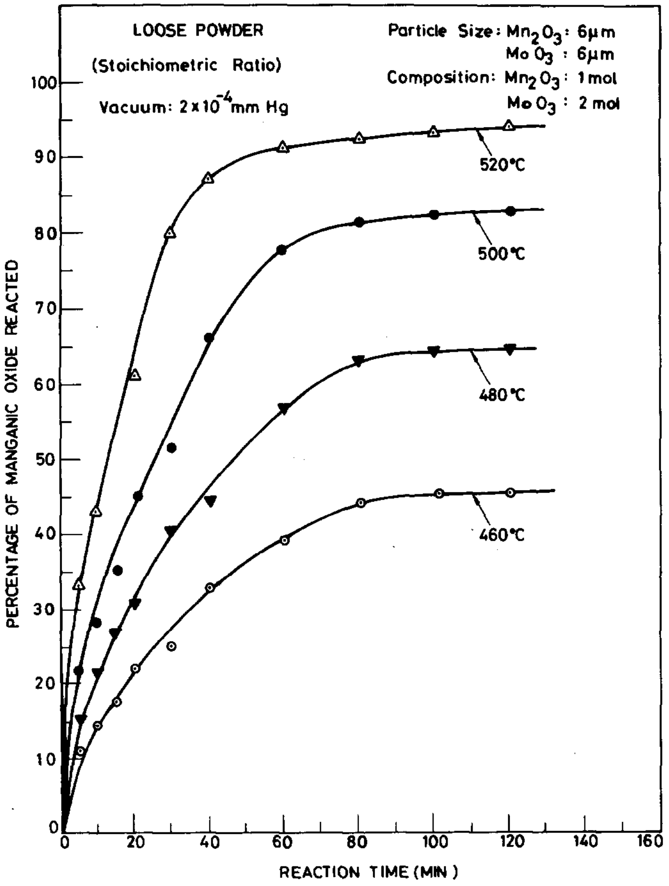

Fig. 2. Effect of temperature and time on conversion in the mixed powder system.

TABLE 4

Arrhenius equations

No.	Surrounding pressure	Arrhenius equation
1	Atmospheric air pressure	$K_E = 11.37 \times 10^9 \exp(-44700/RT)$
2	Vacuum = 2×10^{-4} mm Hg (initial)	$K_E = 10.548 \times 10^8 \exp(-40700/RT)$

plots are shown in Fig. 5 and Arrhenius equations are given in Table 4.

The mobile species reaction between the compacted reactants was determined as follows. A weighed sample of manganic oxide (Mn_2O_3) was placed in the mould of a die plunger system and a certain compaction pressure was applied. A weighed quantity of molybdenum trioxide was then

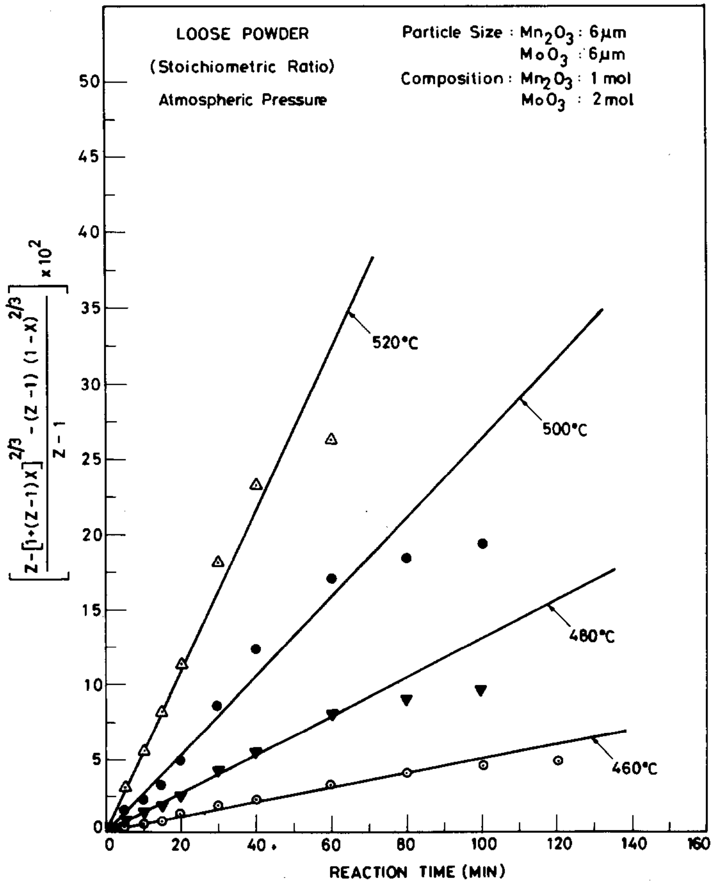

Fig. 3. Correlation of conversion data of the mixed powder system based on the Valensi–Carter model.

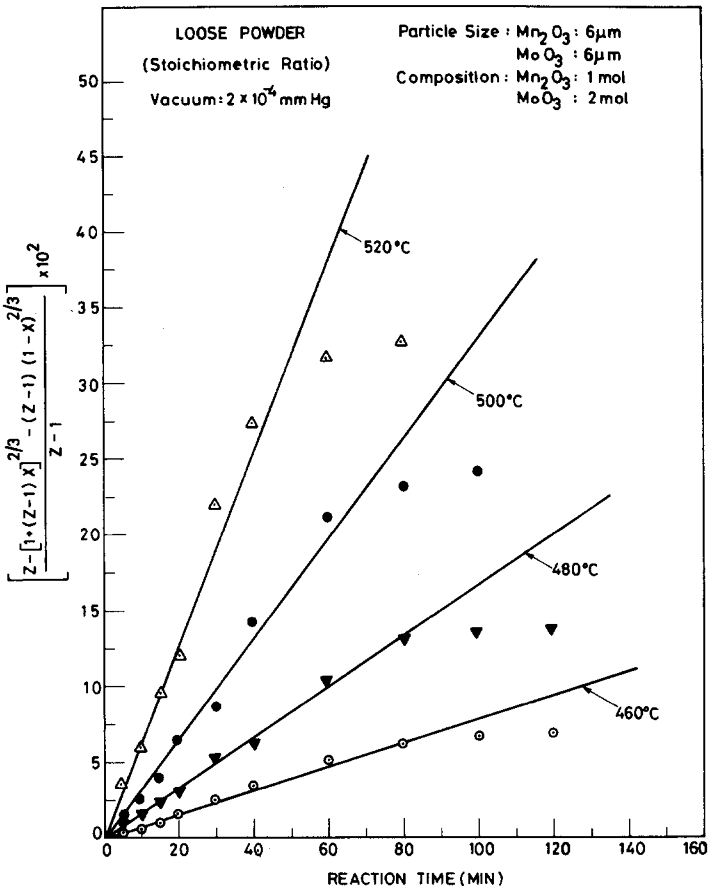

Fig. 4. Correlation of conversion data of the mixed powder system based on the Valensi–Carter model.

placed over the manganic oxide and the same compaction pressure was applied. The combined pellets were heated at 550 °C for 6 h, then separated at the interface. Growth of product was found on the manganic oxide side only, evident from the colour (brown) of the product $MnMoO_4$. There was no change on the face of the MoO_3 pellet. Thus, it was concluded that MoO_3 was the mobile species in the reaction.

CONCLUSIONS

(1) The reaction between Mn_2O_3 and MoO_3 is diffusion controlled, and the Valensi–Carter model is found to be the most suitable.

(2) Conversions are increased if the reaction is carried out under vacuum.

(3) The activation energy for the reaction is found to be lower under

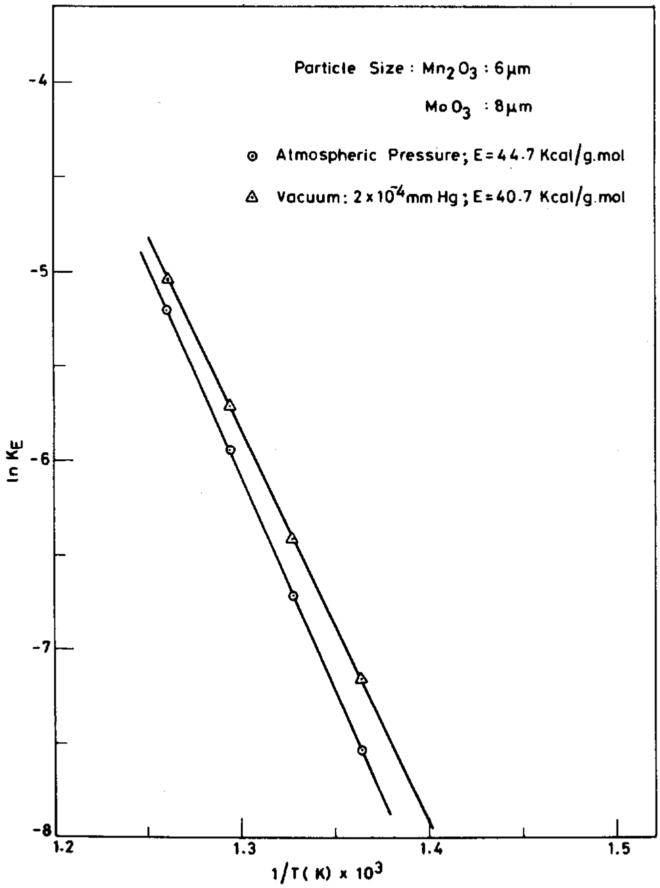

Fig. 5. Arrhenius plots for the mixed powder system.

vacuum (40.7 kcal g^{-1} mol^{-1}) than under atmospheric pressure (44.7 kcal g^{-1} mol^{-1}).

(4) MoO_3 is the mobile species in the reaction between Mn_2O_3 and MoO_3.

NOTATION

K_E	reaction rate constant equivalent (min^{-1})
R	gas constant
t	reaction time (min)
T	absolute temperature (K)
x	fraction of Mn_2O_3 reacted
Z	volume of the reaction product per unit volume of the reactant formed (in eqn. 5)

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