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# THERMAL DECOMPOSITION OF AMMONIUM TRIFLUOROMANGANATE(II)

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## ABSTRACT

Thermal decomposition of $NH_4MnF_3$ has been studied by TG, DSC and isothermal weight change. The reaction with $MnF_2$ as a final product was found to be phase-boundary controlled beyond $\alpha = 0.167$. The activation energy was calculated, and almost the same values were found for eleven integrated kinetic equations. The changes in surface area and density which occur during decomposition are also given.

## INTRODUCTION

The thermal decomposition of ammonium fluoromanganates(III) can be described by the sequence $(NH_4)_3MnF_6 \rightarrow (NH_4)_2MnF_5 \rightarrow NH_4MnF_4 \rightarrow MnF_2$ [1].

In this paper we report isothermal and dynamic thermal decomposition of ammonium trifluoromanganate(II), a perovskite structure compound [2].

## EXPERIMENTAL

The compound was prepared as described elsewhere [2]. The crystals were washed with concentrated acetic acid, dried in a vacuum desiccator over KOH and homogenized in a mortar prior to use.

The isothermal weight changes were determined by means of a Mettler TA1 thermoanalyzer. Experimental conditions: TG-Ma sample holder, platinum flat crucible 12 mm in diameter, sample weights 50 mg, atmosphere of dry air with 5 l $h^{-1}$ flow rate. Phases with different degrees of decomposition were obtained in a tube furnace supplied and regulated by a Mettler TM 16 digital regulator. The 3-g samples were heated at 200 °C in a dynamic atmosphere of dry air.

TG and DSC curves were obtained using a Mettler 2000 C thermoanalyzer. Experimental conditions: platinum crucibles, sample weights 10

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mg, heating rate 10 °C $min^{-1}$, atmosphere of dry air with 30 ml $min^{-1}$ flow rate. Intermediate phases were obtained by heating the initial compound at a heating rate of 10 °C $min^{-1}$ to the desired mass loss, and cooling the samples.

Crystallographic powder spectra were obtained with a Guinier-de Wolff camera using Cu $K\alpha$ radiation.

The density of the samples was obtained by displacement of xylene at 20 °C. The samples were evacuated and then xylene was poured into the bottle whilst the sample was still under vacuum.

The surface areas were obtained by the B.E.T. method on a Strohlein sorptometer. Measurements were carried out at the boiling point of nitrogen at atmospheric pressure. A cross-sectional area of 16.24 $Å^2$ was taken for the nitrogen molecule.

Electron micrographs were taken on a JSM-U2 JEOL electron raster microscope.

## RESULTS

Thermal decomposition of $NH_4MnF_3$ results in $MnF_2$ as final product as shown by X-ray powder photographs. A mass loss from the TG curve (Fig. 1) of 28.5% agreed with the theoretical value of 28.50%. The TG curve has two steps. However, intermediate phases with 7.0, 8.5, 10.0, 14.0 and 22.7% mass losses are mixtures of $NH_4MnF_3$ and $MnF_2$, as shown by X-ray powder photographs; no other phase was detected. The DSC curve (Fig. 1) is endothermal in the first step of decomposition. The exothermal peak at the end of decomposition may be due to the oxidation of ammonia.

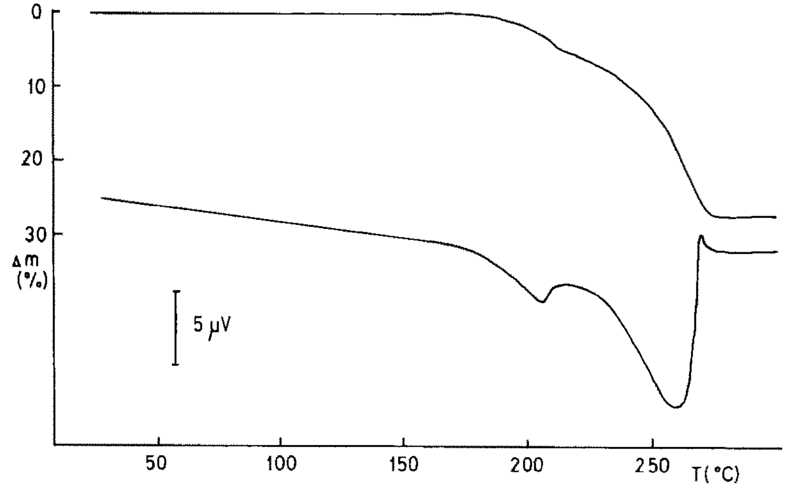

Fig. 1. TG and DSC curves of $NH_4MnF_3$.

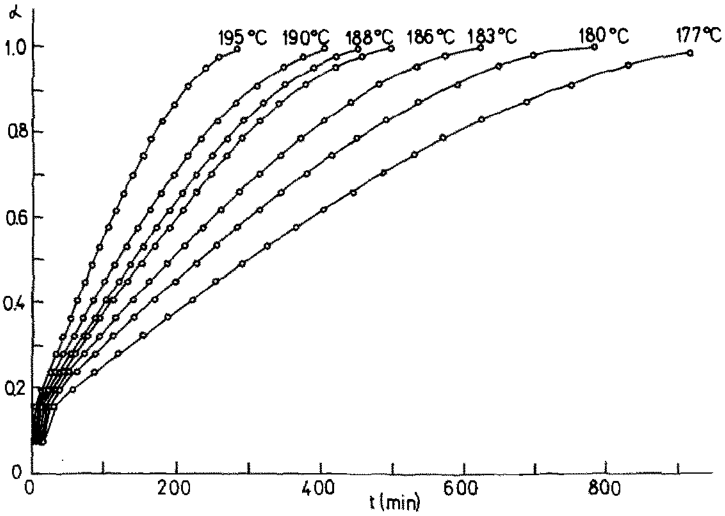

Fig. 2. Isothermal decomposition of $NH_4MnF_3$.

The kinetics of thermal decomposition $NH_4MnF_3 \rightarrow MnF_2$ were studied by isothermal decomposition between 177 and 195 °C. The $\alpha$–$t$ curves are shown in Fig. 2. The rate of decomposition drops approximately five times at $\alpha = 0.167$. For $\alpha$, $t$ points with $\alpha$ above 0.167 ($\alpha' = 0$) kinetic equations were tested in the range $0.05 < \alpha' < 0.98$. The best agreement according to correlation coefficients, was found for a phase-boundary controlled reaction for a disc, $1 - (1 - \alpha')^{1/2} = kt$, ($R_2$) (Table 1).

Dollimore suggested the general form of equation for a phase-boundary controlled reaction as $1 - (1 - \alpha)^{1/n} = kt + b$ [3]. We found the best agreement for $n = 1.58$ ($R_{1.58}$) (Table 1). The $k$ values were calculated also for kinetic equations $D_1$, $D_2$, $D_3$, $D_4$, $R_3$, $F_1$, $A_2$, $A_3$ and zero (Z) order of reaction [3] with correlation coefficients between 0.9055 and 0.9961. The

TABLE 1

Experimental values for $k$

| $T$ (°C) | $1-(1-\alpha')^{1/2} = kt$ | | $1-(1-\alpha')^{1/1.58} = kt + b$ | |
|---|---|---|---|---|
| | $k \times 10^3$ (min$^{-1}$) | Correlation coefficient | $k \times 10^3$ (min$^{-1}$) | Correlation coefficient |
| 177 | 0.967 | 0.9989 | 1.050 | 0.9998 |
| 180 | 1.236 | 0.9979 | 1.342 | 0.9999 |
| 183 | 1.498 | 0.9977 | 1.628 | 0.9999 |
| 186 | 1.920 | 0.9982 | 2.085 | 0.9998 |
| 188 | 2.082 | 0.9983 | 2.261 | 0.9999 |
| 190 | 2.308 | 0.9991 | 2.504 | 0.9998 |
| 195 | 3.375 | 0.9980 | 3.667 | 0.9999 |

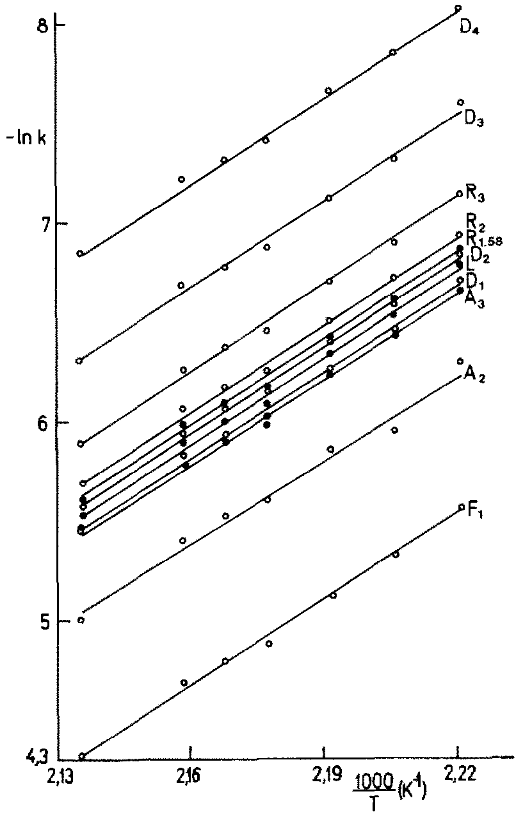

Fig. 3. Arrhenius plot for $NH_4MnF_3$ decomposition above $\alpha = 0.167$.

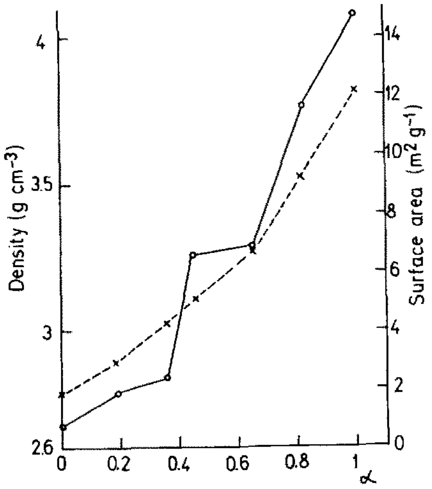

Fig. 4. Plot of surface area (solid line) and density (broken line) as a function of the fraction decomposed.

TABLE 2

Activation energies

| Arrhenius equation | | Wiedemann's method | |
|---|---|---|---|
| Mechanism | $E_a$ (kJ mol$^{-1}$) | $\alpha$ | $E_a$ (kJ mol$^{-1}$) |
| | | 0.0709 | 108 ± 7 |
| | | $\alpha'$ | |
| $D_1$ | 119 ± 4 | 0.05 | 117 ± 3 |
| $D_2$ | 119 ± 3 | 0.10 | 117 ± 5 |
| $D_3$ | 119 ± 3 | 0.15 | 116 ± 3 |
| $D_4$ | 119 ± 4 | 0.20 | 115 ± 6 |
| $R_2$ | 120 ± 4 | 0.25 | 114 ± 6 |
| $R_3$ | 119 ± 3 | 0.30 | 115 ± 3 |
| $F_1$ | 119 ± 3 | 0.35 | 120 ± 1 |
| $A_2$ | 115 ± 6 | 0.40 | 122 ± 2 |
| $A_3$ | 119 ± 3 | 0.45 | 120 ± 3 |
| Z | 119 ± 4 | 0.50 | 121 ± 4 |
| $R_{1.58}$ | 119 ± 3 | 0.55 | 121 ± 4 |
| | | 0.60 | 125 ± 2 |
| | | 0.65 | 123 ± 4 |
| | | 0.70 | 113 ± 6 |
| | | 0.75 | 114 ± 5 |
| | | 0.80 | 118 ± 7 |
| | | 0.85 | 119 ± 7 |
| | | 0.90 | 127 ± 9 |
| | | 0.95 | 123 ± 10 |

Arrhenius plot (Fig. 3) and activation energies show (Table 2) no differences between values calculated with different kinetic equations.

The whole range of values of $\alpha$ was analyzed according to the method of Wiedemann et al. [4] (Table 2). There is a good agreement between the $E_a$ values obtained by Wiedemann's method and those calculated from integrated kinetic equations. The first part of the isothermal decomposition ($\alpha < 0.167$) has the same mass loss as the first step of the TG curve, and exhibits lower $E_a$ values when calculated by Wiedemann's method.

The plot of surface area and density as a function of the fraction decomposed are given in Fig. 4, while the corresponding electron micrographs are given in Fig. 5. These electron micrographs show approximately the same particles size for all fractions and the breaking up of particles was not observed. The increase in surface area can be explained with reference to the porous structure of $MnF_2$. Change to $F_1$ mechanism in the last part of thermal decomposition, which is typical for the breaking up to small particles [5], was not observed.

Values of $n$ different from 2 or 3 in the general equation for phase-boundary controlled reaction $1-(1-\alpha)^{1/n} = kt + b$ were explained with

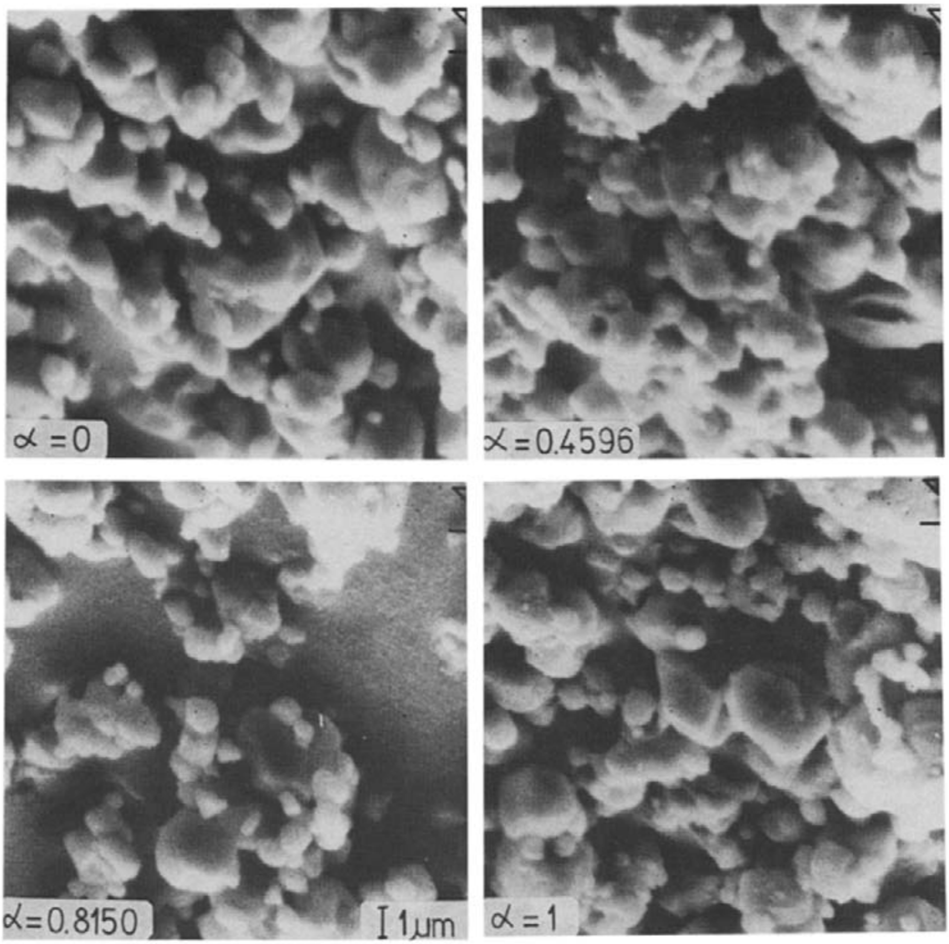

Fig. 5. Electron micrographs.

reference to the irregular shape of the reaction surface [3] caused by different volumes of solid products and educts of thermal decomposition. The difference of densities of $NH_4MnF_3$ and $MnF_2$ (fraction with $\alpha = 0$ and $\alpha = 1$ from Fig. 4), [2,6] results in different volumes of educts and products, and an irregular reaction surface in the case of the thermal decomposition of $NH_4MnF_3$; this may be the explanation of the $n = 1.58$ value.

## ACKNOWLEDGMENT

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