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EFFECT OF METAL OXIDE ADDITIVES ON THE THERMAL DECOMPOSITION OF $KMnO_4$

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ABSTRACT

The study of the thermal decomposition of potassium permanganate in air has been studied using DTA, TG and isothermal decomposition between 150 and 400°C. Rate constants were evaluated and found to be affected by the presence of foreign ions. Oxides such as Fe_2O_3 and Cr_2O_3 resulted in a lowering of the decomposition temperature. The modified catalytic mechanisms were proposed by considering the electron transfer and the oxygen-abstraction models.

INTRODUCTION

The thermal decomposition of $KMnO_4$ has been the subject of many investigations [1—3]. It was found that the elementary stages of the thermal decomposition of $KMnO_4$, which is a semiconductor of the *n*-type, are associated with electron transition from one anion to another. It was proposed [4] that the decomposition proceeds according to the equation

$$\begin{tikzcd} 2\,MnO_4^- \rightleftharpoons & MnO_4 \arrow[d] & + e(MnO_4^{2-}) \\ & MnO_2 + O_2 & \end{tikzcd}$$

which is in agreement with the experimentally determined composition of the permanganate thermolysis products. The influence exerted by additives on the rate of the process was discussed by Roginsky and Schultz [3] who found that NiO and CuO accelerate the process of chemical decomposition. They assumed that there is drop in the concentration of free electrons resulting from contact between the additive and permanganate.

Boldyrev [5] studied the electrical conductivity change during the course of the thermal decomposition reaction and came to the conclusion that at the deeper stages of decomposition, there is a change in the ratio of the donor and acceptor levels of the system.

The present investigation deals with the kinetics of isothermal decomposition of pure and doped $KMnO_4$. The reactivity of Fe_2O_3 and Cr_2O_3 as catalysts in the course of the thermolysis of $KMnO_4$ were investigated by means of TG and DTA.

EXPERIMENTAL

Thermogravimetric measurements were carried out in air using an apparatus described by Park [6]. DTA curves were obtained using the same instrument as previously employed [7]. Experiments were carried out at a heating rate of 5° C min^{-1} in air using α-Al_2O_3 as a reference material.

Fe_2O_3 and Cr_2O_3 catalysts were prepared by heating the hydroxides at 500° C in air for 5 h. The catalysts were characterized by means of surface area measurements using nitrogen adsorption at —196° C. Their S_{BET} values amount to 7 and 33 m^2 g^{-1} for Fe_2O_3 and Cr_2O_3 catalysts, respectively. The parent hydroxides were prepared from the corresponding nitrate salts. The AR $KMnO_4$ used was ground in an agate mortar with the catalysts (10 mole %) and sieved. The sieve fraction less than 200 mesh was retained and dried at 110° C before storage.

RESULTS AND DISCUSSIONS

Differential thermal analysis and thermogravimetric analysis

Figures 1 and 2 show DTA and TG curves of $KMnO_4$ with and without additives. DTA, Fig. 1 curve a, of pure $KMnO_4$ shows one endothermic peak at 300° C and an exothermic peak at 610° C. These peaks correspond to the thermal decomposition [8] and phase transformation of MnO_2 to Mn_2O_3 [9], respectively. In the DTA of the $KMnO_4$—Fe_2O_3 and $KMnO_4$—Cr_2O_3 systems, curves b and c, the peaks corresponding to the decomposition temperature are 45 and 125° C, respectively, lower than that for pure $KMnO_4$. On the basis of these data, it may be speculated that Fe_2O_3 and Cr_2O_3 promote the decomposition of $KMnO_4$.

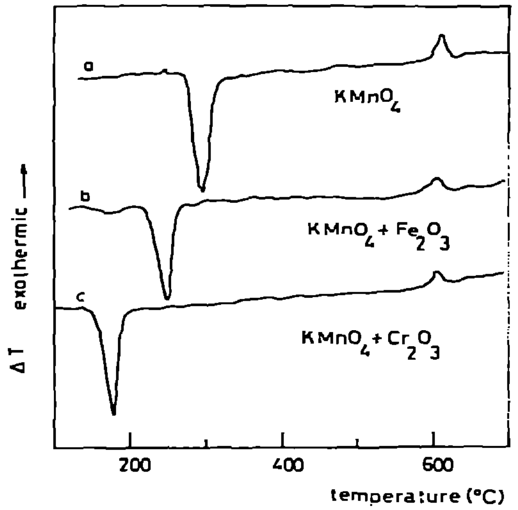
The TG curves for pure $KMnO_4$ and $KMnO_4$ doped with 10 mole % of Fe_2O_3 and Cr_2O_3 catalysts are given in Fig. 2. They show a decrease in weight corresponding to the equation

$$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

An interesting result is that the decomposition stage differs considerably. Cr_2O_3-doped $KMnO_4$ was decomposed at a temperature around 175° C while, with Fe_2O_3, the thermal decomposition temperature was around 275° C. This deviation can be related to the nature of the oxide catalyst. Study of the isothermal decomposition kinetics will therefore add more information to this point.

Kinetics of isothermal decomposition

The TGA and DTA data indicated a suitable range of 150—400° C for isothermal decomposition studies. It was found in general that the decomposition curves are of the usual sigmoid type for both the pure and doped samples and over the decomposition period, which corresponds to 80 or 90% of the complete decomposition reaction. The process can be represented by



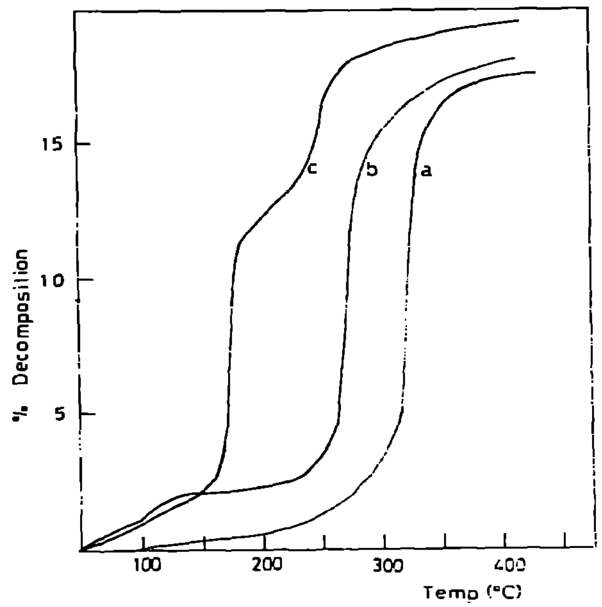


Fig. 1. DTA for pure $KMnO_4$, $KMnO_4 + Fe_2O_3$, and $KMnO_4 + Cr_2O_3$ in air.

Fig. 2. Thermogravimetric analysis curves for (a) pure $KMnO_4$, (b) $KMnO_4 + Fe_2O_3$, and (c) $KMnO_4 + Cr_2O_3$ in air.

the equation

$$\left(\frac{m}{m_0}\right)^{1/3} = kt + a \tag{1}$$

which can be written as

$$1 - (1 - \alpha)^{1/3} = kt + b \tag{2}$$

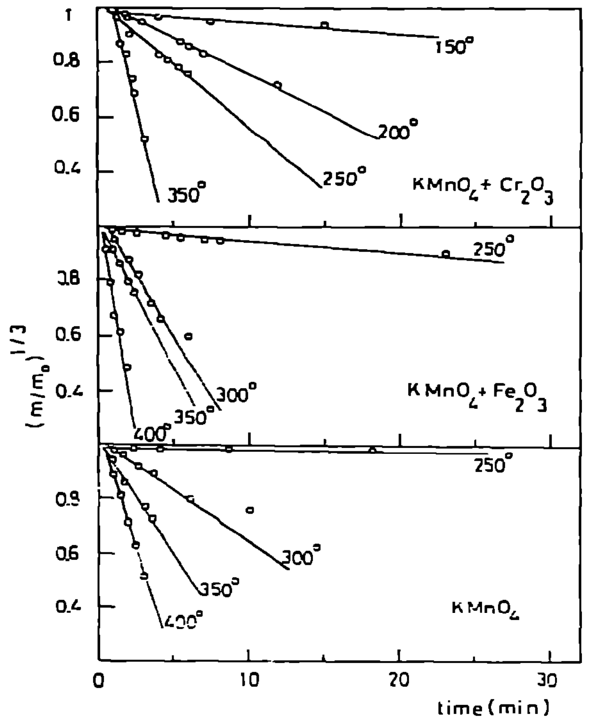
Differentiation of eqn. (1) gives

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = k_0 m^{2/3} \tag{3}$$

where the velocity constant = $3\,k\,m_0^{1/3}$, k, a and b are constants, m_0 is the weight of the volatile component of $KMnO_4$ before decomposition, and m is the weight of this component remaining at time t.

In every case investigated, plotting $(m/m_0)^{1/3}$ against t gave a good straight line, the slopes of which gave k.

Mampel [10] and Langmuir [11] state that decomposition of solids is initiated at certain centers or nuclei, usually formed on the external surface of the solid and, in some cases, also in the surface of cracks and lattice imperfections. The reaction then spreads from these nuclei both along the surface and into the interior of the solid, and along the interface between the reactant and its decomposition products. Representative Mampel plots are shown in Fig. 3. Good straight lines are obtained from which it is possible to evaluate the velocity constants, k (min^{-1}), for the decomposition reaction at various temperatures. From these k values, a plot of log k



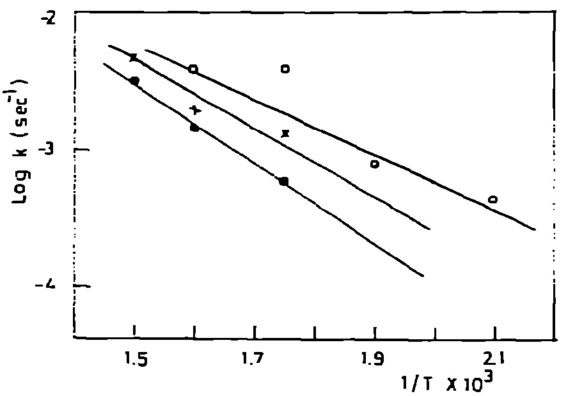


Fig. 3. Application of eqn. (1) to the thermolysis of pure and doped KMnO$_4$ in air.

Fig. 4. Arrhenius plot for the rate constant obtained by fitting the data to eqn. (1). ●, Pure KMnO$_4$; ×, KMnO$_4$ + Fe$_2$O$_3$; ○, KMnO$_4$ + Cr$_2$O$_3$.

against the reciprocal of the absolute temperature gives a good straight line as in the Arrhenius equation. The values of E_a were found to be 13.82, 11.2 and 9.4 kcal mole^{-1} for KMnO$_4$, KMnO$_4$ doped with Fe$_2$O$_3$ and Cr$_2$O$_3$, respectively (see Fig. 4).

In discussing the significance of the results presented for the effect of Fe$_2$O$_3$ and Cr$_2$O$_3$ on the rates of isothermal decomposition of KMnO$_4$, two facts are well established, namely that the decomposition still follows the interfacial mechanism, and that the energy of activation is strongly affected by the additive action.

Similar to the methods previously applied in studying permanganate thermolysis [1,2,12]. Boldyrev [5] studied the effect of MnO$_2$ as an oxidative catalyst for permanganate decomposition. He found that MnO$_2$ isolated from the products of the thermal decomposition of KMnO$_4$ proved to be the most active catalyst in the process. It was proposed by Markowitz and Boryta [13] that the effect of metal oxide on the thermal decomposition is attributed to the abstraction of atomic oxygen. On the other hand, Freeman et al. [14,15] considered it to be due to the charge transfer mechanism. Therefore, the reaction can be represented for *p*-type catalysts as

$$2\ominus_{\text{oxide}} + 2\,\text{MnO}_4^- = 2\,\text{O}_{\text{oxide}} + \text{MnO}_4 + \text{MnO}_2 = \text{O}_2 + \text{MnO}_4^{2-} + \text{MnO}_2 + 2\,\oplus_{\text{oxide}}$$

where $\oplus$ is a positive hole in the oxide, O_{oxide} is an oxygen atom abstracted by the oxide and MnO_4^- is a radical.

Since the decomposition rate increases with an increase of the product which has acceptor properties in the course of the reaction [6], one can expect that with the increase of this tendency, the chemical reaction rate will increase. Consequently, the additive action can be visualized as a solid state interaction between Fe_2O_3 or Cr_2O_3 and the active MnO_2 to increase the hole concentration as follows.

$$1/2\ O_2 + Fe_2O_3 \rightarrow 2\ Fe|Mn|' + 2\ MnO_2 + 2\ |e|^{\bullet} \tag{4}$$

$$1/2\ O_2 + Cr_2O_3 \rightarrow 2\ Cr|Mn|' + 2\ MnO_2 + 2\ |e|^{\bullet} \tag{5}$$

and

$$Cr_2O_3 \rightarrow Cr|Mn|' + MnO_2 + Cr^{6+} + 1/2\ O_2 \tag{6}$$

where $Fe|Mn|'$ and $Cr|Mn|'$ are Fe^{3+} or Cr^{3+} ions substituted in Mn^{4+} positions and $|e|^{\bullet}$ refers to a hole. If we assume that such substitution of additives into the surface layer has taken place, we come to the conclusion that the increase of holes in the surface layer of active MnO_2 produced would lead to such effects. In the case of the Cr_2O_3 catalyst, together with step 5, step 6 also occurs and creates Cr^{6+} ions which are considered to be an acceptor center [16]. This eventually leads to a higher decomposition rate. These results are in accordance with the statement of Dowden [17] that the most active oxides for oxygen abstraction are the p_d-type with vacancies in the d-orbital; p-type semiconductors would tend to increase the decomposition rate due to the presence of positive holes in the d-orbitals which would be available to accept electrons.

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