

ALKALI METAL OXIDES ACTION ON V_2O_5 CATALYSTS USED IN 2-PROPANOL DECOMPOSITION. I. THERMAL DECOMPOSITION AND ELECTRICAL CONDUCTIVITY STUDIES

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ABSTRACT

The effect of monovalent ions on the decomposition stages of ammonium metavanadate was studied using TG and electrical conductivity measurements. It has been determined that Li^+ ions affect the decomposition process in a different manner from Na^+ or K^+ ions. The mechanism by which these ions affect the decomposition process is discussed in relation to the defect structure created by the doping process.

INTRODUCTION

The thermal decomposition mechanisms of many substances pass through a number of stages between the initial and final products [1–3]. The reaction kinetics can be determined using isothermal [4] or non-isothermal weight-loss measurements [5]. Recently, it has been observed by several authors, that doping of solids can markedly influence the reaction rate and the activation energy of solid-phase reactions [6]. The effect of doping has been attributed to the change in the defect structure of reacting substances [7,8]. Decomposition of ammonium metavanadate yields vanadium pentoxide. The intermediates have been studied [9]. It is well known that ammonium metavanadate is very sensitive to the presence of different foreign substances [10], especially alkali metal oxides where the net solid products can be used effectively as a catalyst for SO_2 oxidation [11]. Hence, our goal in the current work is to study the influence of the addition of alkali metal oxides on the different decomposition stages of ammonium metavanadate through TG and electrical conductivity measurements.

EXPERIMENTAL

The parent materials doped with Li^+ , Na^+ or K^+ ions were prepared by adding calculated amounts of the nitrates of Li^+ , Na^+ or K^+ ions in ratios

ranging from 0.01 up to 5 mol% to NH_4VO_3 (AMV). The salts were admixed using bidistilled water in a porcelain dish and evaporated on a waterbath, then dried in an oven at 110°C to constant weight.

Thermogravimetric measurements were carried out at atmospheric pressure using Sartorius thermobalance (type 7085-02). The electrical conductivity measurements were carried out using the method which has been discussed previously [10].

RESULTS AND DISCUSSIONS

Thermogravimetric analysis

The TG curves of pure AMV and AMV doped with 0.5 mol% Li^+ , Na^+ or K^+ ions were traced and the decomposition temperatures are cited in Table 1.

It can be seen that the thermal decomposition process proceeds via two steps. First, the formation of the intermediate $(\text{NH}_4)_2 \cdot 0.2 \text{V}_2\text{O}_5$, secondly, the formation of intermediate ammonium hexavanadate $(\text{NH}_4)_2 \cdot 0.3 \text{V}_2\text{O}_5$, and finally, the intermediate decomposes to a V_2O_5 crystal lattice [9]. From the data in Table 1, it is also found that the addition of Li^+ ions enhances the decomposition process and Na^+ or K^+ ions produce a slight retardation effect on the decomposition process. These results could be explained via the diffusion of these ions through the AMV lattice where the ionic radii of the ions increase in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$.

Kinetics of isothermal decomposition

The kinetic process of AMV decomposition or of material doped with 0.5 mol% Li^+ , Na^+ or K^+ was studied isothermally over the temperature range $180\text{--}340^\circ\text{C}$. It has been determined that, in general, the decomposition curves are of the usual sigmoidal type. Britton et al. [12] have proposed an equation for such decomposition process as follows

$$(m/m_0)^n = Kt + b \quad (1)$$

TABLE 1

Catalytic thermal temperature for first and second intermediate processes corresponding to pure and doped AMV

Sample	First peak	Second peak
Pure AMV	198	280
AMV + 0.5 mol% Li^+	172	272
AMV + 0.5 mol% Na^+	202	292
AMV + 0.5 mol% K^+	215	326

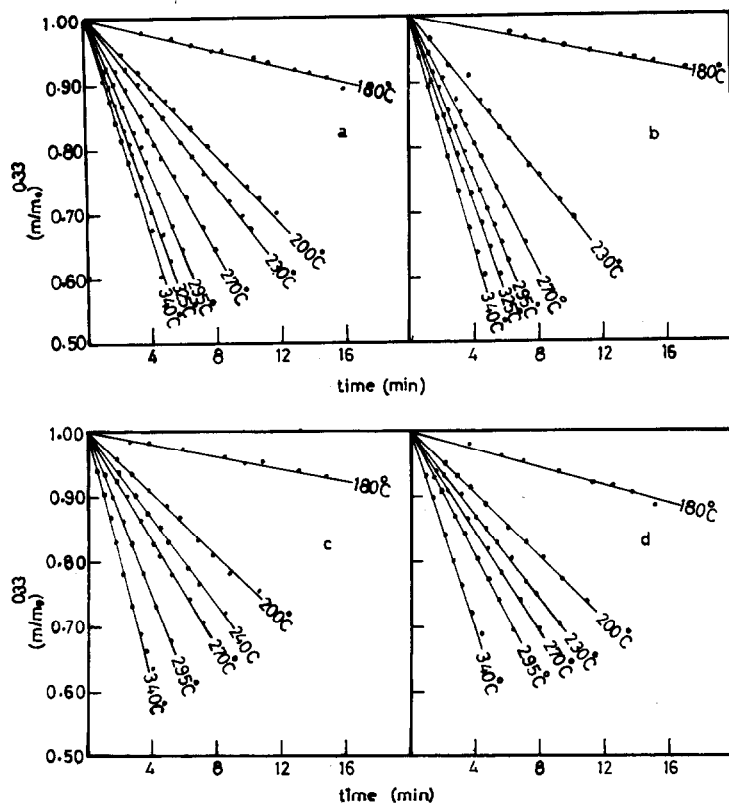


Fig. 1. $(m/m_0)^{0.33}$ versus time at various temperatures for (a) pure NH_4VO_3 , (b) NH_4VO_3 doped with 0.5 mol% Li^+ , (c) NH_4VO_3 doped with 0.5 mol% Na^+ and (d) NH_4VO_3 doped with 0.5 mol% K^+ .

where m is the weight of undecomposed volatile product at time t , m_0 is the weight of total volatile product in the initial sample, K , b and n are constants. b is found to be close to unity and n equal to 0.33. Plotting $(m/m_0)^{0.33}$ against t gives straight lines, the slopes of which give the specific rate constant, K .

Analysis of such cases was originally performed on the basis that the reactant molecules are situated at lattice imperfections which are situated

TABLE 2

E_a (kJ) values of pure AMV and AMV doped with 0.5 mol% foreign ions

Sample	E_{a_1}	E_{a_2}	$E_{a \text{ total}}$
Pure AMV	26.3	16.3	42.6
AMV + 0.5 mol% Li^+	22.6	22.6	37.4
AMV + 0.5 mol% Na^+	29.3	17.3	46.6
AMV + 0.5 mol% K^+	31.1	20.6	57.5

mainly on the surface of the solid where it possesses a low activation energy [13,14]. From the plots in Fig. 1, the velocity constants, K (min^{-1}), were estimated. Using the conventional Arrhenius plot, E_a values were obtained. These are given in Table 2.

It appears that the values of $E_{a\text{total}}$ are in accordance with the results obtained in TG analysis.

Electrical conductivity measurements

The electrical conductivity variation accompanying the thermal decomposition process was carried out and plotted in Fig. 2. Curve a, shows an increase in σ values with the temperature increase having two maxima. The two peaks discussed earlier are attributed to the formation of the bi- and hexavanadate intermediates. The effect of the additives on the conductivity variation of (AMV) during its decomposition is shown in curves b, c and d. It appears that Li^+ ions largely affect the stability of the intermediates where

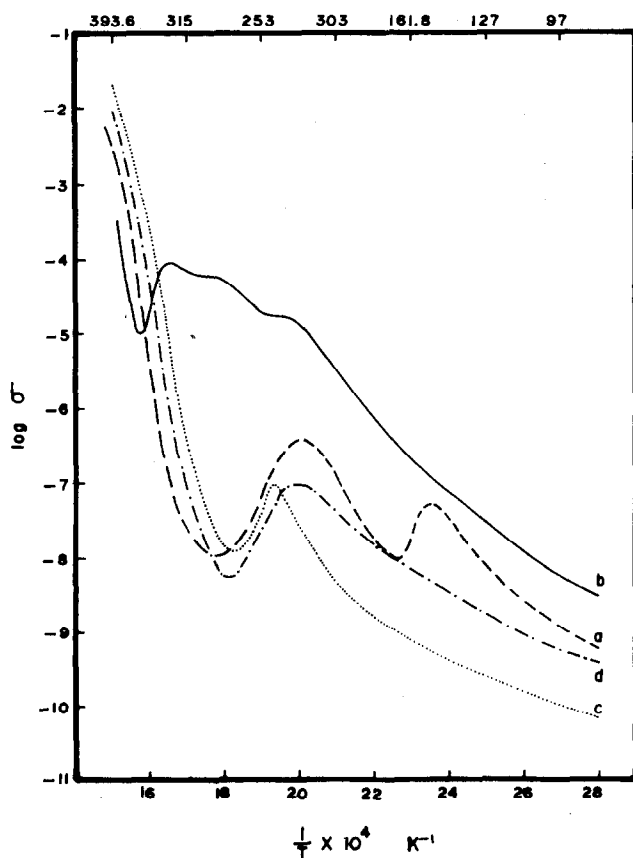
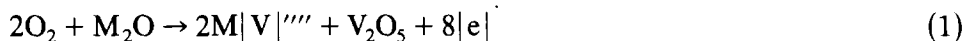


Fig. 2. $\log \sigma$ versus $1/T$ for pure NH_4VO_3 (a) and for NH_4VO_3 doped with 0.5 mol% Li^+ (b), 0.5 mol% Na^+ (c) and 0.5 mol% K^+ (d).

the two steps which appeared in the spectrum of the pure AMV disappeared. At the same time σ values were higher than those corresponding to Na^+ or K^+ ions. Addition of Na^+ or K^+ ions gives one peak which corresponds to the formation of the hexavanadate with a slight shift to higher temperature.

To discuss the effect of increasing the percentage of doping material in the lattice of the V_2O_5 structure, the values of conductance of different mixed ratios calcined at 500°C for 2 h in air were measured at 300°C as shown in Fig. 3. In spite of the fact that all the dopants are monovalent ions, the σ values are entirely different as shown. Adopting the band theory of semiconductors, the mechanism of doping can be represented as follows



Where M represents a monovalent ion such as Li^+ , Na^+ or K^+ ions and $|e|$ is a defect electron created in the doping process and $\text{M}|\text{V}|''''$ represents substitution of monovalent ions for vanadium(V) ions in the lattice points of the catalyst. Since the cross sectional area of the ions have a wide spectrum of variation, their rates of diffusion will not all be the same. Consequently it appears that the Na^+ and K^+ ions vary in such a way that Na^+ ions diffuse into the V_2O_5 lattice to a much larger extent than K^+ ions. In the case of Li^+ ions, the variation seems to be caused by the high degree of diffusion into the lattice where the defects created retard the movement of the charge carriers (which are the electrons for the n-type oxide) for conduction.

For the proportion 0.1 mol% doping it appears that there is a high degree of lattice disturbance of the V_2O_5 structure and the sequence of additive

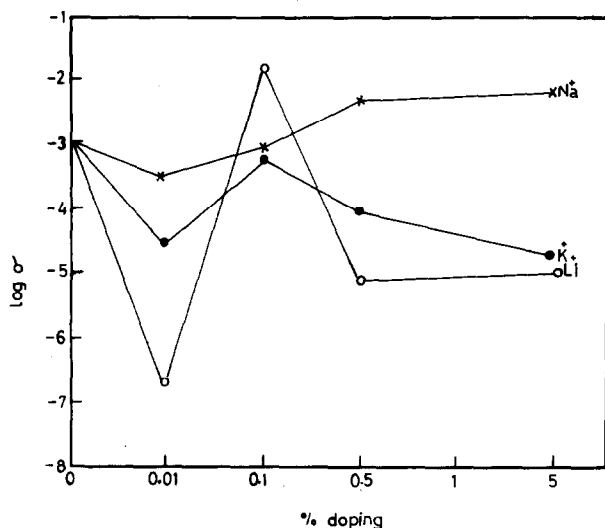


Fig. 3. Variation of $\log \sigma$ versus percentage doping for (○) V_2O_5 doped with Li^+ , (×) V_2O_5 doped with Na^+ and (●) V_2O_5 doped with K^+ ions.

variation is different. This case can add another factor to the doping mechanism where the vanadium ions released from the lattice will be in the oxidation state V^{4+} . Also, the electrons released on removal of the lattice oxygen via mechanism (2).



(where $V|V|'$ are V^{4+} ions replaces V^{5+} in its normal positions) will lead to an increase in the electron concentration in the lattice, i.e., increasing the conductivity values as was predicted experimentally.

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