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EFFECT OF SODIUM OXIDE DOPING ON SOLID-SOLID INTERACTIONS BETWEEN V_2O_5 AND Al_2O_3

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Abstract

A V_2O_5/Al_2O_3 mixed solids sample was prepared with a molar ratio of 0.4:1 Na_2O (4 and 10 mol%) was added in the form of sodium nitrate prior to calcination in air in the temperature range 500–1000°C. Solid–solid interactions between V_2O_5 and Al_2O_3 were studied using DTA and TG curves and their derivatives together with XRD techniques.

The results obtained showed that Na_2O interacted with V_2O_5 at temperatures starting from 500°C to yield a sodium/vanadium compound, $Na_{0.3}V_2O_5$ which remained stable and decomposed in part by heating at 1000°C. V_2O_5 exists in orthorhombic and monoclinic forms in the case of pure mixed solids and those containing 4 mol% of Na_2O and preheated at 500°C, and in monoclinic form in the case of the mixed solid doped with 10 mol% of Na_2O.

Heating of pure and doped mixed oxide solids at 650°C resulted in the conversion of most of the V_2O_5 into $AlVO_4$. Doping with sodium oxide enhanced the solid–solid interaction between V_2O_5 and Al_2O_3 at 650°C to produce $AlVO_4$. The produced $AlVO_4$ decomposed completely on heating at 700°C to form α-Al_2O_3 and V_2O_5, (orthorhombic and monoclinic forms).

The presence of Na_2O was found to decrease the relative intensity of the diffraction lines of α-Al_2O_3 (corundum) produced at 750°C which indicated some kind of hindrance of the crystallization process.

Heating of pure and doped mixed solids at 1000°C resulted in a further crystallization of α-corundum together with V_2O_5 and sodium vanadate, $Na_{0.3}V_2O_5$. However, the intensities of diffraction lines relative to those of the sodium vanadium compound were found to decrease markedly by heating at 1000°C, indicating partial thermal decomposition into vanadium and aluminium oxides.

Keywords: solid-solid interactions, V_2O_5/Al_2O_3, Na_2O-doping

Introduction

The thermal decomposition of ammonium metavanadate has been found to be affected by the atmosphere in contact with the solid [1–4]. In an inert atmos-

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phere or under a reduced pressure of 10^{-6} torr, it decomposed giving V_3O_7 [1, 5], while in air it decomposed producing V_2O_5 through an intermediate compound [1, 3]. The presence of a supporting material like Al_2O_3 might result in modification of the thermal decomposition process due to possible solid–solid interactions between V_2O_5 and Al_2O_3. This process could also be influenced by treating the supporting material by doping with certain foreign oxides. In fact, it has been reported in our recent investigation [6] that Li_2O-doping stimulated the solid–solid interactions between Al_2O_3 and V_2O_5 at 650°C to form $AlVO_4$. Li_2O-doping was also found to increase the thermal stability of the produced aluminium vanadate.

The present paper is devoted to studies on the effects of Na_2O-doping on the thermal decomposition of ammonium vanadate supported on Al_2O_3 and solid–solid interactions between V_2O_5 and Al_2O_3. The techniques employed were TG, DTG, DTA, dDA and X-ray diffraction.

Experimental

Materials

A known mass of $Al(OH)_3$, supplied by Prolabo Company, was heated in air at 500°C. The obtained solid was impregnated in a solution containing a calculated amount of ammonium metavanadate dissolved in dilute NH_4OH solution. The nominal molar composition of the impregnated solid was $0.4NH_4{:}VO_3{:}Al_2O_3$ and the solids were dried at 110°C to constant weight. The doped mixed solids were prepared by treating a known mass of alumina with a solution containing a calculated amount of $NaNO_3$ dissolved in the least amount of distilled water, drying at 110°C and heating in air at 500°C for 5 h. The doped alumina samples were then impregnated in ammonium metavanadate solution. The amounts of sodium, expressed as Na_2O were 4 and 10 mol%. Pure and doped mixed solids were then heated in air at different temperatures between 500 and 1000°C for 5 h.

Techniques

Differential thermal analysis of various pure and doped solids was carried out with a V2.2 A DuPont 9900 Thermal Analyzer. The rate of heating was kept at 20°C min^{-1}. A 100 mg sample of each solid specimen was employed in each experiment.

An X-ray investigation of the thermal products of pure and doped mixed solids was performed with a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation $\lambda = 1.545$ Å at 40 kV and 25 mA with a scanning speed of 2° in 2θ min^{-1}.

Results and discussions

Thermal behaviour of pure and doped mixed solids

The TG and DTA curves and their derivatives were measured for pure and doped mixed solids. The curves obtained for various solid samples were similar. Figures 1 and 2 show the thermal curves of a pure mixed solid sample and that doped with 10 mol% of Na_2O. The DTA curves of pure and doped mixed solids exhibit five endothermic and one exothermic peaks. The maxima of endothermic peaks are at 106–148°C, 231–241.7°C, 331–341°C, 636–652°C and 690–720°C. The exothermic peak appears at 390°C and is not accompanied by any change in mass. The endothermic peaks were accompanied by different

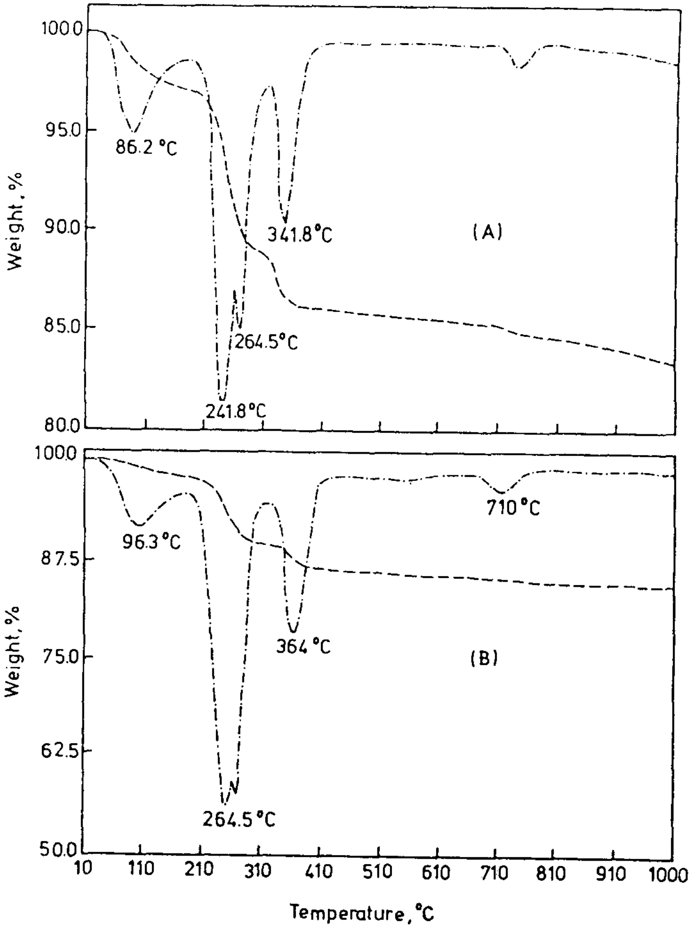

Fig. 1 TG and DTG curves of pure and doped mixed solids. (A) pure mixed solids having the formula $0.4NH_4VO_3:Al_2O_3$. (B) pure mixed solids doped with 10 mol% Na_2O

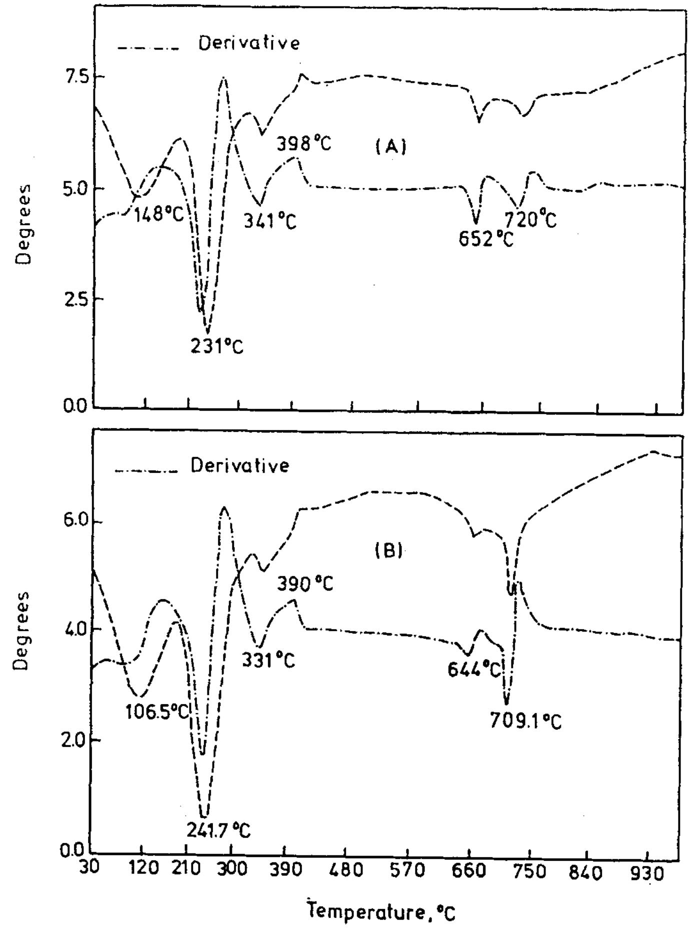

Fig. 2 DTA and d DTA curves of pure and doped mixed solids. (A) pure mixed solids having the formula $0.4NH_4VO_3{:}Al_2O_3$. (B) pure mixed solids doped with 10 mol% Na_2O

losses in mass, namely, 2–4%, 5–10%, 1–3%, 14% and 1–2%, respectively, for pure and doped mixed solids. The first peak indicates the removal of physisorbed water, the second peak corresponds to the formation of an intermediate according to:

$$6NH_4VO_3 \xrightarrow{231-241^\circ C} (NH_4)_2V_6O_{16} + 2H_2O + 4NH_3$$

The third peak characterizes the thermal decomposition of the intermediate according to:

$$(NH_4)_2V_6O_{16} \xrightarrow{331-341^\circ C} 3V_2O_5 + 2NH_3 + H_2O$$

The fourth peak indicates a solid–solid interaction between V_2O_5 and Al_2O_3 to produce aluminium vanadate, while the last peak might characterize the thermal decomposition of the produced aluminium/vanadium compound.

The exothermic peak, not accompanied by any loss in mass, might indicate a phase transformation of vanadium oxide or more probably crystallization of V_2O_5. These assumptions will be confirmed below through XRD analysis of various solids.

XRD investigation of various mixed solids

The XRD investigation of pure and doped mixed solids preheated at different temperatures was carried out on pure and doped mixed solids preheated in air at 500, 650, 750 and 1000°C.

The results obtained showed that the pure mixed solids preheated at 500°C consist of orthorhombic and monoclinic V_2O_5 and amorphous alumina (c.f. Fig. 3). This figure also shows that the doped mixed solids preheated at 500°C consist of sodium vanadate in a well crystallized form ($Na_{0.3}V_2O_5$) together with orthorhombic and monoclinic V_2O_5 [7]. However, the mixed solids treated with 10 mol% of Na_2O consist of monoclinic V_2O_5 and $Na_{0.3}V_2O_5$ phases. It seems that sodium oxide catalyzes the phase transformation, V_2O_5 (orthorhombic) → V_2O_5 (monoclinic).

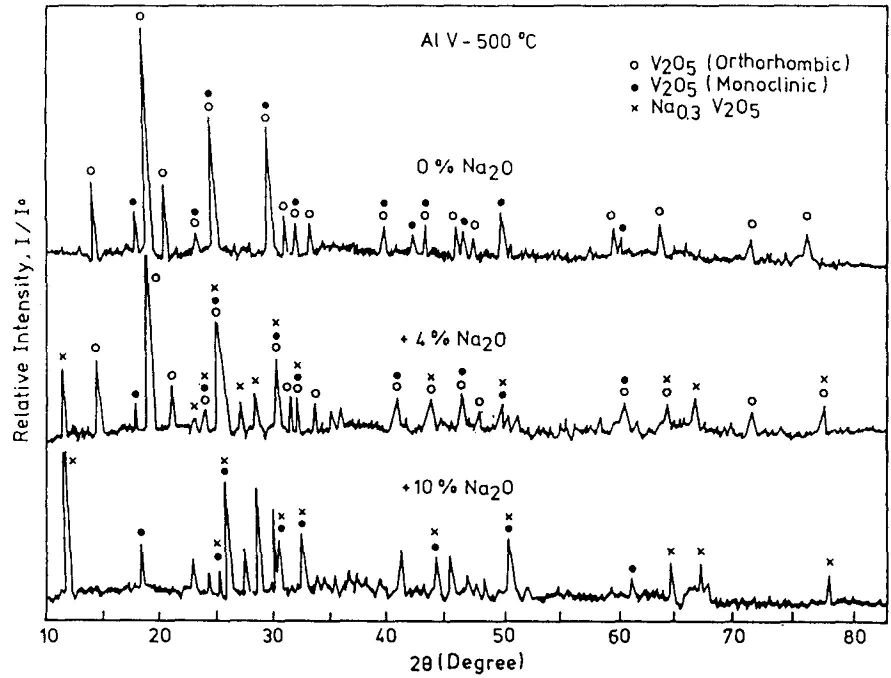

Fig. 3 XRD diffractograms of pure and doped mixed solids preheated in air at 500°C

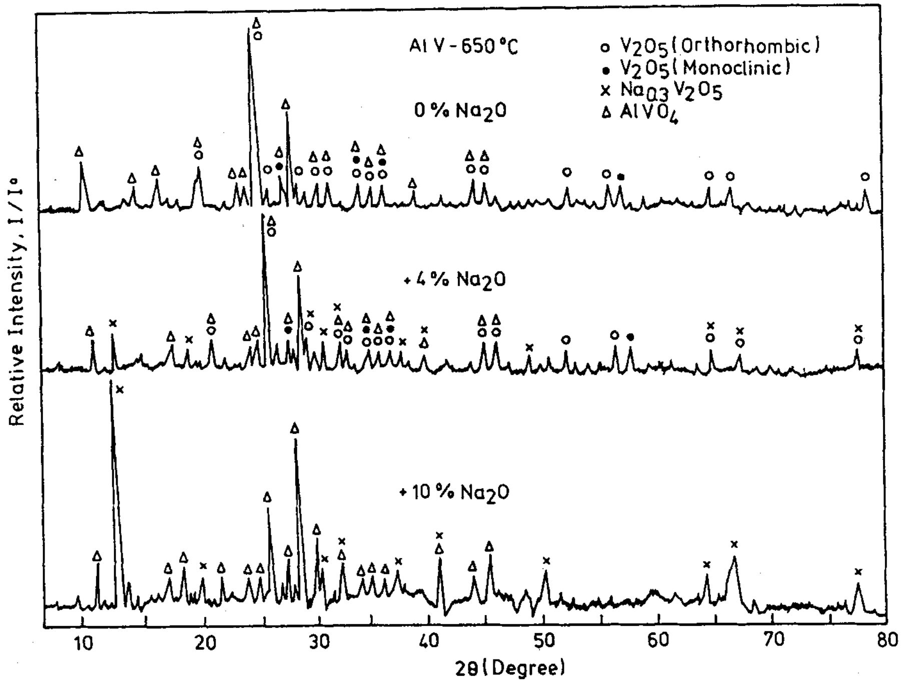

Fig. 4 XRD diffractograms of pure and doped mixed solids preheated in air at 650°C

Figure 4 shows the X-ray diffractograms of pure and doped mixed solids preheated in air at 650°C. It is clear from this Figure that the pure mixed solids preheated in air at 650°C consist of a mixture of well crystallized $AlVO_4$, $Na_{0.3}V_2O_5$ together with a small portion of unreacted V_2O_5. The presence of sodium oxide (10 mol%) resulted in a complete disappearance of all diffraction lines of the V_2O_5 phase. The endothermic peak at 644–652°C observed in the DTA curves of various solids investigated corresponds to the formation of $AlVO_4$ according to:

$$V_2O_5 + Al_2O_3 \xrightarrow{644\text{–}652^\circ C} 2AlVO_4$$

The presence of a small portion of unreacted V_2O_5 in the case of the pure mixed solid preheated at 650°C indicates that the completion of the above mentioned reaction producing $AlVO_4$ requires a prolonged heating at this temperature. The presence of 10 mol% Na_2O was found to be enough for the completion of the solid–solid interaction between Al_2O_3 and V_2O_5. The promotion effect of Na_2O could not be directly related to the dissolution of sodium ions in the V_2O_5 lattice, sodium ions being much bigger than V^{+5} ions (the ionic radii of Na^+ and V^{+5} are 0.95 and 59 Å, respectively [8]). However, sodium oxide has been observed to catalyze the phase transformation of orthorhombic

V_2O_5 to monoclinic V_2O_5. It seems that monoclinic V_2O_5 interacted with Al_2O_3 more easily than orthorhombic V_2O_5 to produce $AlVO_4$.

Figure 5 shows the XRD patterns of pure and doped solids preheated at 750°C. The diffractograms of pure mixed solids include all the diffraction lines of Al_2O_3 (α-corundum) together with the lines of the monoclinic and orthorhombic V_2O_5 phases. The relative intensities of the diffraction lines of the orthorhombic and monoclinic phases are almost the same which might indicate their presence in equimolar proportion. It seems that V_2O_5 enhances the crystallization of Al_2O_3 into α-corundum at 750°C. Inspection of Fig. 5 also reveals that the intensity of the diffraction lines of α-corundum decreases by increasing amount of the sodium oxide present. In other words, Na_2O hinders the crystallization of α-corundum. The retardation effect of the crystallization process due to doping with sodium oxide might result from the formation of an amorphous film of sodium aluminate which covers the aluminium oxide grains, this film might act as a barrier opposing the crystallization of α-Al_2O_3 (corundum). In fact, it has been reported (9) that doping of the CuO/Al_2O_3 system with sodium oxide decreases markedly the crystallization process of α-Al_2O_3 (corundum) at 900°C.

Figure 6 shows the XRD patterns of pure and doped mixed solids preheated in air at 1000°C. It can be seen in this Figure that all the diffraction lines of the well crystallized α-Al_2O_3 (corundum) and V_2O_5 (monoclinic and orthorhombic) were detected in the patterns of the pure mixed solids.

The doping process brought about the complete disappearance of free V_2O_5 phases. It can be seen from Fig. 6 that the intensities of the diffraction lines

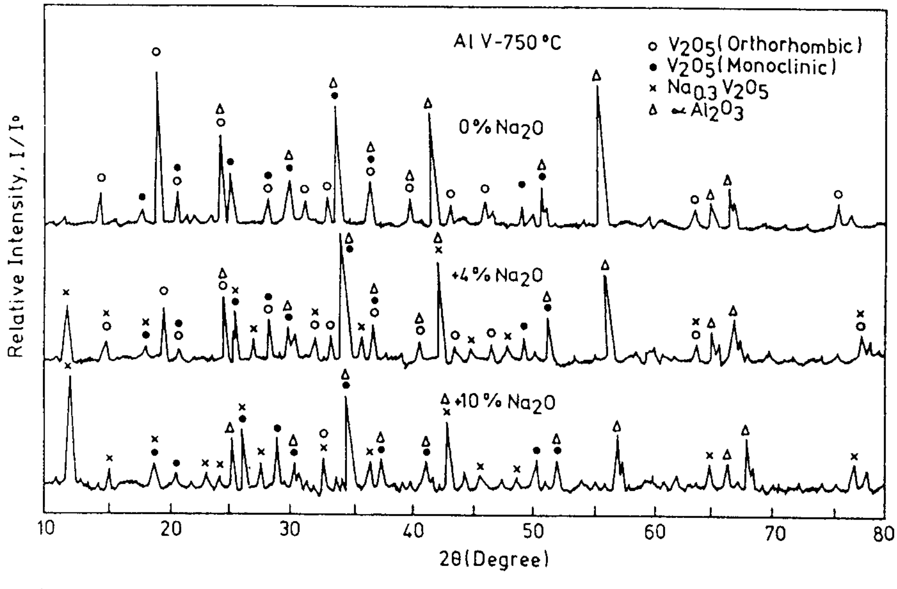

Fig. 5 XRD diffractograms of pure and doped mixed solids preheated in air at 750°C

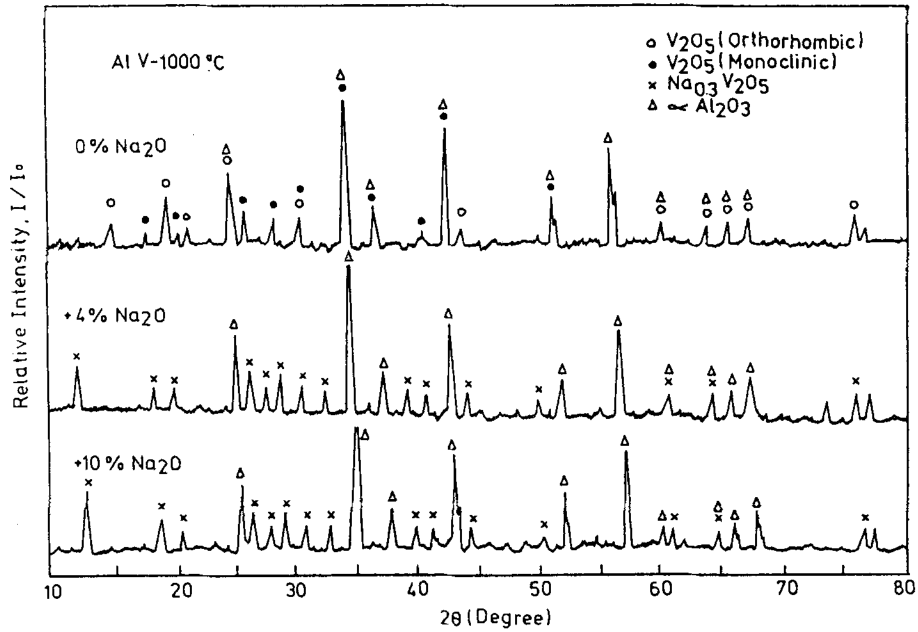

Fig. 6 XRD diffractograms of pure and doped mixed solids preheated in air at 1000°C

compared to those of sodium vanadate $Na_{0.3}V_2O_5$ decrease significantly which indicates its partial decomposition into V_2O_5 and Na_2O. The disappearance of all the diffraction lines of V_2O_5 phases due to doping with sodium oxide at 1000°C might be attributed to either its presence as an amorphous phase or its dissolution in the α-Al_2O_3 lattice. The presence of an amorphous V_2O_5 phase at 1000°C is quite improbable, so the dissolution of V_2O_5 in the Al_2O_3 lattice might account for its absence as a separate phase. It seems that doping with sodium oxide enhances the dissolution of V_2O_5 in the Al_2O_3 lattice.

It has been previously reported [10] that α-Al_2O_3 can dissolve 41.4 weight% of MoO_3 by heating the mixed oxides in air at 1000°C, forming a solid solution.

Conclusions

The results permit the following conclusions:

1 – V_2O_5 interacts with sodium oxide at temperatures starting from 500°C, yielding sodium vanadate $Na_{0.3}V_2O_5$ which remains stable during heating at temperatures below 1000°C, then decomposes in part at this temperature producing V_2O_5 and Na_2O.

2 – V_2O_5 interacts readily with Al_2O_3 at 650°C to give $AlVO_4$, doping with sodium oxide enhances this solid–solid interaction.

3 – Doping of the V_2O_5/Al_2O_3 system with sodium oxide catalyzes the V_2O_5 (orthorhombic) → V_2O_5 (monoclinic) phase transformation at temperatures starting from 500°C.

4 – Doping of vanadium/aluminium mixed oxides with sodium oxide at 1000°C enhances the dissolution of V_2O_5 in the Al_2O_3 lattice, producing a homogeneous solid solution.

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