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Effects of alkali-metal ions on the thermal decomposition of ammonium metavanadate supported on alumina

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The thermal decomposition of ammonium metavandate (AMV) supported on γ-alumina (1 : 1 mol) and treated with alkali-metal ions was investigated using differential thermal analysis (DTA), thermogravimetric analysis (TGA), infrared (i.r.) absorption spectroscopy and X-ray diffraction (XRD). The results revealed that the presence of alkali-metal ions did little to affect the thermal decomposition processes of AMV supported on alumina. However, these ions enhanced creation of V^{4+} ions by heating the samples in air at 400 °C. The oxides produced underwent a solid–solid interaction at 500–700 °C, forming alkali-metal vanadates. The formation of these spinels was found to be strongly dependent on the degree of diffusion and the concentration of the alkali-metal ions. Moreover, the addition of a higher concentration of alkali-metal ions inhibits the formation of aluminium vanadate while enhancing the crystallinity of γ- to δ-alumina.

1. Introduction

Vanadium-pentoxide catalysts of the monolayer type have aroused considerable attention during the last few years. Many studies have been concerned with the structure of the catalysts, and it appears that the choice of the support and its loading are the most important factors [1, 2]. γ-alumina is known to greatly increase the degree of depression of most catalytically active phases, so it is commonly employed as a catalyst support for a large variety of catalysts [3–6]. The influence of alumina supports on the thermal decomposition of ammonium metavanadate (AMV) has been recently reported [7, 8]. The results obtained [8] indicated that alumina supports affect the thermal decomposition of AMV as well as the surface site V = O. The addition of small additives of certain foreign cations to the aluminas has been found to influence the chemical interaction between the loaded oxides and their support [9–11]. However, the effect of the alkali-metal-ion dopants on the thermal decomposition of AMV supported on alumina or the solid–solid interaction between V_2O_5 and Al_2O_3 have not yet been investigated to our knowledge. Therefore, this work was conducted to study the effect of Li^+, Na^+ or K^+ ion dopants on the thermal decomposition of AMV, supported on γ-alumina, and on the mutual solid–solid interaction between V_2O_5 and Al_2O_3. The techniques employed were thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction (XRD) and infrared (i.r.) absorption spectroscopy.

2. Experimental procedure

2.1. Materials

The starting materials were AnalaR-grade chemicals. γ-alumina was prepared by thermal decomposition of pure $Al(OH)_3$ at 500 °C in air for 5 h. AMV supported on γ-alumina (1:1 mol), was prepared by an impregnation method and dried at 100 °C. Supported AMV specimens were then treated with solutions containing known amounts of alkali-metal hydroxides, and then dried at 100 °C. Supported AMV and modified samples were calcined in air at 400 and 700 °C for 4 h. The amounts of alkali-metal hydroxides added were 1, 3 and 7 wt %.

2.2. Techniques

TGA and DTA of AMV, supported on alumina and treated with alkali-metal ions, were carried out with a Shimadzu computerized thermal analysis system DT-40. The system includes programs which process data from the thermal analyser with the chromatopac C-R3A. The rate of heating was kept at 10 °C min^{-1}. α-alumina powder for DTA standard material was applied as a reference.

XRDs for the thermal products of AMV, supported on alumina and treated with 7 wt % alkali-metal ions, were obtained using a Philips XRD model PW 2103, applying a Cu target and Ni filter. The distances were calculated and compared with data in ASTM cards [12].

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I.r. spectra of the solid products were recorded using a Pye Unicam Sp3-300 spectrophotometer in the range 1600–200 cm^{-1} with a KBr-disk technique.

3. Results and discussion

3.1. Thermal decomposition of AMV supported on alumina and treated with alkali-metal ions

Fig. 1 shows the TGA and DTA curves of AMV supported on γ-alumina and treated with Li$^+$ ions. Fig. 1a shows that the decomposition of untreated AMV supported on alumina exhibits four stages, with maxima at 190, 224, 304 and 660 °C. The TGA curve shows that AMV loses weight on heating in three steps. The first endothermic peak, with about a 5.8% loss in weight, indicates the decomposition of AMV to the intermediate ammonium bivanadate $(NH_4)_2V_4O_{11}$. The second endothermic peak was accompanied by a loss of 1.8%, corresponding to the decomposition of ammonium bivanadate to the intermediate ammonium hexavanadate $(NH_4)_2V_6O_{11}$. The third endothermic peak, which was followed by a 3.8% weight loss, corresponds to the decomposition of ammonium hexavanadate to V_2O_5 [8, 13, 14]. The fourth endothermic peak, which is not followed by any change in weight, is attributed to the formation of very crystalline aluminium vanadate spinel [7, 8].

Fig. 1b, c, d shows TGA and DTA of AMV supported on γ-alumina and treated with 1, 3 and 7 wt % Li$^+$ ions. Analysis of the data on the thermal behaviour of these solids indicates that: (i) the addition of 1 or 3 wt % Li$^+$ ions has little affect on the decomposition of AMV, while the addition of 7 wt % Li$^+$ ions leads to a decrease in the peak area of all decomposition stages on heating up to 350 °C; (ii) the TGA curves indicate that the decomposition proceeds in three steps; (iii) the exothermic peaks located at 625, 615 and 610 °C (for 1, 3 or 7 wt % Li$^+$ ions, respectively) correspond to the formation of lithium vanadate, LiV_6O_{15} [15] and, moreover, the formation of this spinel increases on increasing the concentration of Li$^+$ ions; and (iv) a broad endothermic peak covers the

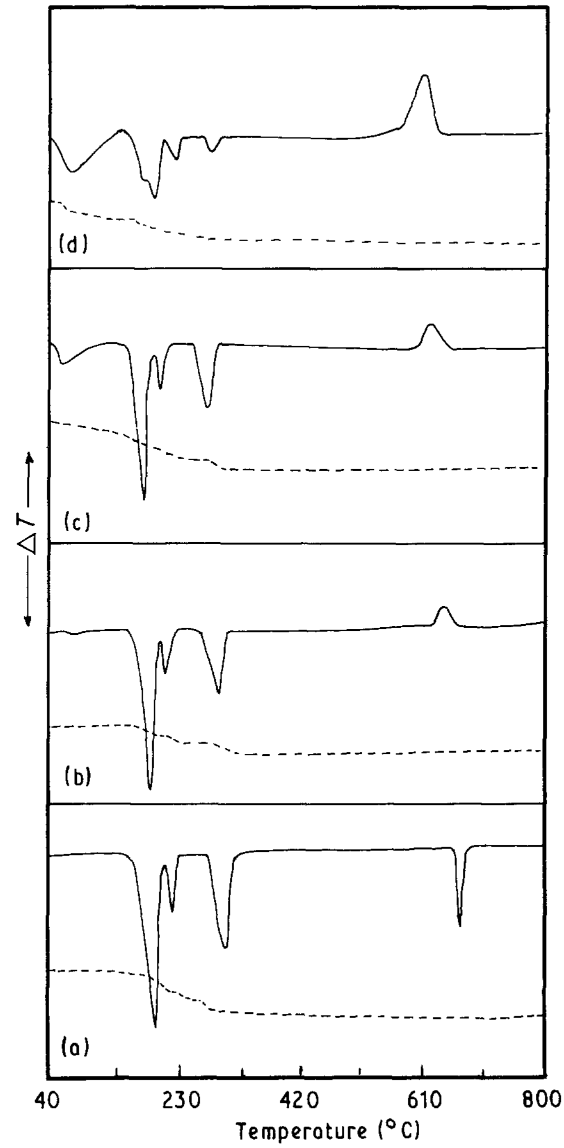

Figure 1 DTA (——) and TGA (- - -) curves of AMV supported on alumina (a) (1 : 1); and doped with LiOH (b) 1 wt %, (c) 3 wt %, and (d) 7 wt %.

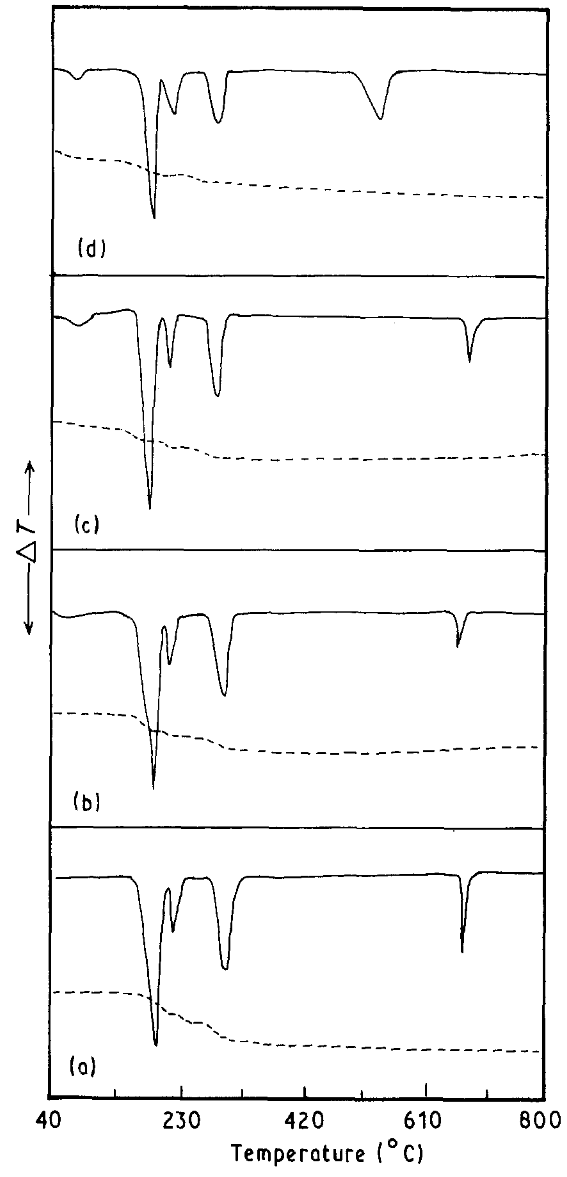

Figure 2 DTA (——) and TGA (- - -) curves of AMV supported on alumina: (a) (1 : 1), and doped with NaOH (b) 1 wt %, (c) 3 wt %, and (d) 7 wt %.

temperature range 50–150 °C, resulting from the evolution of physically adsorbed water.

Fig. 2 shows the thermal decomposition of AMV supported on γ-alumina doped with 1, 3 or 7 wt % Na^+ ions, (Fig. 2b, c, d, respectively). The following observations can be made. (i) The thermal decomposition stages of supported AMV are little affected by the different ratios of Na^+ ions; (ii) The endothermic peaks at 650 and 645 °C (Fig. 2b, c) correspond to the formation of aluminium vanadate [7, 8]. This means that the presence of Na^+ ions in low ratios may enhance the solid–solid interaction between V_2O_5 and Al_2O_3 giving $AlVO_4$. (iii) On increasing the ratio of Na^+ ions (Fig. 2d), a broad endothermic peak appears at 560 °C; it can be attributed to the formation of sodium vanadate $Na_2V_{12}O_{31}$ [16]. (iv) The broad endothermic peak covering the range of 50–125 °C can be attributed to physisorbed water.

Fig. 3 represents the thermal decomposition of supported AMV in the presence of 1, 3 or 7 wt % ions Fig. 3b, c, d, respectively). These results indicate the following. (i) The behaviour of the thermal decomposition of supported AMV treated with K^+ ions is similar to that of the untreated sample (Fig. 3a) on heating up to 350 °C. (ii) On heating the samples above 350 °C in the presence of 1 wt % K^+ ions, the position of the endothermic peak corresponding to aluminium vanadate is unchanged while addition of 3 wt % K^+ enhances the formation of this spinel a little. (iii) On addition of 7 wt % K^+ ions, and heating above 350 °C, the endothermic peak located at 520 °C can be attributed to the formation of potassium vanadate, $K_2V_8O_{21}$ [17].

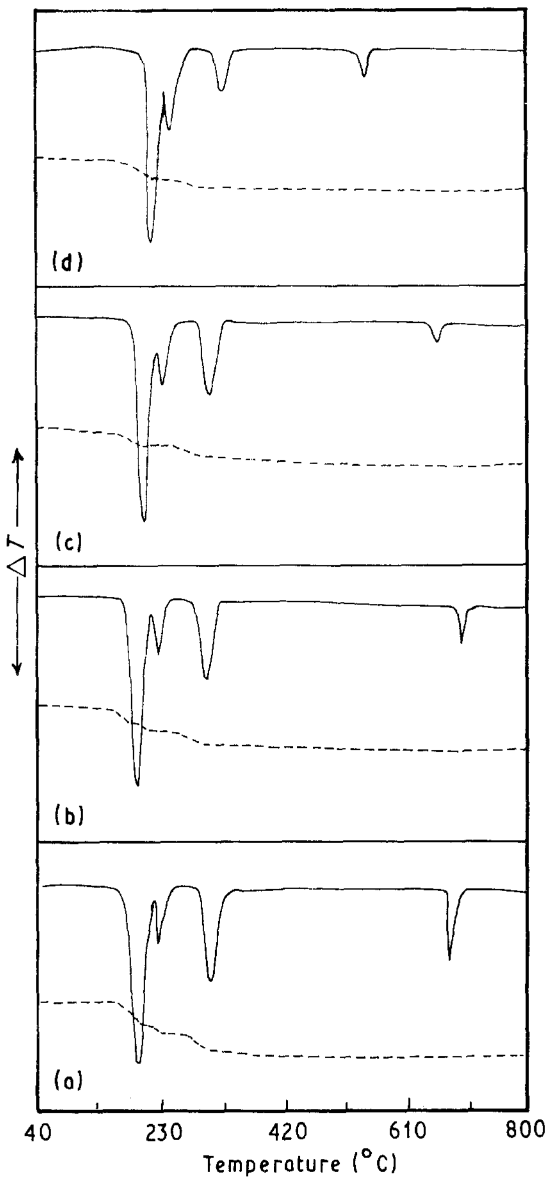

Figure 3 DTA (——) and TGA (– – –) curves of AMV supported on alumina: (a) (1:1); and doped with KOH (b) 1 wt %, (c) 3 wt %, and (d) 7 wt %.

From the above results it can be concluded that the presence of alkali-metal ions during the thermal decomposition of AMV supported on alumina has little affect on the formation of the intermediate products while it significantly affects the solid–solid interaction between V_2O_5 and Al_2O_3. A noticeable effect is observed in presence of Li^+ ions compared to Na^+ or K^+ ions. This may be explained on the basis of the ionic radii of these ions which increases from Li^+ to K^+.

3.2. I.r. spectra investigation of calcined samples of AMV supported on alumina and treated with alkali-metal ions

Fig. 4 shows the i.r. spectra of AMV supported on alumina and treated with alkali-metal ions when calcined at 400 °C for 4 h. Curve b, AMV supported on alumina, shows a spectrum similar to pure AMV calcined at 400 °C (curve a). Moreover, the band assigned at 1020 cm^{-1} corresponds to a V=O stretching vibration while the band assigned at 840 cm^{-1} can be attributed to the combination band V–O–V (stretching and lattice vibration) [8, 14, 18]. Fig. 4c, d, e, f, g, h correspond to the addition of 3 or 7 wt % of Li^+, Na^+ or K^+ ions. It can be easily seen from these curves that the general features of the i.r. spectrum of V_2O_5 supported on alumina is greatly influenced by the presence of these ions. The appearance of new bands and the decrease in the intensity of the band corresponding to V=O could by interpreted in the light of the incorporation of Li^+, Na^+ or K^+ ions in the V_2O_5 lattice. The new bands assigned at 950 and 740 cm^{-1} are due to the lattice vibrations of V_2O_4 [14, 19]. In addition, it appears that the creation of V^{4+} depends on the diffusion degree of the Li^+ ions; the variation seems to be caused by the high degree of diffusion into the lattice of V_2O_5 [20]. It is known that V_2O_5 is an oxygen-deficient semiconductor which contains V^{4+} ions as defects in the structure [21]. Thus, the addition of alkali-metal ions should increase the number of V^{4+} ions and consequently increase the ratio of V^{4+} to V^{5+} which is responsible for the catalytic activity of V_2O_5 catalysts [22]. El-Shabaky *et al.* [7] suggested that some of V^{5+} ions of the V_2O_5 lattice are reduced into V^{4+} and V^{3+} ions in presence of Al_2O_3. The results obtained here indicate that the Al_2O_3 support present in a catalyst stabilizes vanadium in the fifth state of oxidation and hinders reduction to V^{4+}. However the presence of alkali-metal ions

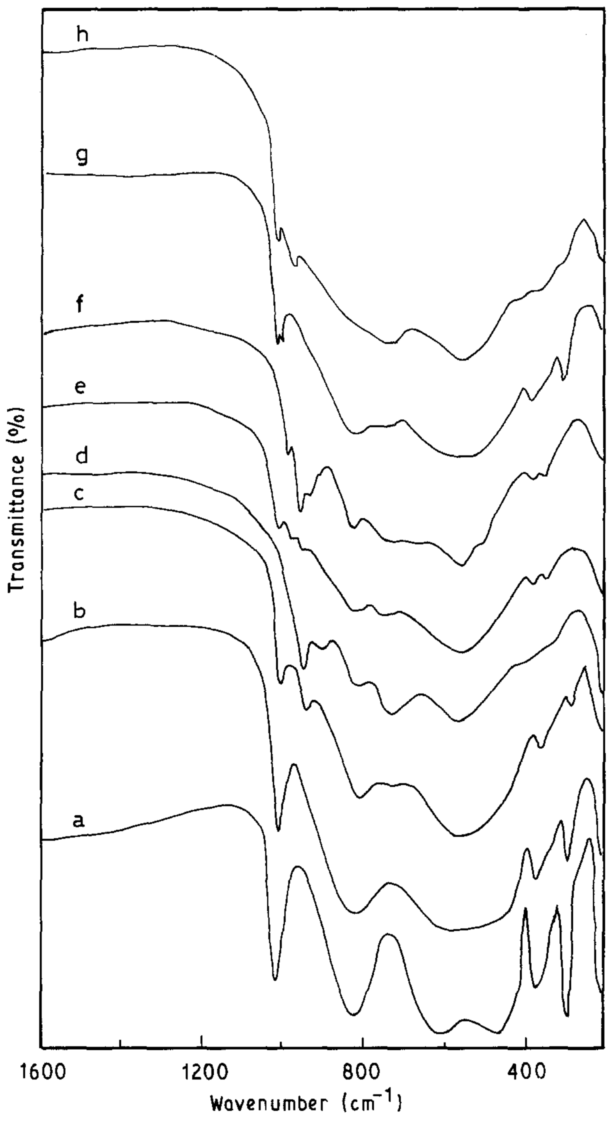

Figure 4 I.r. spectra of: (a) AMV, (b) AMV supported on alumina (1 : 1) and doped with (c) 3 wt % LiOH; (d) 7 wt % LiOH; (e) 3 wt % NaOH; (f) 7 wt % NaOH; (g) 3 wt % KOH; and (h) 7 wt % KOH [Samples calcined at 400 °C for 4 h].

during the decomposition of supported AMV up to 400 °C leads to an observable decrease in the intensity of the V=O band, while the concentration of V^{4+} ions increases.

Fig. 5 shows the i.r. spectra of AMV supported on alumina, and AMV modified with 3 or 7 wt % Li^+, Na^+ or K^+ and calcined at 700 °C for 4 h. It can be seen that calcination of these samples at 700 °C produces a noticeable change in the spectrum of AMV supported on alumina (curve a) in the range 1020–800 cm^{-1}. This could be due to the solid–solid interaction between V_2O_5 and Al_2O_3 or alkali-metal oxides. However, the new bands assigned at 1000 and 950 cm^{-1} correspond to the formation of alkali-metal bronzes [23, 24, 25]. The degree to which they form depends on the degree of alkali-metal-ion diffusion into the lattice of V_2O_5, as well as their concentrations. It is worth noting that the band assigned at 950 cm^{-1} is observed in the samples calcined at 400 and 700 °C. This can be explained by the fact that the alkali metal in bronze compounds is ionized and V^{4+} is formed [23].

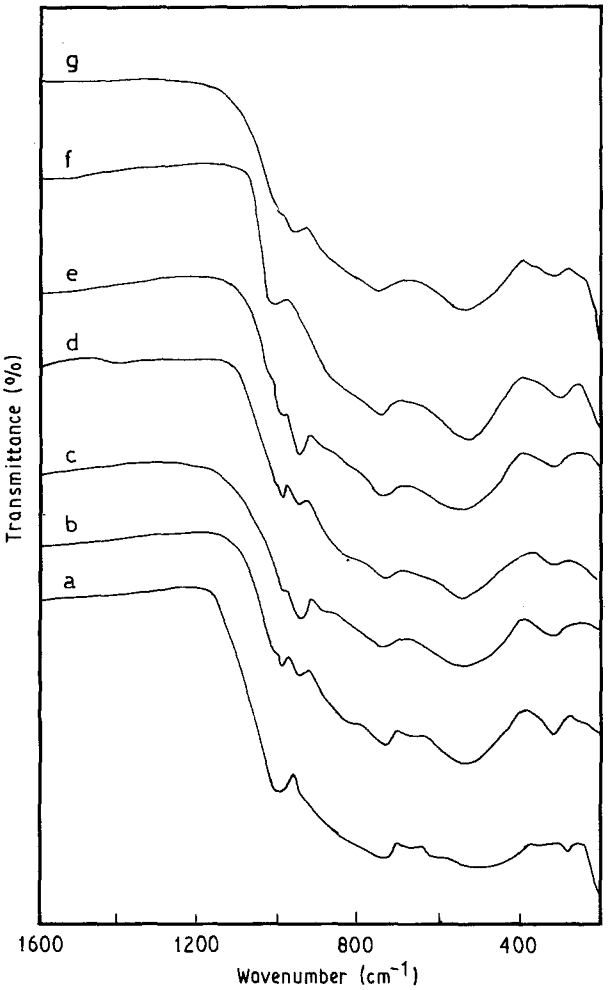

Figure 5 I.r. spectra of (a) AMV; (b) AMV supported on alumina (1 : 1); and doped with 3 wt % LiOH, (c) 7 wt % LiOH, (d) 3 wt % NaOH, (e) 7 wt % NaOH, (f) 3 wt % KOH, and (g) 7 wt % KOH [Samples calcined at 700 °C for 4 h].

3.3. X-ray investigation of the thermal products of AMV supported on alumina and modified with alkali-metal ions

Fig. 6 shows the XRD lines of AMV supported on alumina and modified with 7 wt % Li^+, Na^+ or K^+ ions calcined at 700 °C in air for 4 h. It can be seen that Fig. 6a indicates the solid–solid interaction between V_2O_5 and Al_2O_3 led to the formation of $AlVO_4$ together with a small portion of unreacted V_2O_5 and δ-alumina [8]. Therefore, the endothermic peak observed at 660 °C in the DTA curve Fig. 1a is due to the interaction between V_2O_5 and the support giving $AlVO_4$. The X-ray investigation of supported AMV treated with alkali-metal ions showed a noticeable change in the crystal structure of the untreated sample. All the diffraction lines characteristic of $AlVO_4$ disappeared, and the diffraction lines of alkali-metal vanadate [15–17] persisted in the diffraction patterns. Moreover, there was a noticeable increase in the intensity of the diffraction lines of δ-alumina; i.e. it increases its crystallinity. It has been reported that Al_2O_3 calcined at 500 °C was poorly crystalline γ-alumina and its degree of crystallinity increased on increasing the calcination temperature to 900 °C [26]. Therefore, alkali-metal oxides catalyse the crystalliza-

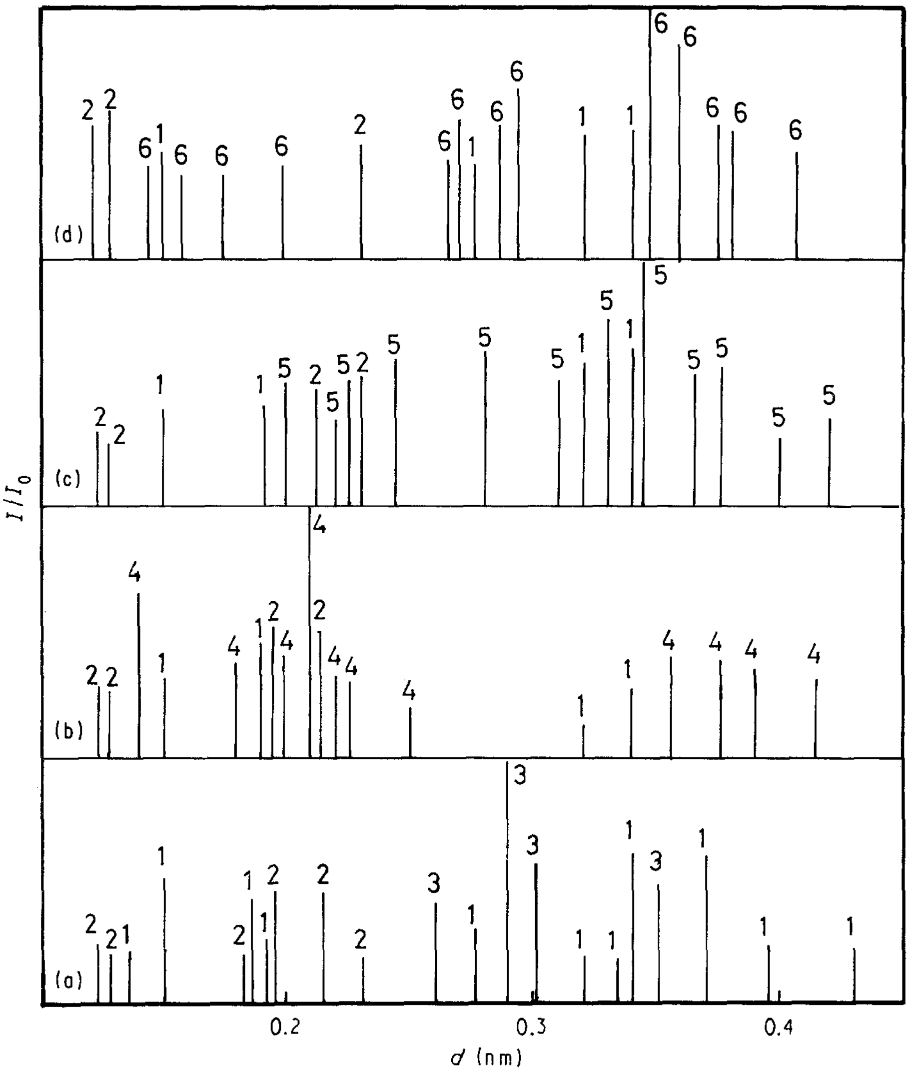

Figure 6 XRD patterns of AMV: (a) supported on alumina (1 : 1); and doped with (b) 7 wt % LiOH; (c) 7 wt % NaOH, and (d) 7 wt % KOH. Calcined at 700 °C for 4 h: (1) V_2O_5, (2) δ-Al_2O_3, (3) $AlVO_4$, (4) LiV_6O_{15}, (5) $Na_2V_{12}O_{31}$, and (6) $K_2V_8O_{21}$.

tion process of the alumina support. This means that the presence of these dopants inhibits the interaction between V_2O_5 and Al_2O_3 while enhancing the crystallinity of γ- to δ-alumina. It is also observed that lines characteristic of V_2O_5 are detected in all samples treated with alkali-metal ions. However, the peaks observed in the DTA curves at temperatures of 610, 560 or 520 °C correspond to 7 wt % Li^+, Na^+ or K^+ ions, respectively, and are attributed to the formation of alkali-metal vanadates. Moreover, the results of the i.r. spectra in Fig. 5 indicate that V^{4+} ions form during the decomposition of AMV supported on alumina in the presence of alkali-metal ions. Thus the formation of V^{4+} may be enhanced in the solid–solid interaction between V_2O_5 and the alkali-metal oxides.

4. Conclusions

1. Thermal decomposition processes of AMV supported on alumina are little affected in the presence of alkali-metal-ion dopants up to 400 °C. However, the solid products at this temperature are accompanied by creation of V^{4+} ions.

2. On heating the treated samples at 700 °C alkali-metal vanadates form. This process depends on the degree of diffusion of the alkali-metal ions and on their concentrations.

3. The presence of alkali-metal oxides (7 wt %) inhibits the formation of aluminium vanadate while enhancing the crystallinity of Al_2O_3.

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