

Influence of Al_2O_3 support on the thermal decomposition of ammonium metavanadate

A. A. SAID*

Department of Chemistry, Faculty of Science, United Arab Emirates University, Al-Ain, P.O. Box 17551, United Arab Emirates

The thermal decomposition of ammonium metavanadate (AMV) supported on aluminium oxide was investigated using differential thermal analysis, thermogravimetry, infrared and X-ray diffraction techniques. The results obtained revealed that the decomposition of AMV supported on alumina proceeded in three decomposition stages. Alumina was found to enhance only the decomposition of the intermediate ammonium hexavanadate to produce V_2O_5 . In addition, the values of activation energies of the various decomposition stages were accompanied by a significant decrease on decreasing the concentration of AMV. The infrared spectra indicated that the band corresponds to the surface site $\text{V}=\text{O}$ strongly affected by the presence of Al_2O_3 . Finally, an interaction between Al_2O_3 and V_2O_5 occurred at 660°C giving well-crystallized AlVO_4 .

1. Introduction

Supported metal oxide catalysts exhibit differing degrees of catalysis depending on the kind of support and on the composition of the catalyst [1, 2]. Vanadium pentoxides supported on alumina are one of the most important classes of solid catalysts [3–6]. They are usually prepared by impregnation of an alumina support from an aqueous solution of ammonium metavanadate. The thermal decomposition of ammonium metavanadate without support has been the subject of several investigations [7–10]. It has been reported that the thermal decomposition of ammonium metavanadate takes place according to different mechanisms depending mainly upon the atmosphere in contact with the solid [11, 12] and the presence of foreign ion additives [7, 10]. However, a little work has been done on the effect of a support on the thermal decomposition of ammonium metavanadate. Therefore, the present paper reports a study on the thermal decomposition of ammonium metavanadate supported on γ -alumina. The techniques employed were thermogravimetry (TG), differential thermal analysis (DTA), infrared (IR) spectroscopy and X-ray diffraction (XRD).

2. Experimental procedure

The starting materials were Analar grade chemicals. Gamma-alumina precalcined in air at 500°C , was impregnated with different proportions of ammonium metavanadate (AMV) dissolved in doubly distilled water. The samples were dried in an oven at 110°C to constant weight. The composition of the impregnated solids was $0.1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$, $0.2 \text{ NH}_4\text{VO}_3:$

$1 \text{ Al}_2\text{O}_3$, $0.3 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$ and $1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$.

TG and DTA of pure AMV and various impregnated solids were carried out using a Shimadzu Computerized Thermal Analysis System DT-40. The system includes programmes which process data from the thermal analyser, with the chromatopac C-R3A. The rate of heating of samples was kept at $10^\circ\text{C min}^{-1}$ using an air atmosphere at 40 ml min^{-1} . α -alumina for the DTA standard was applied as a reference.

X-ray investigation of the thermal products of pure AMV and AMV supported on γ -alumina was performed with a Philips diffractometer type PW 2103, applying a copper target and a nickel filter.

IR spectra of the thermal products of pure AMV and AMV supported on γ -alumina were recorded from KBr discs using a Pye Unicam SP 2000 spectrophotometer.

3. Results and discussion

3.1. Thermal decomposition of pure AMV and AMV supported on alumina

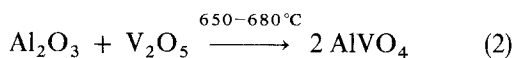
The TG and DTA curves of pure AMV and AMV supported on Al_2O_3 are shown in Fig. 1 while Table I gives the maximum temperatures for the decomposition stages together with the corresponding activation energies. Pure AMV (curve a) exhibits four endothermic peaks, the maxima of these are located at 193, 224, 315 and 685°C , respectively. The TG curve shows that AMV loses weight on heating in three steps. The first peak, which was followed by 11.7% loss in weight, indicated the decomposition of AMV to the intermediate ammonium bivanadate (ABV). The second

* Permanent address: Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt.

4. Generally, the values of the activation energies of different decomposition stages (Table I) decrease with decreasing content of AMV. A noticeable decrease in E values was observed in case of the decomposition of $0.1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$ and $0.2 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$. This can be explained as due to an increase in the contact surface between the intermediate compounds and the support, which results in the decomposition being favoured energetically at the expense of the decomposition of the intermediate compounds. Thus, these results can suggest that the support which has a high surface area may strongly affect the activation energy, accompanied by the thermal decomposition of the solid materials.

3.2. XRD investigation of the thermal products of AMV and AMV supported on Al_2O_3

Fig. 2 shows XRD lines of AMV, Al_2O_3 and $1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$ calcined at 500 and 670 °C in air for 4 h. It can be seen from these lines that the diffraction lines of V_2O_5 were only detected in the sample calcined at 500 °C, while Al_2O_3 calcined at 500 °C revealed that δ -alumina was poorly crystalline [15]. On the other hand, Al_2O_3 mixed with AMV ($1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$) calcined at 500 °C indicated the absence of a solid–solid interaction between Al_2O_3 and V_2O_5 at 500 °C. Increasing the calcination temperature to 670 °C led to the formation of well-crystallized aluminium vanadate, AlVO_4 [15], together with a small portion of unreacted V_2O_5 and δ -alumina. Therefore, an endothermic peak was observed at 660 °C in the DTA curves (Fig. 1) of various supported samples due to the solid–solid interaction between Al_2O_3 and V_2O_5 , giving AlVO_4 . This reaction, proceeds according to



These results are in agreement with results reported by El-Shobaky *et al.* [9].

3.3. IR investigation of calcined samples of pure AMV and AMV supported on Al_2O_3

Fig. 3 represents the IR spectra of pure AMV and AMV supported on alumina calcined at 400 °C in air for 4 h. Curve a shows that the decomposition of AMV to V_2O_5 is complete. Moreover, V_2O_5 exhibited a

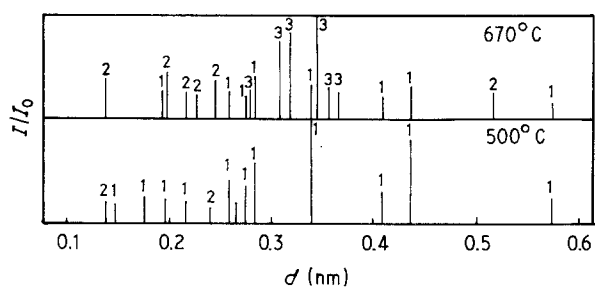


Figure 2 X-ray diffraction patterns of the thermal products of $1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$, (1) V_2O_5 , (2) Al_2O_3 and (3) AlVO_4 .

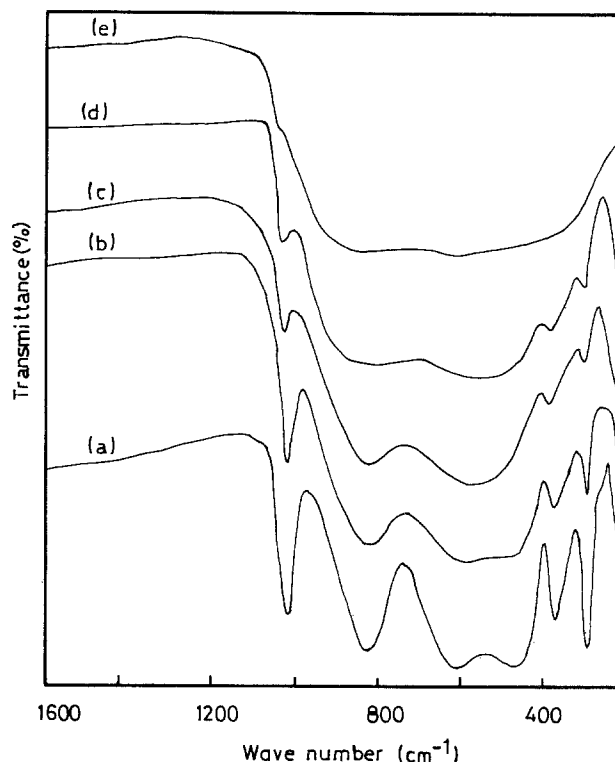


Figure 3 IR spectra of (a) AMV, (b) $1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$, (c) $0.3 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$, (d) $0.2 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$ and (e) $0.1 \text{ NH}_4\text{VO}_3:\text{Al}_2\text{O}_3$ (samples calcined at 400 °C for 4 h).

band at 1020 cm^{-1} which is assignable to the $\text{V}=\text{O}$ stretching vibration [16, 17]. The band assigned at 840 cm^{-1} was attributed to a combination band of $\text{V}-\text{O}-\text{V}$ stretching and lattice vibration. Curves b–e for AMV supported on Al_2O_3 indicate that the composition $1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$, curve b, exhibits a similar spectrum to pure AMV. On decreasing the percentage loading of AMV, a decrease in the percentage transmission of the absorption bands occurs, reaching a minimum in the case of the composition $0.1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$. These results are in agreement with the DTA results in which the area of the third endothermic peak (formation of V_2O_5) decreased with decreasing AMV content. Accordingly, the decrease in the percentage transmission of the absorption band assigned at 1020 cm^{-1} can be interpreted on the basis of the formation of a disordered V_2O_5 phase. The disappearance of this band in the case of composition $0.1 \text{ NH}_4\text{VO}_3:1 \text{ Al}_2\text{O}_3$ (curve e) indicates that the monolayer was not formed [12]. Therefore, the increase in V_2O_5 content leads mainly to the accumulation and thickening of vanadium oxide and an increase in the surface $\text{V}=\text{O}$ active sites [18].

Recently [19–22], it was found that the structure of the loaded vanadium species, the morphology of catalysts, and the interaction between vanadium oxide and its support all play a significant role in the catalytic activity and selectivity of V_2O_5 catalysts. In addition, it was reported [23] that the vanadium oxide coverage of the support surface was dependent on the type of the support and the percentage loading of V_2O_5 . Therefore, V_2O_5 on Al_2O_3 loses its active $\text{V}=\text{O}$ sites until the formation of the multilayer occurs, i.e. strong interaction between V_2O_5 and the Al_2O_3 support.

Fig. 4 shows the IR spectra of AMV supported on alumina calcined at 670 °C in air for 4 h. It can be seen that the percentage transmission of the band assigned at 1020 cm⁻¹ corresponding to V=O, decreases with decreasing AMV concentration. However, the appearance of this band confirms the presence of V₂O₅ in the XRD lines of the composition 1 NH₄VO₃:1 Al₂O₃ calcined at 670 °C (Fig. 2). A remarkable change in the spectra of these solids was observed in the range 1000–500 cm⁻¹. This change may be related to the formation of aluminium vanadate spinel structure.

4. Conclusions

The main conclusions that can be derived from the experimental results are as follows.

1. The decomposition of pure AMV and AMV supported on Al₂O₃ proceeds in three stages and the Al₂O₃ support enhances the decomposition of the third stage, i.e. decomposition of AHV to V₂O₅.

2. The values of activation energies of the various decomposition steps showed a significant decrease with decreasing AMV content.

3. The IR results show important evidence that the active surface site V=O can disappear in the presence of low concentrations of AMV on the Al₂O₃ support.

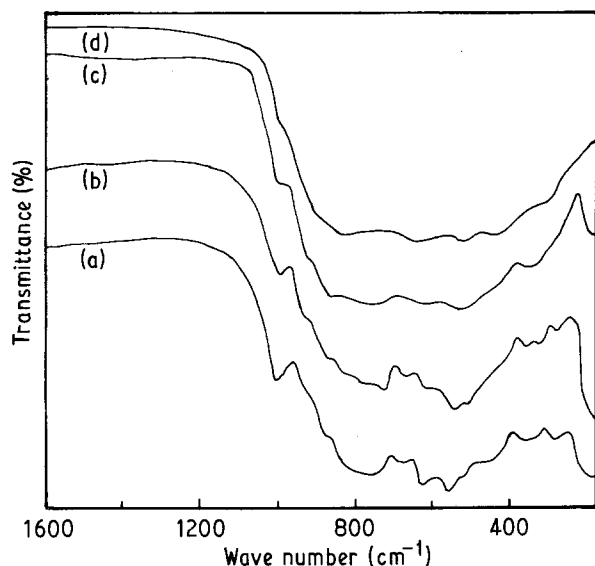


Figure 4 IR spectra of (a) 1 NH₄VO₃:1 Al₂O₃, (b) 0.3 NH₄VO₃:1 Al₂O₃, (c) 0.2 NH₄VO₃:1 Al₂O₃ and (d) 0.1 NH₄VO₃:1 Al₂O₃ (samples calcined at 670 °C for 4 h).

Therefore, the content of V₂O₅ must be considered during the preparation of the supported catalysts.

4. Aluminium vanadate can be formed by the calcination of V₂O₅ and Al₂O₃ at 670 °C. In addition, its amount was found to be dependent upon the percentage loading of AMV.

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