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# Structures accompanying the solid–solid interactions in the $V_2O_5$–MgO system

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## Abstract

Magnesium hydroxide samples were treated with solutions containing different proportions (0.5–50 mol%) of ammonium metavanadate (AMV), dried at 80°C, and then calcined in air at temperatures of 400, 550 and 700°C for 4 h. The solid–solid interactions between the resulting mixed oxides were investigated using DTA, TG, IR and XRD techniques. The results obtained revealed that AMV and $Mg(OH)_2$ decompose readily at 300 and 375°C respectively to produce $V_2O_5$ and MgO solids. The presence of the support enhances the decomposition to $V_2O_5$ while the presence of $V_2O_5$ retards the decomposition of $Mg(OH)_2$. With ratios of less than 20 mol% AMV, no peaks in the DTA curves related to the decomposition of AMV were found. However, the two oxides interacted at a composition of 20 mol% AMV above 500°C to form $Mg_3V_2O_8$ spinel, but this decreased on increasing the percentage content of AMV. Moreover, samples containing 20 or 30 mol% AMV calcined at 700°C mainly led to the formation of $Mg_3V_2O_8$, whereas an $MgV_2O_6$ spinel was the predominant product formed on increasing to 50 mol% AMV.

*Keywords:* Ammonium metavanadate; Binary system; Calcination; Magnesium oxide; Spinel; Vanadium pentoxide

## 1. Introduction

Magnesia MgO is frequently used as a compatible support material for monolayer-type metal catalysts [1]. It is therefore extremely important to determine the

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structure of such supported metal oxides. For supported vanadium pentoxide, a number of studies have been undertaken to study the structure of loaded vanadium species [2,3], the morphology of catalysts [4–6] and interactions between vanadium oxide and its support [7,8]. Recently [9], we reported that the surface site, V=O, is strongly affected by the presence of an $Al_2O_3$ support. Thus, it is important to determine the phase structural changes that would accompany the thermal decomposition of parent materials. However, a literature survey has shown that little work has been done on the structure changes accompanying the thermal decomposition of ammonium metavanadate supported on magnesia. Therefore, the present paper reports on a study of the solid–solid interactions in the $V_2O_5$–MgO system. The techniques employed were DTA, TG, XRD and IR spectroscopy.

## 2. Experimental procedure

The starting materials were Analar grade chemicals. Magnesium hydroxide was prepared by precipitation from nitrate solution using ammonium hydroxide (1:1) with occasional stirring at room temperature. The precipitate was dried in an oven at 80°C to constant weight. The mixed solid specimens were prepared by impregnation of a known mass of solid $Mg(OH)_2$ with aqueous solutions of ammonium metavanadate (AMV) of different calculated proportions. The prepared mixed samples were dried in an oven at 80°C followed by heating in air at 400, 550 and 700°C for 4 h. The vanadium oxide contents of these solids, expressed as mol% $V_2O_5$ were in the range 0.5–50.

TG and DTA of pure $Mg(OH)_2$ and its mixtures with AMV were carried out using a Shimadzu Computerized Thermal Analysis System DT-40. The system includes programs which process data from the thermal analyser with chromatopac C-R3A. The rate of heating was kept at 10°C $min^{-1}$ using an air atmosphere flowing at 40 ml $min^{-1}$. $\alpha$-Alumina powder was applied as the DTA standard.

X-ray investigations of the thermal products of pure $Mg(OH)_2$ and AMV supported on magnesia were performed with a Philips diffractometer (Model PW 1710) using a copper target and a nickel filter. The diffraction lines of the samples were matched with the ASTM cards [10].

The IR spectra of pure $Mg(OH)_2$ and of the supported samples calcined at 400, 550 and 700°C were recorded using a Pye Unicam SP3-300 spectrophotometer in the range of 4000–200 $cm^{-1}$ in KBr discs.

## 3. Results and discussion

### *3.1. Thermal decomposition of ammonium metavanadate–magnesium hydroxide mixed solids*

Fig. 1 shows the DTA and TG curves for $Mg(OH)_2$. These curves indicate that $Mg(OH)_2$ starts its decomposition at 286°C and this is complete at 373°C. The

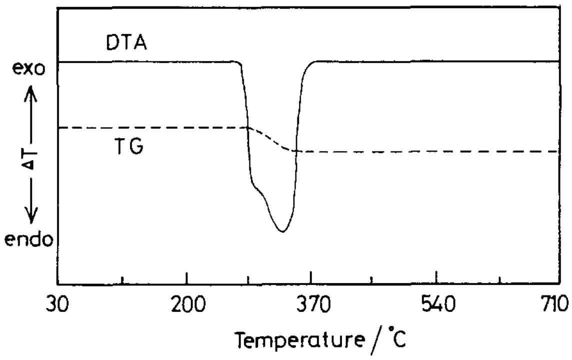

Fig. 1. TG–DTA curves of the thermal decomposition of magnesium hydroxide.

decomposition seems to proceed in two steps, a minor one at 301°C and the main step maximized at 338°C. Weber and Roy [11] have observed a two-step dehydration of $Mg(OH)_2$ and presumed it to result from the formation of an intermediate phase in the dehydration process. Ball and Taylor [12] suggested the formation of an intermediate phase with a spinel-like structure, e.g. $(MgO)_3H_2O$, resulting from cation migration during dehydration. The weight loss accompanying these two steps was found to be 24% which is less than the theoretical value (31%) for the complete dehydration. This result shows that the dehydration of $Mg(OH)_2$ is not completed and that the structure of magnesia following the decomposition stages is $MgO \cdot 0.4H_2O$.

Fig. 2, curves a and b show the DTA and TG curves of AMV supported on $Mg(OH)_2$ in different compositions. Analysis of the resulting data for the different solids indicates some trends, and conclusions may be drawn as follows.

(i) The addition of 0.5–10 mol% AMV into $Mg(OH)_2$ support, curves a–d, shows that the decomposition of $Mg(OH)_2$ proceeds in two steps in the presence of 0.5 or 1 mol% AMV, while in the presence of more than 1 mol% AMV, it decomposes in one stage. Moreover, the presence of $V_2O_5$ produced from the decomposition of AMV retards the decomposition of $Mg(OH)_2$ to a higher temperature. However, no peaks are observed corresponding to the decomposition of AMV.

(ii) On increasing the content of AMV from 20 to 50 mol%, curves e–h, new peaks appear corresponding to the thermal decomposition of AMV and a solid–solid interaction between MgO and $V_2O_5$. The thermal decomposition of AMV has recently been studied [9,13]: the first endothermic peak between 182 and 188°C corresponds to the decomposition of AMV to the intermediate ammonium bivanadate, $(NH_4)_6 \cdot V_{12}O_{33}$; the second endothermic peak at 220–225°C is attributed to the decomposition of ammonium bivanadate into ammonium hexavanadate, $(NH_4)_4 \cdot V_{12}O_{32}$; the third endothermic peak at 288–298°C is due to the decomposition of ammonium hexavanadate to $V_2O_5$. It is clear that the presence of $Mg(OH)_2$ support enhances only the decomposition of ammonium hexavanadate to $V_2O_5$. The fourth peak which corresponds to the decomposition of $Mg(OH)_2$ is unaffected by the increase in AMV content.

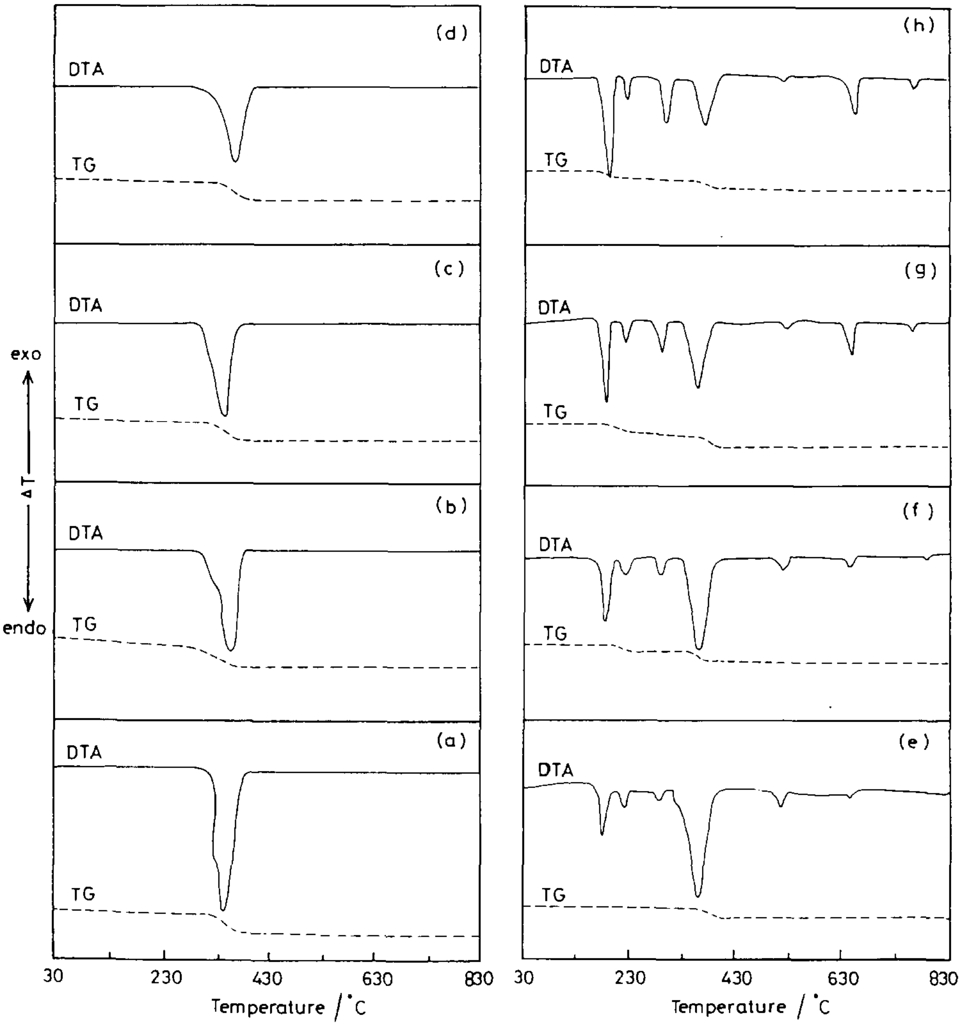

Fig. 2. TG–DTA curves of the thermal decomposition of magnesium hydroxide mixed with 0.5 (a), 1 (b), 5 (c), 10 (d), 20 (e), 30 (f), 40 (g) and 50 (h) mol% AMV.

(iii) The fifth endothermic peak at 514–522°C is attributed to the formation of $Mg_3V_2O_8$ spinel [14,15]. Moreover the area of this peak decreases on increasing the % content of AMV.

(iv) The sixth endothermic peak at 650°C is attributed to the formation of $MgV_2O_6$ spinel [14,15]. The formation of this compound increases on increasing the % content of AMV as observed from the increase in the peak area.

(v) The last small endothermic peak observed in the case of 30, 40 and 50 mol% AMV, at about 750°C, is due to the melting of $V_2O_5$ [9,14]. It is noted that this

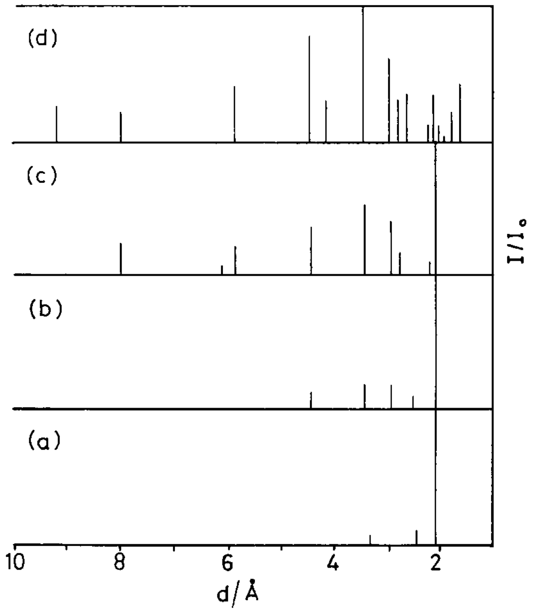

Fig. 3. XRD lines of magnesium hydroxide (a) and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (b, c and d respectively) and calcined at 400°C.

temperature is higher than the value reported before. This strongly suggests that the presence of MgO retards the melting of $V_2O_5$.

### *3.2. X-ray investigation of the thermal products of ammonium metavanadate supported on magnesium hydroxide*

Fig. 3 shows the XRD lines for AMV supported on magnesium hydroxide calcined at 400°C in air for 4 h. It can be seen from curve a that the diffraction lines corresponding to those of pure MgO were detected at $d/(\text{Å}) = 2.11$, 2.40 and 3.30. These lines were detected on increasing the mixing ratio of AMV up to 50 mol%. However, the diffraction lines at $d/(\text{Å}) = 3.40$, 4.38 and 2.88 which start to appear on mixing $Mg(OH)_2$ with 20 mol% AMV correspond to the $V_2O_5$ lattice structure [10]. These lines increase in intensity on increasing the % content of AMV and become the main lines at 50 mol%. This is in accord with the results of DTA, i.e. the absence of any peaks related to the decomposition of AMV and to solid–solid interaction between $V_2O_5$ and MgO mixtures with less than 20 mol% AMV. Fig. 4 shows the X-ray diffraction lines of $Mg(OH)_2$ mixed with 20, 30 and 50 mol% AMV calcinated at 550°C for 4 h. It shows that the diffraction lines due to the presence of MgO are detected up to 50 mol% AMV. Moreover, the lines corresponding to $V_2O_5$ start to appear on mixing $Mg(OH)_2$ with 20 mol% AMV, and they increase on increasing the percentage content of $V_2O_5$. However, the new lines detected at $d/(\text{Å}) = 2.55$, 3.04, 3.22, 2.85 and 2.50 depend on the % mixing and

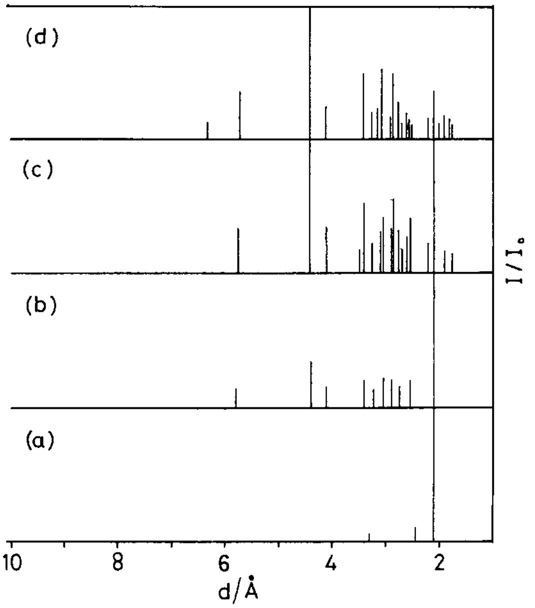

Fig. 4. XRD lines of magnesium hydroxide (a) and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (b, c and d respectively) and calcined at 550°C.

correspond to the formation of $Mg_3V_2O_8$ spinel structure [10,15,16]. The solid–solid interaction between MgO and $V_2O_5$ takes place as follows

$$3MgO + V_2O_5 \xrightarrow{550^\circ C} Mg_3V_2O_8$$

Therefore, the endothermic peak observed at 514–522°C in the DTA curves corresponds to the above equation. Fig. 5 represents the XRD lines of AMV supported on $Mg(OH)_2$ calcined at 700°C for 4 h. It shows that increasing the calcination temperature to 700°C leads to a significant change in the intensity of the diffraction lines corresponding to $V_2O_5$ and MgO. Also, the diffraction lines at $d/(\text{Å}) = 2.55$, 2.50, 3.04 and 3.30 for $Mg(OH)_2$ mixed with 20 or 30 mol% AMV correspond with the formation of magnesium orthovanadate, $Mg_3V_2O_8$. It is worth noting that the crystallinity and stability of this spinel increases on increasing the calcination temperature from 550 to 700°C. However, the sample containing 50 mol% AMV shows new diffraction lines at $d/(\text{Å}) = 3.05$, 4.29, 3.12, 6.16 and 2.70. These lines are attributed to the interaction between $V_2O_5$ and MgO to produce well crystallized $MgV_2O_6$ phase [10,14,15]. The formation of this spinel takes place as follows

$$MgO + V_2O_5 \xrightarrow{700^\circ C} MgV_2O_6$$

This equation is consistent with the endothermic peak observed at 650°C in the DTA curves. Moreover, the two lines detected at $d/(\text{Å}) = 2.11$ and 2.88 correspond to the presence of MgO and $V_2O_5$ respectively. The detection of $V_2O_5$ solid

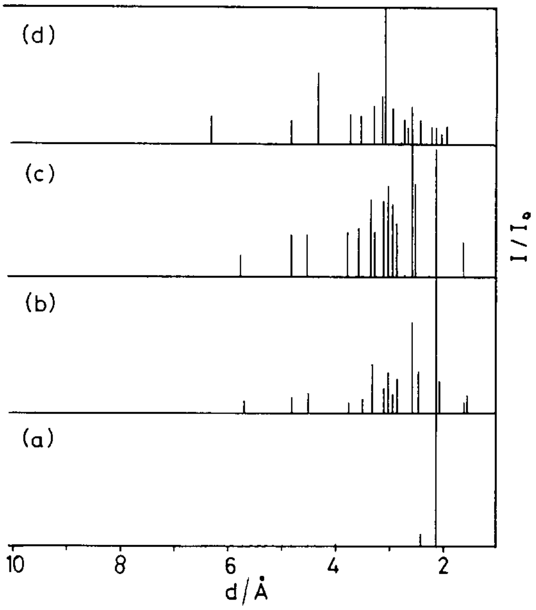

Fig. 5. XRD lines of magnesium hydroxide (a) and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (b, c and d respectively) and calcined at 700°C.

confirms the endothermic peak observed in the DTA curves at about 750°C. Furthermore, the diffraction line detected at $d/(\text{Å}) = 2.55$ corresponds to the presence of $Mg_3V_2O_8$ together with the other phases. However, the two lines detected at $d/(\text{Å}) = 1.55$ and 5.78 in the case of 20 and 30 mol% AMV may due to the presence of hydrated vanadium pentoxide, $V_2O_5 \cdot H_2O$ [10,15]. It was noted that in the mixed samples with less than 20 mol% AMV, no lines are detected that correspond to $V_2O_5$ or that suggest any solid–solid interaction. The absence of any XRD lines corresponding to $V_2O_5$ is attributed to monolayer dispersion of this oxide on the surface of the MgO support.

### *3.3. IR investigation of the thermal products of ammonium metavanadate supported on magnesium hydroxide*

Fig. 6 shows the IR spectra of pure $Mg(OH)_2$ and of AMV supported on $Mg(OH)_2$ calcined at 400°C in air for 4 h. The spectrum of the original sample of $Mg(OH)_2$ (curve a) shows bands at 3680, 3470, 1400 and 850 $cm^{-1}$. The sharp absorption band located at 3680 $cm^{-1}$ is assigned to free hydroxyl groups [17] while the broad band at 3470 $cm^{-1}$ is characteristic of OH stretching vibration [18]. The absorption band at 1400 $cm^{-1}$ corresponds to the combined water molecules [19]. The broad band located at 900–300 $cm^{-1}$ corresponds to the Mg–O vibration [20]. However, curve b shows that the calcination of $Mg(OH)_2$ at 400°C results only in the disappearance of the band corresponding to the free hydroxyl groups. This

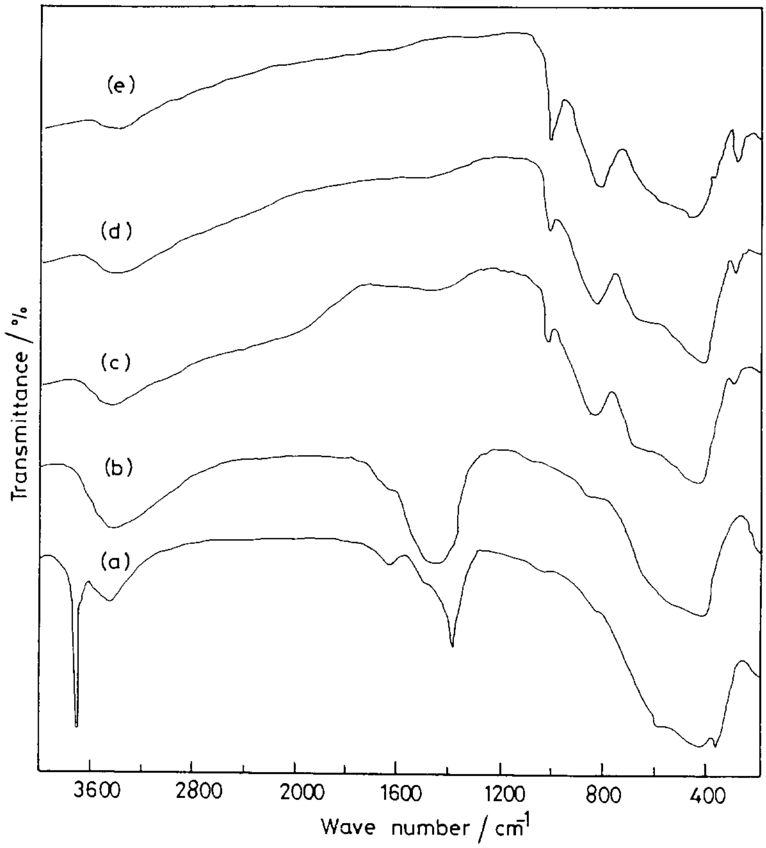

Fig. 6. IR spectra of the original magnesium hydroxide (a), the thermal products of magnesium hydroxide (b), and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (d, c and e respectively) and calcined at 400°C.

confirms the TG in which the structure of $Mg(OH)_2$ after heating at 400°C still contains combined water. The spectra of AMV supported on $Mg(OH)_2$ at 20, 30 and 50 mol%, curves c–e respectively, show that the intensity of the band located at 3430 cm$^{-1}$ decreases with increasing mol% AMV. Moreover, the intensity of the band located at 1450 cm$^{-1}$ sharply decreases on addition of 20 mol% AMV and disappears in the presence of 30 mol% AMV. The two bands at 1030 and 830 cm$^{-1}$ that appear on mixing $Mg(OH)_2$ with 20 mol% AMV are assignable to the V=O stretching vibration and to the V–O–V stretching and lattice vibrations respectively [9,21]. On increasing the % loading of AMV up to 50 mol%, an increase in the percentage transmission of these two bands occurs. Thus, curve e exhibits a similar spectrum to that of pure $V_2O_5$ [9], together with the band corresponding to Mg–O. Fig. 7 shows the IR spectra of AMV supported on magnesia calcined at 550°C in air for 4 h. It is clear that, in general, the IR spectra of $V_2O_5$ supported on magnesia are greatly influenced by the presence of the support. The vibration bands

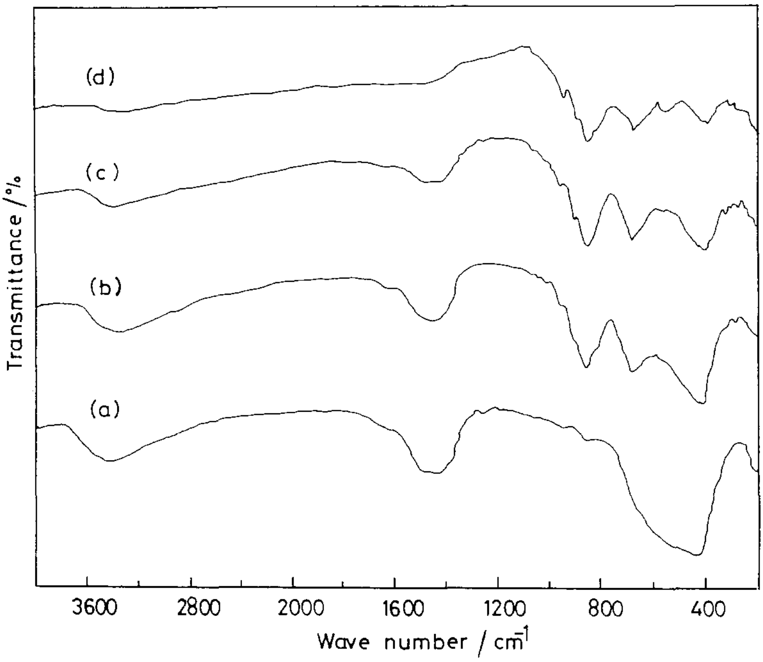

Fig. 7. IR spectra of the thermal products of magnesium hydroxide (a) and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (b, c and d respectively) and calcined at 550°C.

located at 3430 and 1450 cm$^{-1}$ are observed at 20 and 30 mol% AMV, disappearing on increasing the AMV content to 50 mol%. However, the absorption band corresponding to Mg–O vibrations is observed in all the mixed samples but its intensity decreases on increasing the AMV content. The new bands at 920, 690 and 570 cm$^{-1}$ are presumed to be characteristic of the formation of $Mg_3V_2O_8$ spinel [16]. The formation of this spinel greatly affects the position of the absorption bands corresponding to V=O or V–O–V vibrations. Fig. 8 shows the IR spectra of samples calcined at 700°C for 4 h. It appears that the vibration band located at 3430 cm$^{-1}$, assignable to the OH groups, is detected only on addition of 20 or 30 mol% AMV. In addition, the intensity of the band corresponding to Mg–O vibration decreases on increasing the content of AMV up to 30 mol%. The bands corresponding to the formation of $Mg_3V_2O_8$ become more sharp in the case of 20 or 30 mol% AMV, while the spectrum of the sample containing 50 mol% is completely changed. The two new broad bands at 915 and 815 cm$^{-1}$ may be characteristic of the lattice vibration of $MgV_2O_6$ [16].

## 4. Conclusions

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

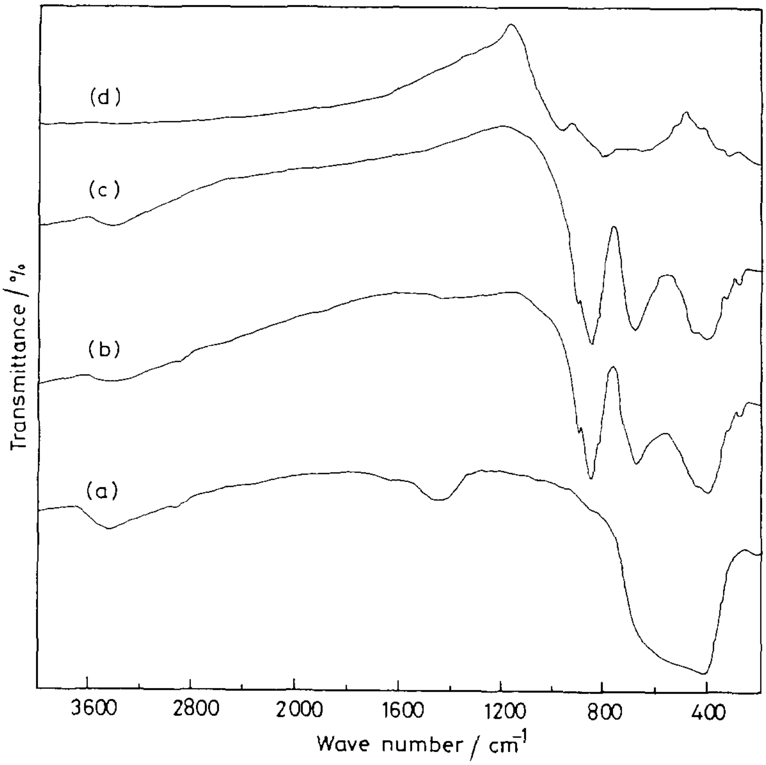

Fig. 8. IR spectra of the thermal products of magnesium hydroxide (a) and magnesium hydroxide mixed with 20, 30 and 50 mol% AMV (b, c and d respectively) and calcined at 700°C.

(i) On mixing $Mg(OH)_2$ with <20 mol% AMV, no peaks are observed on the DTA curves that correspond to the decomposition of AMV, due to the dispersion capacity of MgO. This is confirmed by the absence of the surface active site V=O, as indicated by the IR results.

(ii) On increasing the AMV content up to 50 mol%, the decomposition of AMV proceeds in three stages and the $V_2O_5$ produced retards the decomposition of $Mg(OH)_2$. However, the presence of the support only enhances the formation of $V_2O_5$ and increases its melting point.

(iii) $V_2O_5$ readily starts to react with MgO above 500°C yielding mainly well crystallized $Mg_3V_2O_8$ spinel, the amount of which decreases on increasing the content of AMV.

(iv) The calcination of samples at 700°C increases the crystallinity of the $Mg_3V_2O_8$ spinel in the presence of 20 or 30 mol% AMV, while in the presence of 50 mol%, only the well crystallized $MgV_2O_6$ spinel is produced.

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