Thermoanalytical study of vanadyl and vanadium acetoacetonates

Gamal A.M. Hussein

Chemistry Department, Faculty of Science, Minia University, El-Minia 61519, Egypt

Abstract

The thermal decomposition reactions of vanadyl and vanadium acetoacetonates in dry nitrogen have been thoroughly studied. Thermal processes occurring throughout the decomposition range (100–500°C) were monitored by means of TG, DTA and IR spectroscopic analysis of the gaseous products. These processes were characterized on the basis of the solid product analyses using X-ray diffractometry and IR spectroscopy. The results showed that $VO(C_5H_7O_2)_2$ had completely decomposed to V_2O_3 at 325°C through the intermediates $VO(CH_3COO)(C_5H_7O_2)$ at 290°C, $VO(CH_3COO)_2$ at 300°C and $V_2O(CO_3)_2$ at 315°C. In contrast, $V(C_5H_7O_2)_3$ decomposed via the acetate at 280°C and the carbonate at 292°C as intermediates. The carbonate decomposed immediately to give V_2O_5 at 305°C. Part of the V_2O_5 underwent a reduction process through an endothermic effect at 325°C. The ultimate solid products at 400°C were V_2O_3 and V_2O_5. Gas phase products included propyne, acetone, carbon oxides, methane and isobutene. Methane and isobutene resulted from interfacial reaction involving the initial product (acetone).

1. Introduction

Acetoacetonates (beta-diketonates) are coordination compounds containing a bidentate ligand which are often thermally stable [1] and can be easily prepared for a wide range of metals [2]. The stability constant of this type of complex is notably high [3]. This implies that the acetoacetonate is capable of abstracting metals from media in which its concentration is low. As a consequence, rare metals can be effectively isolated and saved for other applications. For instance, acetoacetonates find use in the preparation of supported metal or metal oxide catalysts [4,5].

Recently, a metal acetoacetonate has been used as a precursor in organometallic chemical vapor deposition (OMCVD) for processing thin films of superconductor materials [6]. It is therefore important to know the thermal behavior of such precursors. Little information is available in the literature about the thermal decomposition reactions [7,8] of the metal acetoacetonates, a promising class of catalyst precursors. In an earlier study [7] of the thermal decomposition of $Zn(acac)_2$ dihydrate in an N_2 atmosphere, it was found that dehydration was complete at 110°C and the compound melted at 143°C, followed by decomposition to $Zn(CH_3COO)_2$ at 209°C. The acetate decomposed at 240°C forming a mixed phase, $ZnCO_3-ZnO$. On further heating at 655°C, ZnO was formed as the final product.

Vanadium oxides, the thermal genesis of which is to be studied in the present investigation, find numerous applications in various industrial and technological fields, e.g., as a catalyst and a catalyst support [9,10] in methanol formation reactions and as a refractory oxide [11] in the formation of ceramics [12].

The present investigation explores the thermal decomposition reaction of $VO(acac)_2$ and $V(acac)_3$, which have distinctly different structures [2]. The formation of vanadium oxides V_2O_x by the thermal decomposition of vanadyl and vanadium acetoacetonates is monitored by thermogravimetry (TG), differential thermal analysis (DTA) and IR gas phase analyses. The solid reaction products are analyzed by means of IR spectroscopy and X-ray diffractometry in the hope of attaining a deeper understanding of the thermal decomposition mechanisms.

2. Experimental

2.1. Materials

The $VO(C_5H_7O_2)_2$ and $V(C_5H_7O_2)_3$ were pure (95% and 97% respectively) products from Aldrich (USA). They are denoted in the text as $VO(acac)_2$ and $V(acac)_3$, respectively. From the thermal analysis (see below), the solid phase decomposition products were obtained by heating at 280–500°C for 1 h in a dynamic atmosphere of nitrogen (20 ml min^{-1}). The nitrogen atmosphere was used to avoid charring the organic moieties.

2.2. Apparatus and techniques

2.2.1. Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of the test samples were performed with an automatically recording Shimadzu 30H analyzer (Japan). A 20 mg portion of test sample was used for the TG, and highly sintered α-Al_2O_3 was the reference material for the DTA measurements. TG and DTA curves were recorded during heating to 500°C at various rates (2–20 °C min^{-1}) in a dynamic atmosphere of nitrogen (20 ml min^{-1}).

2.2.2. Infrared spectroscopy

The IR spectra of the test sample and its solid calcination products were obtained at a resolution of 5.3 cm^{-1} over the wavenumber range 4000–500 cm^{-1} by means of a Perkin-Elmer model 580B spectrophotometer (UK). The spectra were taken from thin (<20 mg cm^{-2}), lightly loaded ($<1\%$) KBr supported disks of the test samples.

IR identification of the decomposition gaseous products was achieved with the help of spectra taken from the gas phase surrounding of 0.5 g test sample being heated at 10 °C min^{-1} to various temperatures (280–400°C) for 5 min in a specially designed IR cell [13]. Prior to recording the gas phase spectra, the cell was briefly evacuated at room temperature and 10^{-2} mbar for 5 min. The cell background spectrum was ratioed out of the gas phase spectra using an on-line Perkin-Elmer Data Station, model 3700.

2.2.3. X-ray diffractometry

The XRD analysis of test samples and their calcination products was carried out by means of a model JSX-60 PA JEOL diffractometer (Japan), equipped with a source of Ni-filtered Cu Kα radiation. For identification purposes, diffraction patterns (I/I_0) vs. d-spacing (Å) obtained were matched with ASTM standards [14].

3. Results and discussion
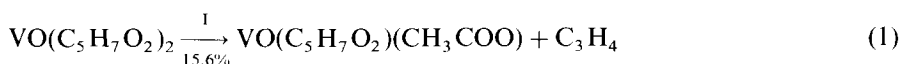
Fig. 1 shows the TG and DTA curves recorded for VO(acac)$_2$ [A] and V(acac)$_3$ [B] at 20 °C min^{-1} in a dynamic atmosphere of nitrogen. The curves indicate that VO(acac)$_2$ decomposes via four overlapping endothermic weight loss (WL) processes with maxima at 290 (I), 300 (II), 315 (III) and 325°C (IV). On the other hand, V(acac)$_3$ is shown to decompose via four overlapping endothermic WL processes occurring at 280 (I), 292 (II), 305 (III) and 325°C (IV). Fig. 2 shows the IR spectra taken from the gas phase surrounding the metal acetoacetonates after heating to various temperatures (280–400°C) for 5 min. The IR spectra and X-ray powder diffractograms obtained for the solid phase decomposition products at 280–500°C are presented in Figs. 3 and 4 respectively.

3.1. Characterization of the thermal processes

3.1.1. VO(acac)$_2$ [VO(C$_5$H$_7$O$_2$)$_2$]

Process I. The IR spectrum taken from the gas phase released at 280°C (Fig. 2A) has absorption bands at 1650, 1450, 930, 908 and 760 cm^{-1} assignable to CH$_3$–C=CH(C$_3$H$_4$) [15]. The WL (15.6%) determined by thermal process I (Fig. 1A) is close to that (15.8%) expected for the release of 1 mol of C$_3$H$_4$. The release of C$_3$H$_4$ indicates that the decomposition of VO(acac)$_2$ starts with the formation of the oxoacetate–acetoacetonate complex of vanadium

$$\text{VO(C}_5\text{H}_7\text{O}_2)_2 \xrightarrow[15.6\%]{1} \text{VO(C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{COO}) + \text{C}_3\text{H}_4 \qquad (1)$$

The solid phase IR spectrum of unheated $VO(acac)_2$ displays bands (cm^{-1}) due to $v_{C-CO} + v_{C-O}$ in combination with $v_{C-O} + v_{C-C}$ (1565, 1550, 1530); $\delta_{CH} + v_{C=C} + \delta_d CH_3$ (1430); $\delta_s CH_3$ (1380, 1360); $v_{C-CH_3} + v_{C-C}$ (1285); $\delta_{CH} + v_{C-CH_3}$ (1190); $\rho_r CH_3$ (1020); $v_{C-C} + v_{C-O}$ (940); π_{CH} (795, 780); $v_{C-CH_3} +$ ring deformation $+ v_{MO}$ (790); $\pi_{CH_3 COC}$ (655); ring deformation and v_{MO} (610) [2].

The IR spectrum of the solid product at 280°C (Fig. 3A) displays the same band structure as the $VO(acac)_2$ complex [2] but with lower intensity; in addition, absorption bands due to acetate have appeared at 1703, 1460, 1380 and 1150 cm^{-1} [16]. However, XRD of the solid product at 280°C (Fig. 4A), when compared with that of untreated $VO(acac)_2$, indicates an effective loss of crystal coherency. In fact, the product has a predominantly amorphous nature. These results may provide an
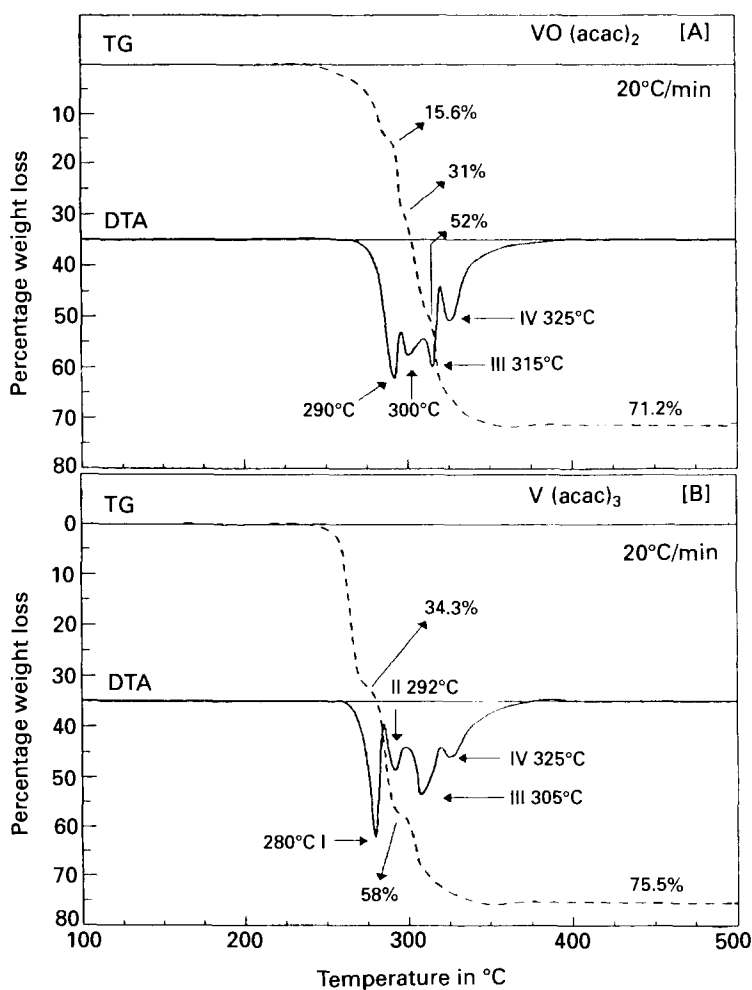

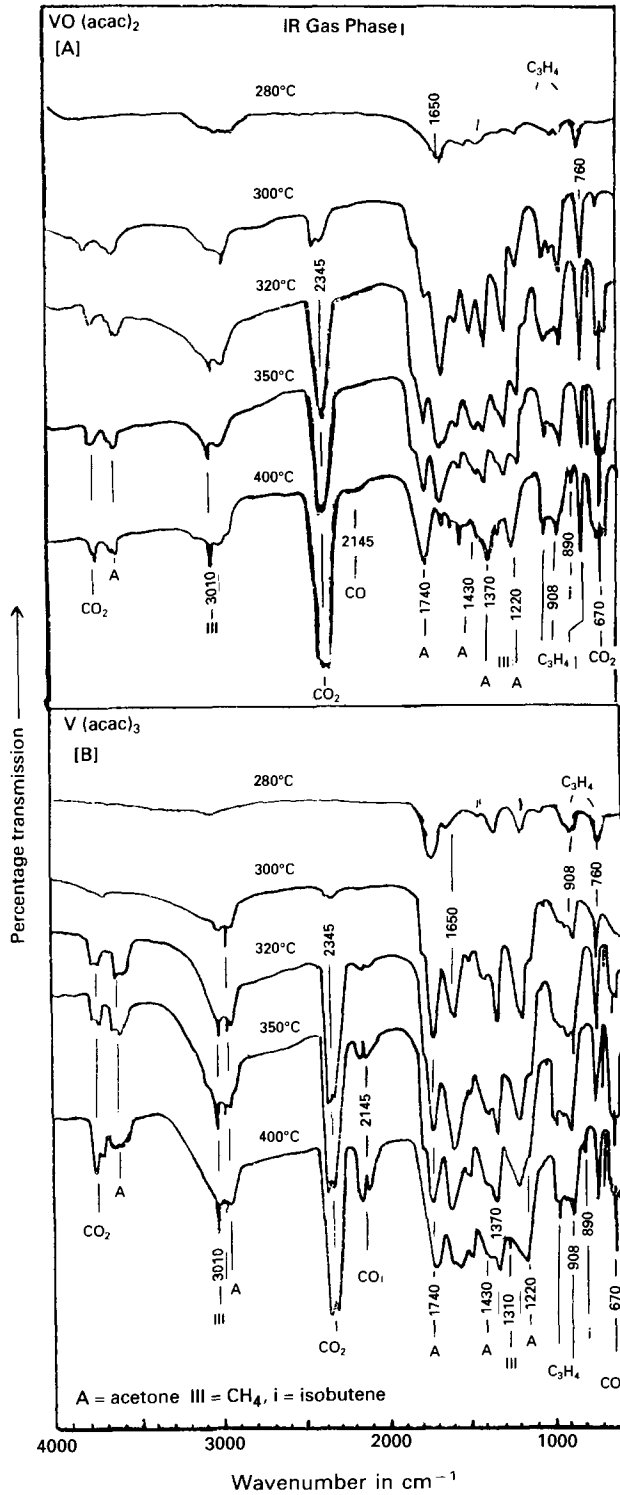Fig. 1. TG and DTA curves for $VO(acac)_2$ [A] and $V(acac)_3$ [B] heated at 20 °C min^{-1} in dry nitrogen.

Fig. 2. IR spectra taken from the gas phase products of heating VO(acac)$_2$ [A] and V(acac)$_3$ [B] at the temperatures indicated for 5 min.
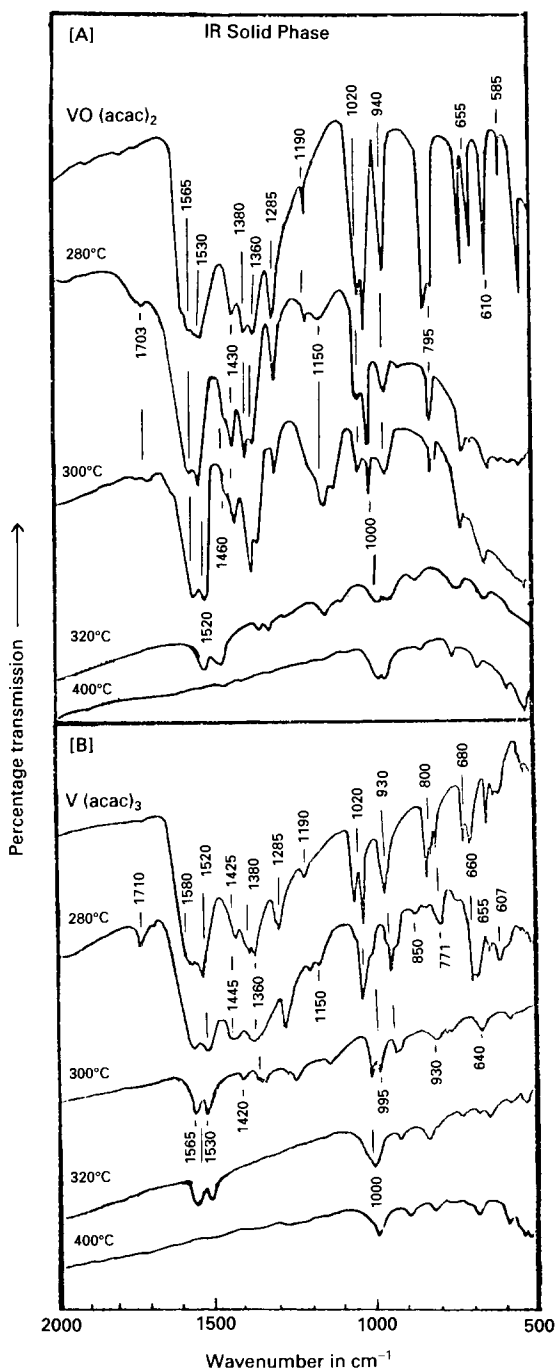
Fig. 3. IR spectra taken from the solid phase products of heating VO(acac)₂ [A] and V(acac)₃ [B] at the temperatures indicated for 1 h in dry nitrogen.
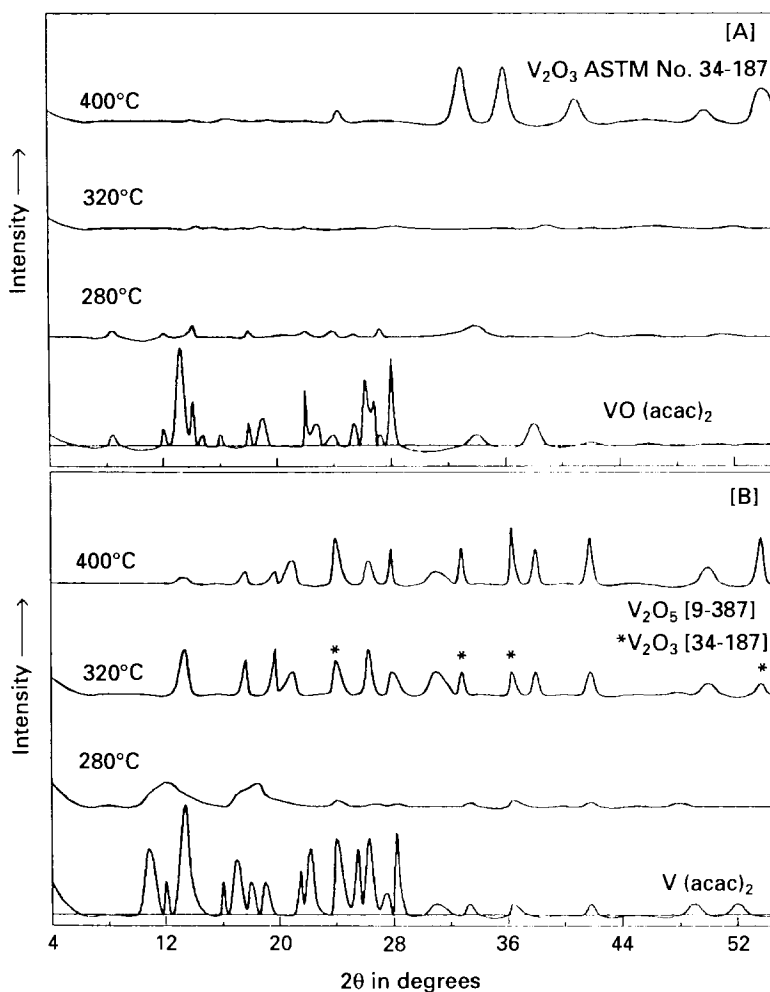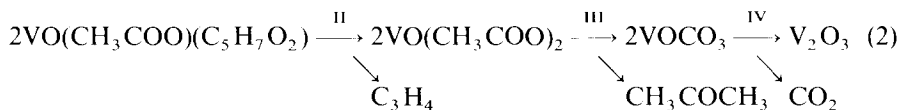
Fig. 4. X-ray powder diffractograms of the solid phase decomposition products of VO(acac)₂ [A] and V(acac)₃ [B] at the temperatures indicated for 1 h in dry nitrogen.

indication that the presence of the oxygen atom bonded to the vanadium metal causes strain in one of the two acetoacetonates, making its decomposition easier, and/or that the two acetoacetonate groups are bonded to the vanadyl group by bonds of two different strengths [17].

Processes II, III and IV. From the TG and DTA curves (Fig. 1A), it can be seen that processes II, III and IV are endothermic weight losses and are strongly overlapped even with process I. They show maxima at 300, 315 and 325°C respectively. These processes bring the total WL up to 71.2%, which is very close to that of 71.75% expected for the formation of V_2O_3. The WL observed through process II is $\approx 31\%$, very close to that expected (30.0%) for the formation of $VO(CH_3COO)_2$. Also, process III involves a WL of $\approx 52\%$, which is very close to
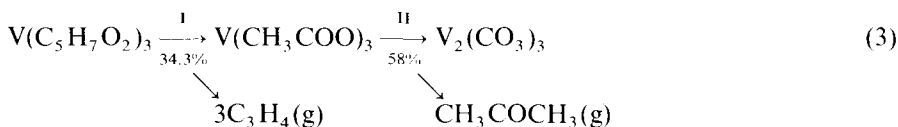
that expected for the formation of $VOCO_3$ from $VO(acac)_2$. Thus, the reactions involve the decomposition of $VO(CH_3COO)(C_5H_7O_2)$ to V_2O_3 as follows

$$2VO(CH_3COO)(C_5H_7O_2) \xrightarrow{\text{II}} 2VO(CH_3COO)_2 \xrightarrow{\text{III}} 2VOCO_3 \xrightarrow{\text{IV}} V_2O_3 \quad (2)$$
$$\searrow \qquad\qquad\qquad\qquad \searrow \qquad\qquad \searrow$$
$$C_3H_4 \qquad\qquad\qquad CH_3COCH_3 \quad CO_2$$

In support, the IR spectra of the gas phase at 300 and 320°C (Fig. 2A) display bands due to acetone at 1740, 1430, 1370 and 1220 cm^{-1} [15] and bands due to CO_2 at 2345 and 670 cm^{-1} [15]. Moreover, the C_3H_4 absorption bands are intensified. Reaction (2) is further corroborated by the IR spectra taken from the solid phase at 300 and 320°C (Fig. 3A), in which absorptions characteristic of $VO(CH_3COO)_2$ (at 1565, 1520, 1460, 1380 and 1150 cm^{-1}) [16] are observed in the 300°C spectrum but have disappeared in the 320°C spectrum, forming carbonate species (absorption bands at 1530, 1460 and 830 cm^{-1} [7,16,18]. At 400°C the spectrum displays only the characteristic bands of V_2O_3 [19]. Consistently, the corresponding XRD patterns at 400°C (Fig. 4A) match solely with the pattern (ASTM No. 34-187) of V_2O_3. However, the XRD patterns for the 300 and 320°C products are typical of amorphous materials.

3.1.2. V(acac)₃ [V(C₅H₇O₂)₃]

Processes I and II. Processes I and II are shown by the TG and DTA curves (Fig. 1B) to be overlapping, endothermic, weight losses, with respective maxima at 280 and 292°C. The WL effected (34.3%) through process I is fairly close to that expected (34.48%) for the formation of $V(CH_3COO)_3$. The IR gas phase spectra at 280 and 300°C (Fig. 2B) exhibit absorption bands assignable to C_3H_4 and acetone [7,15]. The release of C_3H_4 accounts for the decomposition of V(acac)₃ to vanadium acetate, and the release of acetone is probably due to the decomposition of the acetate [7,16] to carbonate through process II. The measured WL on completion of process II is 58%, which is near to the theoretical value of 59.5% expected for the formation of $V_2(CO_3)_3$, i.e.

$$V(C_5H_7O_2)_3 \xrightarrow[34.3\%]{\text{I}} V(CH_3COO)_3 \xrightarrow[58\%]{\text{II}} V_2(CO_3)_3 \quad (3)$$
$$\searrow \qquad\qquad\qquad \searrow$$
$$3C_3H_4(g) \qquad\quad CH_3COCH_3(g)$$

The IR solid phase spectrum of unheated V(acac)₃ (Fig. 3B) bears a great deal of similarity to that obtained for VO(acac)₂ (Fig. 3A). The spectrum of the solid product at 280°C (Fig. 3B) displays characteristic bands due to acetate at 1710, 1565, 1420, 1150 and 1030 cm^{-1} [16,20]. The difference ($\Delta v = 145$ cm^{-1}) between v_{as} (1565 cm^{-1}) and v_s (1420 cm^{-1}) of the COO$^-$ vibrations suggests that the acetate groups are bidentate acetate (bridged-bonded) to V ions [20]; also, the appearance of the absorption band at 1710 cm^{-1} gives indication of the transformation of unidentate acetate [18,20]. The solid products at 300 and 320°C yield IR spectra (Fig. 3B) documenting the disappearance of the acetate absorption bands and the appearance of absorptions assignable to carbonate species at 1565, 1420, 830 and 640 cm^{-1} [16]. The corresponding XRD patterns at 280 and 320°C (Fig. 4B) reveal the amorphous nature of the acetate and carbonate thus formed.

Processes III and IV. The thermal analysis results (Fig. 1B) show that processes III and IV are endothermic weight loss maximized at 305 and 325°C respectively, and are strongly overlapped even with process II. The TG curve indicates the total WL observed at the end of process IV at 75.4%, which lies between that of 73.8% expected for the formation of V_2O_5 from $V(acac)_3$ and that of 78.4% expected for the formation of V_2O_3 from $V(acac)_3$, i.e. process III is responsible for the decomposition of $V_2(CO_3)_3$ to form V_2O_5. Part of the V_2O_5 is reduced to V_2O_3 through process IV as follows

$$V_2(CO_3)_3 \xrightarrow{\text{III}} V_2O_5 + CO_2 + 2CO \tag{4}$$

$$V_2O_5 + 2CO \xrightarrow{\text{IV}} V_2O_3 + 2CO_2 \tag{5}$$
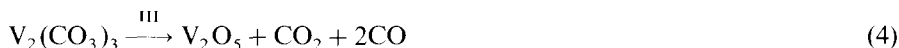
These findings are in agreement with the TPR studies [21] for the different types of oxygen in vanadium oxides (in an atmosphere of 6% H_2/Ar); the results indicate that the TPR profile of pure V_2O_5 has one single reduction peak located at 530°C. The presence of CO (reducing agent) as a gaseous decomposition product affected and accelerated (325°C) the reduction process in our case.

In support, the XRD analysis of the solid products obtained at 300–400°C (Fig. 4B) detected two crystalline phases, V_2O_3 [ASTM No. 34-187] and V_2O_5 [ASTM No. 9-387].

The IR spectrum of the solid product at 400°C (Fig. 3B) shows that the bands due to carbonate species have completely disappeared. Bands are detected at ≈ 1000, 830 and 625 cm^{-1} due to V_2O_5 and V_2O_3 [22].

In support, consider the IR spectrum of the gas phase at 300 and 320°C (Fig. 2B), where the characteristic bands due to CO_2 and CO (band at 2145 cm^{-1}) are markedly increased in intensity with increases in the heating temperature.

## 3.2. Chemical reactivity at the gas/solid interface

The gas phase IR spectra at 400°C for $VO(acac)_2$ and $V(acac)_3$ (Figs. 2A and 2B) display absorption bands diagnostic for methane and isobutene; their locations are indicated in Fig. 2. The assignments are according to Zaki and Sheppard [23]. These gases are not among the initial decomposition products of the vanadyl and vanadium acetoacetonates. The spectra show a notable drop in the intensity of the absorptions of gas phase acetone relative to the spectra at 300°C.

It has been shown [7,16,18,23,24] that the formation of methane and isobutene in the presence of metal oxide catalysts arises from the involvement of acetone molecules in a surface-mediated bimolecular reaction, in which acetone is adsorbed, and hence activated for an aldol condensation type of reaction

$$(CH_3)_2CO_{(s)} + OH^-_{(s)} + (CH_3)_2CO_{(g)} \rightarrow (CH_3)_2C{=}CH_{2(g)} + CH_3COO^-_{(s)}$$
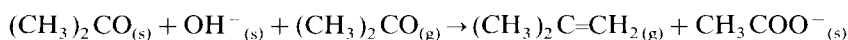
where g = gas and s = surface.
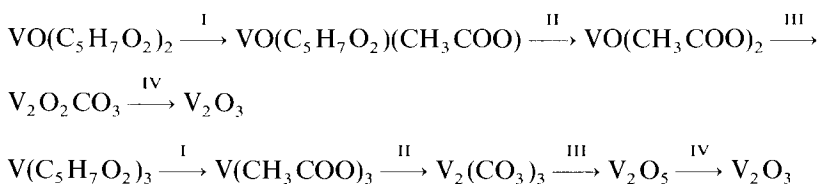
In addition, adsorbed acetone can also be activated for nucleophilic attack by an adjacent surface OH to split off a methyl group in the form of CH_4 [23]

$$(CH_3)_2CO_{(s)} + OH^-_{(s)} \rightarrow CH_{4(g)} + CH_3COO^-_{(s)}$$
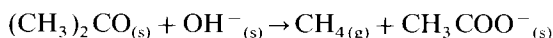
These or similar reactions on V_2O_3 and/or V_2O_5 may explain the simultaneous production of isobutene and methane and the decrease of acetone in the gas phase.

4. Conclusions

1. The thermal decomposition course of vanadyl and vanadium acetoacetonates in a dry nitrogen atmosphere may include the following pathways

$$VO(C_5H_7O_2)_2 \xrightarrow{\text{I}} VO(C_5H_7O_2)(CH_3COO) \xrightarrow{\text{II}} VO(CH_3COO)_2 \xrightarrow{\text{III}}$$

$$V_2O_2CO_3 \xrightarrow{\text{IV}} V_2O_3$$

$$V(C_5H_7O_2)_3 \xrightarrow{\text{I}} V(CH_3COO)_3 \xrightarrow{\text{II}} V_2(CO_3)_3 \xrightarrow{\text{III}} V_2O_5 \xrightarrow{\text{IV}} V_2O_3$$

2. Unidentate and bidentate structures of acetate are formed as intermediates through the decomposition of both vanadyl and vanadium acetoacetonate.

3. $VO(acac)_2$ is a selective precursor for the formation of V_2O_3. However, vanadium acetoacetonate forms a mixture of V_2O_5 and V_2O_3 as a final product.

4. The final decomposition product, vanadium oxides from both $VO(acac)_2$ and $V(acac)_3$, can catalyze the surface reaction of acetone to give methane and isobutene.

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