Thermal characterization of individual and mixed basic copper carbonate and ammonium metavanadate systems

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ABSTRACT

The thermal behaviour of individual and mixed solids, with different molar ratios, of basic copper carbonate and ammonium metavanadate was reported. The pure and mixed solids were thermally treated at 300, 500, 750 and 1000 °C. The thermal products at various calcination temperatures were characterized by means of thermal analyses (TG–DTG–DTA), X-ray diffraction (XRD) and electron spin resonance (ESR) techniques. The catalytic activity of all solids was measured using hydrogen peroxide decomposition at 30, 40 and 50 °C. The results revealed that pure basic copper carbonate decomposed to CuO at 300 °C and to Cu2O at temperature above 950 °C, where as pure ammonium vanadate decomposed to (NH4)2V6O16 and NH4V2O4 as an intermediate compound at 250 and 350 °C before the formation of V2O5 at 300 °C. CuO enhanced the formation of V2O5 at 300 °C. A series of copper vanadate phases were detected, Cu9V2O10, Cu2V2O7 and Cu3V5O14, for the mixtures 3Cu:1V, 1Cu:1V and 1Cu:3V preheated at 750 °C, respectively. These phases were formed as a result of solid–solid interactions between copper and vanadium oxides. The calcination temperature and the composition of the Cu–V mixtures affect the degree of crystallinity and pattern intensities of different phases detected at treatment temperatures ranged between 300 and 1000 °C. The catalytic activity of mixed CuO–V2O5 was found to be greater than that of single oxides obtained at the same calcination temperatures. This might be attributed to increase in the concentration of active sites by creation of new ion pairs. No measurable catalytic activity was observed for all solids calcined at 750 and 1000 °C. This might be attributed to restriction of catalytically active constituents.

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1. Introduction

The decomposition reactions of various compounds are of major importance because of their frequent applications in metallurgy and in the production of large-surface materials for used as solvent and catalyst [1,2]. The so-called mixed catalysts are often produced by thermal decomposition of mixed components of transition metals [3,4]. The thermal treatment of mixed solids may also lead to the formation of new compounds as a result of solid–solid interaction between the thermal products [5,6]. The compound formed may have new physicochemical and catalytic properties better than that of the pure components. Therefore, the catalytic activities of mixed catalysts were often much higher than those of mechanically mixed solids having the same composition [7,8].

Thermal analysis of two solid systems may be composed of complicated thermograms for several reasons for several possible reasons including the formation of new compound. The thermal reaction between the different solid constituents in the mixtures can be characterized by several techniques such as differential thermal analysis (DTA), X-ray diffraction (XRD), and infrared (IR) and by graphical treatment of derivategravimetric curves of the component in the isolated state and of the multi-component system [8,9].

The solid-state chemistry of the (M xV2O5) vanadium oxide bronze (VOB) represent an extensive family of phases with original variety of chemical or physical properties intimately associated with the variable stoichiometry of the M elements (alkali, alkaline earth, Cu, Ag, Zn—-) and the mixed valence of the vanadium (V5+–V4+). Among these VOBs the copper vanadium bronze family appears to be special [10,11].

This work reports a study of the thermal behaviour of pure and mixed solids composed of copper basic carbonate and ammonium metavanadate as well as the effect of chemical composition and calcination temperature on the course of solid–solid interactions between the thermal products. The pure and mixed solids were thermally treated at 300, 500, 750 and 1000 °C. The thermal products at various temperatures were characterized by means of thermal analyses (TG–DTG–DTA), electron spin resonance (ESR) and X-ray diffraction (XRD) techniques. The catalytic activity of all solids was measured using hydrogen peroxide decomposition as a model reaction at 30, 40 and 50 °C.
2. Experimental

2.1. Materials

The starting materials were solids of basic copper carbonate, CuCO₃, Cu(OH)₂, and ammonium metavanadate, NH₄VO₃. The chemicals employed were analytical grade and supplied by Prolabo Company. Three mixtures of molar ratios; 3:1, 1:1 and 1:3 with respect to CuO–V₂O₅ were prepared by mixing the materials, homogenizing and grinding. The produced powder was thermally treated by a gradual increase of temperature up to 300 °C, and kept in air at that temperature for 4 h. The same heating process was performed at other calcination temperature, namely 500, 750 and 1000 °C.

2.2. Techniques

Thermal analyses, i.e., thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis were carried out on using a Shimadzu Dr-40 thermal analyzer. The sample was placed in platinum crucible (0.1 cm³). The samples were studied under air atmosphere with flowing rate of 30 ml min⁻¹. Constant weights of sample (16–20 mg) were used in order to avoid the effect of variation in sample weight on peak shape and temperature. Alpha alumina was used as a reference material in this technique. The rate of heating was fixed at 10 °C min⁻¹.

An X-ray diffraction investigation of individual and mixed solids preheated in air at 300, 500, 750 and 1000 °C was conducted using a Philips diffractometer (type PW 1390). The patterns were run with iron filtered iron radiation (λ = 1.53 Å) at 30 kV and 10 mA with a scanning speed of 2 °C 2θ in 20 min⁻¹.

The crystallite size of different phases present in the solids at 300 and 500 °C was calculated from Scherer equation [12]:

\[ d = \frac{\beta}{\cos \theta} \]

where d is the average particle size, \( \beta \) the Scherer constant (0.89), \( \lambda \) the wavelength of X-ray beam, \( \theta \) the diffraction angle of the investigated phase and \( 2\theta \) is full width at half maximum (FWHM). Electron spin resonance spectra were taken using (Bruker Elexsys. 500) operated at X-band frequency. The following parameters are generalized to all samples otherwise mentioned in the text. Microwave frequency: 9.79 GHz. Receiver gain: 60. Sweep width: 6000 center at 3480 Cs. Microwave power: 0.202637 W.

The catalytic activity of individual and mixed solids obtained at different calcination temperatures was determined using H₂O₂ decomposition in aqueous solution. Microwave power: 0.202637 W. Otherwise mentioned in the text. Microwave frequency: 9.79 GHz. Receiver gain: 60.

The catalytic activity of individual and mixed solids obtained at different calcination temperatures resulted in the formation of well crystalline CuO phase. The degree of crystallinity of the detected phase was calculated for all solids preheated at 300, 500, 750 and 1000 °C using Scherer equation and was found to be 28, 31, 55 and 44 nm, respectively.

3. Results and discussion

3.1. Thermal analysis and XRD-characterization of pure basic copper carbonate thermally treated at different temperatures

The thermal analysis (TG–DTG–DTA) of pure basic copper carbonate has been carried out and represented in Fig. 1a. The DTG-curve of this solid consists of two endothermic peaks their minima located at 280 and 950 °C. These peaks were accompanied by two weight loss processes [4,13] at temperature ranged between (230)–(300) °C and (910)–(990) °C. The first process corresponds to the complete decomposition of pure basic copper carbonate to CuO with total weight loss of 25%. The second process related to the reduction of CuO to Cu₂O with total weight loss of 28%.

On the other hand, the X-ray diffractograms of pure basic copper carbonate calcined at 300, 500, 750 and 1000 °C are shown in Fig. 1b. It can be seen from this figure that the solid calcined at different temperatures resulted in the formation of well crystalline CuO phase. The degree of crystallinity of the detected phase progressively increased with increasing the calcination temperature up to 750 °C then decreased with increasing temperature treatment to 1000 °C without the detection of any diffraction lines of Cu₂O. The crystallite size of the detected phase was calculated for all solids preheated at 300, 500, 750 and 1000 °C using Scherer equation and found to be 28, 31, 55 and 44 nm, respectively.

3.2. Thermal analysis and XRD-characterization of pure ammonium metavanadate thermally treated at different temperatures

Fig. 2a represents the (TG–DTA) curves of pure NH₄VO₃. From this figure it can be seen that: (i) The TG-curve of this sample consisted of three weight loss processes in temperature ranged between (200)–(280) °C, (300)–(350) °C and (380)–(460) °C. The first two steps represented the thermal decomposition of ammonium metavanadate into different types of vanadyl compounds species as, (NH₄)₂V₆O₁₆ and NH₄VO(10) with a constant weight losses of 12% and 16.5% before the formation of V₂O₅ as a final product with a constant weight loss of 22% at 450 °C. (ii) The DTA-curve of this solid consisted of three endothermic peaks their minima located at 240, 340 and 700 °C. In addition, strong and sharp exothermic peak; its maxima; located at 425 °C was detected without the observation of any weight change in the TG-curve. This peak might correspond to the crystallization of V₂O₅. Furthermore, the endothermic peak located at 700 °C might represent the melting of vanadium oxide. The over all reaction might be written as follows [14,15]:

\[ 2\text{NH}_4\text{VO}_3 \rightarrow \text{V}_2\text{O}_5 + 2\text{NH}_3 + \text{H}_2\text{O} \]

On the other hand, Fig. 2b illustrates the X-ray diffractograms of pure ammonium metavanadate thermally treated at 300, 500, 750 and 1000 °C. These figures showed the formation of vanadyl compound, NH₄VO(10), for pure solid preheated at 300 °C. Increasing the calcination temperature to 500 °C resulted in the detection of diffraction patterns of V₂O₅ phase. The degree of crystallinity of this phase significantly increased with increasing the calcination temperature up to 1000 °C. The crystallite sizes of the detected phases were calculated for pure ammonium metavanadate preheated at 300, 500, 750 and 1000 °C using Scherer equation and were found to be, 45, 68, 82 and 103 nm, respectively.
3.3. Thermal analysis of mixtures of CuCO₃, Cu(OH)₂ and NH₄VO₃

Fig. 3a–c shows the thermal decomposition steps of the mixed solids of copper carbonate and ammonium metavanadate with molar ratios 3:1, 1:1 and 1:3, respectively. The DTA-curve of mixed solids with molar ratio 3Cu:1V consisted of six endothermic peaks their minima located at 223, 287, 337, 759, 796 and 945 °C. In addition, two exothermic peaks their maxima located at 383 and 635 °C were detected. On the other hand, DTA-curve of mixed solids with molar ratio 1Cu:1V consisted of five endothermic peaks their minima located at 234, 276, 542, 592 and 767 °C. In addition, two exothermic peaks having maxima located at 355 and 392 °C were detected. On the other hand, the DTA-curve of mixed solids with molar ratio 1Cu:3V consisted of three endothermic peaks their minima located at 238, 331 and 735 °C. In addition, two exothermic peaks their maxima located at 400 and 511 °C were observed.

The first thermal decomposition step for all the mixtures starts at about 230 °C represents the removal of physisorbed water and ammonia from both salts. The second step starts at temperature ranged between 250 and 330 °C. This step corresponds to the complete decomposition of pure salts to copper and vanadium oxides. Furthermore, the thermograms of all Cu:V mixtures did not show any noticeable mass loss from 500 to 700 °C. This might be attributed to the formation of copper vanadate compounds which formed as a result of solid–solid interactions between the produced oxides. The type of formed copper vanadate phases much influenced by the composition of the mixture and calcination temperature range. These phases will be identified in Section 3.4.

The comparison of thermograms of pure and mixed salts shows that increasing the amount of vanadium oxide in the Cu–V mixtures prevents the reduction of copper oxide to cuprous oxide at temperature more than 950 °C. On the other hand, copper oxide enhanced the thermal decomposition of ammonium vanadate to vanadium oxide at 300 °C. Furthermore, the area of endothermic peak located at temperature ranged between 715 and 765 °C, which represents the melting of V₂O₅, significantly decreased with increasing the amount of CuO in the mixture. On the other hand, the last thermal step for the mixture (3Cu:1V) started at temperature ranged between 800 and 970 °C might reflect the thermal decomposition...
of formed copper vanadate and/or the formation of cuprous oxide.

3.4. XRD-characterization of thermal products obtained by firing mixtures of CuCO₃, Cu(OH)₂ and NH₄VO₃

Fig. 4a–c depicts the X-ray diffractograms of the mixtures of basic copper carbonate and ammonium metavanadate having the molar ratios 3Cu:1V, 1Cu:1V and 1Cu:3V thermally treated at 300, 500, 750 and 1000 °C, respectively. Inspection of these figures shows that: (i) Crystalline CuO (monoclinic) and V₂O₅ (orthorhombic) phases were detected for all the mixtures thermally treated at 300 °C, except that rich in copper (3Cu:1V), only the X-ray patterns of copper oxide phase is observed. The peak height and degree of crystallinity of CuO phase progressively decreased with increasing the amount of vanadium in the mixture. The crystallite sizes of CuO and V₂O₅ phases were calculated using Scherrer equation. The crystallite sizes of CuO phase detected for the mixtures 3Cu:1V and 1Cu:1V calcined at 300 °C were found to be 46 and 41 nm, respectively. On the other hand, the crystallite sizes of V₂O₅ detected for the mixtures 1Cu:1V and 1Cu:3V heated at 300 °C were found to be 34 and 53 nm, respectively. (ii) Increasing of calcination temperature to 500 °C resulted in significant increase in the degree of crystallinity of CuO for all mixed solids while that of V₂O₅ phase decreased. On the other hand, no diffraction lines of V₂O₅ was detected for the mixture, (3Cu:1V) calcined at 500 °C. (iii) The X-ray diffractograms of the mixtures preheated at 750 and 1000 °C show the disappearance of all diffraction lines of CuO and V₂O₅ for all the mixtures except the mixtures, 3Cu:1V and 1Cu:1V, resulted in the formation of poorly crystalline CuO phase. In addition, a series of copper vanadate phases [10,11], Cu₅V₂O₁₀, Cu₂V₂O₇ and Cu₃V₅O₄, were detected for all the mixtures preheated at 750 and 1000 °C (except the mixture 1Cu:1V calcined at 1000 °C). These phases formed as a result of thermal solid–solid interactions between copper and vanadium oxide phases regarding to the composition of the mixture. Furthermore, it can be seen also from Fig. 4a–c that the calcination temperature and the composition of the Cu–V mixtures affect the degree of crystallinity and pattern intensities of copper vanadate phases at 750 and 1000 °C as follows: (i) The X-ray diffractograms of the mixture (3Cu:1V) calcined at 1000 °C resulted in a progressive decrease in all of all diffraction lines of CuO and Cu₂V₂O₇, and Cu₅V₂O₁₀. (ii) Increasing of calcination temperature from 750 to 1000 °C for the mixture (1Cu:1V) led to thermal decomposition of Cu₂V₂O₇ into crystalline CuO and V₃O₅ phases. (iii) While for the mixture 1Cu:3V heated at 1000 °C led to decrease of peak height of Cu₃V₅O₄ without the detection of copper and vanadium oxides phases.

3.5. Catalytic activity measurements of pure and mixed solids precalcined at different temperatures

The experimental results obtained revealed that the decomposition of H₂O₂ over pure and mixed solids under investigation calcined at different temperatures followed first-order kinetics. The kinetics of the catalyzed reaction being monitored for reactions carried out at 30, 40 and 50 °C by measuring the volume liberated oxygen at different time intervals until equilibrium was attained. Table 1 depicts the values of reaction rate constant k min⁻¹ measured at different reaction temperatures. The values of rate constants were obtained from the plots of ln(a/a−x) against time, where a is the initial concentration of H₂O₂ and x is the amount of evolved oxygen (see Fig. 5a). In addition, the effect of chemical composition and calcination temperature on the catalytic activity of CuO–V₂O₅ system under investigation is represented in Fig. 5b.

From the inspection of the data given in Table 1 and Fig. 5a–b, it can be seen that: (i) Individual copper and vanadium oxides obtained by thermal treatment of their salts at 300 and 500 °C exhibit a very small catalytic activity in H₂O₂ decomposition. (ii) The catalytic activities of variously mixed solids progressively
increased with increasing the amount of vanadium in the mixture, increasing the reaction temperature from 30 to 50 °C and with increasing the calcination temperatures from 300 to 500 °C.

(iii) The catalytic activity of mixed CuO–V_2O_5 obtained by thermal treatment of mixed solids at the same calcination temperatures was found to be greater than that of single oxides. This can be interpreted in terms of the concept of bivalent catalytic centers [4,7,13,16,17] by assuming that for CuO, the centers consist of Cu^{2+}–Cu^{+} ion pairs and for V_2O_5, they consist of V^{5+}–V^{4+} ion pairs. The higher catalytic activity of two component oxides may be attributed to the fact that besides the one component sites Cu^{2+}–Cu^{+} and V^{5+}–V^{4+}, there will be also the mixed sites Cu^{+}–V^{5+} and/or Cu^{2+}–V^{4+} ion pairs as a result of mutual charge interaction. In other words, increasing the catalytic activity of mixed oxides might be attributed to increase in the concentration of active sites by creation of new ion pairs. This behaviour will be discussed in Section 3.4 of ESR.

From the above results, the mechanism of H_2O_2 decomposition on (CuO–V_2O_5) mixed oxide catalysts can be summarized as follows [4,7]:

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightleftharpoons \text{H}^+ + \text{HO}_2^- \\
\text{HO}_2^- & \rightarrow \text{HO}^+ + \text{e} \\
\text{Cu}^{2+} + \text{e} & \rightarrow \text{Cu}^+ \\
\text{V}^{5+} + \text{e} & \rightarrow \text{V}^{4+} \\
\text{Cu}^+ + \text{V}^{5+} & \rightarrow \text{Cu}^{2+} + \text{V}^{4+}
\end{align*}
\]

In this case, the presence of reduced copper in the system is capable to reduce V^{5+} (major catalytic center) partly to ions of lower oxidation state (V^{4+}) minor centers being more active species in

**Table 1**

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>Calcination temperature (°C)</th>
<th>30 °C (K/min⁻¹)</th>
<th>40 °C (K/min⁻¹)</th>
<th>50 °C (K/min⁻¹)</th>
<th>(E_a) kJ mol⁻¹</th>
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<tr>
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<td>3Cu:1V</td>
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<td>0.050</td>
<td>0.073</td>
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<tr>
<td>1Cu:1V</td>
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<td>0.056</td>
<td>0.082</td>
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<td>0.070</td>
<td>0.090</td>
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<tr>
<td>Pure V-salt</td>
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<td>0.041</td>
<td>0.059</td>
<td>37</td>
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</tr>
<tr>
<td>Pure Cu-salt</td>
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<td>0.046</td>
<td>0.068</td>
<td>38</td>
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<tr>
<td>3Cu:1V</td>
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<td>0.082</td>
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<tr>
<td>1Cu:3V</td>
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<td>0.055</td>
<td>0.076</td>
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</tbody>
</table>

**Fig. 5.** (a) Dependence of ln((a–x)/x) vs. time for catalyst (1C-3V) calcined at (i) 300 and 500 °C. (b) Dependence of the rate constant (k, 10 min⁻¹) on catalyst composition (Cu–V) calcined at A-300 °C and B-500 °C.
hydrogen peroxide decomposition reaction [7,16]. This means that the observed changes of the catalytic activity are probably due to the changes of valence state of catalytically active components of the catalyst [7,17]. (iv) No measurable catalytic activity observed for all solids calcined at 750 and 1000 °C. This might attributed to restriction of catalytically active constituents by the formation of copper vanadate compounds.

Determination of the apparent activation energy (E_a) for the catalytic decomposition of H_2O_2 in the presence of pure and mixed oxides has shed some light on the possible changes in the mechanism of the catalyzed reaction. Thus, values of k measured at 30, 40, and 50 °C over the variously treated solids have allowed (E_a) to be obtained via direct application of the Arrhenius equation [5,17]. The values of (E_a) thus obtained are listed in Table 1. It can be seen from Table 1 that the addition of increasing amounts of vanadium oxide resulted in a measurable decrease in the value of (E_a). This finding ran parallel to the observed increase in the catalytic activity due to this treatment.

Table 1 also shows that the values of activation energy (E_a) are clustered in the range of 43–30 kJ mol^{-1} for the mixed solids calcined at 300 °C and are clustered in the range of 38–25 kJ mol^{-1} for the mixed solids calcined at 500 °C. The constancy of the values of activation energy points to similar nature of active centers being different from that of single copper or vanadium salts calcined at the same calcination temperatures.

3.6. ESR spectra of pure and mixed solids

Fig. 6a shows ESR spectra of ammonium vanadate calcined at 300, 500 and 750 °C. Although we initiated with V^5+ species, V^4+ species were clearly shown in these samples decreasing with increasing calcination temperatures represented by a sharp isotropic signal (clearly observed in 300 °C sample) centered at magnetic field at 3500 Gs [18].

Introducing Cu in vanadium resulted in the appearance of another broad overlapping signal due to the presence of Cu^{2+} species centered at nearly 3100 Gs [19]. Thus from Fig. 6b of 1Cu:1V system calcined at different temperatures the above observation is clearly shown thus at 300 °C sample both overlapping signals of V^4+ and Cu^{2+} are observed, moreover at 500 °C only V^4+ signal can be seen. This indicate that Cu Species exist either as separate CuO which is antiferromagnetic [19,20] and will not be detected by ESR or as Cu^{+} species which also not detected by ESR. In addition, at 750 °C sample Cu^{2+} species are overlapped clearly with lower amount of V^4+ species. This indicates that at 750 °C interaction occurs between Cu and V resulting in compound contains Cu^{2+} and V^5+ species with lesser amount of V^4+ species. Keeping in mind the above observations and taking a look at H_2O_2 decomposition results, which showed that the catalytic activity of this system increased from 300 to 500 °C, one can explain the above increase by the partial reduction to copper and vanadium oxide system by
increasing temperature which resulted in an electron transfer to $\text{Cu}^{2+}$ and $\text{V}^{5+}$ according to the following equation:

$$\text{Cu}^{2+} + \text{V}^{5+} + 2e^{-} \rightarrow \text{Cu}^{+} + \text{V}^{4+}$$

Although we suggest the partial reduction of $\text{Cu}^{2+}$ and $\text{V}^{4+}$ as evidenced by ESR, this change may not be detected by XRD. This can be explained by the fact that this change in oxidation state may occur in small amount without phase change in the crystals containing vanadium and/or copper ions.

According to the above equation, the increase in the catalytic activity can be explained by the presence of $\text{Cu}^+$ species which has no signal in ESR spectra. It is seemed that the presence of $\text{Cu}^+$ species may be induced by the presence of $\text{V}^{4+}$ species at these temperatures.

Moreover, in case of $3\text{Cu}:1\text{V}$ system (Fig. 6c), also the previous observations can be seen, thus at 300 $^\circ$C both signals of $\text{Cu}^{2+}$ and $\text{V}^{4+}$ can be seen, however at 500 $^\circ$C only species of $\text{V}^{4+}$ can be observed with very low contribution of $\text{Cu}^{2+}$ species. The above observation reflects itself in the catalytic activity thus the catalytic activity increased with increasing calcination temperature from 300 to 500 $^\circ$C. Moreover the absence of $\text{V}^{4+}$ species at 750 $^\circ$C sample predicts that the electronic transfer is not occurred and consequently the catalytic activity is predicted to be null due to the absence of induced $\text{Cu}^+$ species.

Regarding to $1\text{Cu}:3\text{V}$ system (Fig. 6d) it can be observed that in this system the main factor affecting the catalytic activity is the presence of $\text{V}^{5+}$ species and not the electron transfer as the previous two systems, so that, although the $\text{Cu}^{2+}$ are predominant in 500 $^\circ$C sample the catalytic activity increased with increasing calcination temperature from 300 to 500 $^\circ$C indicating that the electron transfer effect is neglected in this system.

4. Conclusions

It can be concluded from the obtained results that pure basic copper carbonate decomposed to CuO at 300 $^\circ$C and to Cu$_2$O at temperature above 950 $^\circ$C. On the other hand, pure ammonium vanadate decomposed to (NH$_4$)$_2$V$_2$O$_7$ and NH$_4$V$_4$O$_9$ as intermediate compounds at 250 and 350 $^\circ$C before the formation of V$_2$O$_5$ at 450 $^\circ$C. The presence of copper oxide in the Cu–V mixtures enhanced the thermal decomposition of ammonium vanadate to V$_2$O$_5$ at 300 $^\circ$C. As well as the presence of great amount of vanadium oxide in the Cu–V mixtures prevents the formation of crystalline Cu$_2$O. A series of copper vanadate phases were detected, Cu$_3$V$_2$O$_{10}$, Cu$_2$V$_2$O$_7$ and Cu$_3$V$_3$O$_{14}$, for the mixtures 3Cu:1V, 1Cu:1V and 1Cu:3V preheated at high calcination temperature, respectively. These phases formed as a result of thermal solid–solid interactions between copper and vanadium oxide phases. The calcination temperature and the composition of the Cu–V mixtures affect the degree of crystallinity and pattern intensities of formed copper vanadate phases. The catalytic activity of mixed CuO–V$_2$O$_5$ obtained by thermal treatment of mixed solids at the same calcination temperatures was found to be greater than that of single oxides. This can be interpreted in terms of the concept of bivalent catalytic centers. No measurable catalytic activity observed for all solids calcined at 750 and 1000 $^\circ$C. This might attributed to the restriction of catalytically active constituents by the formation of copper vanadate compounds.

References