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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 Cu_2O at temperature above 950 °C, where as pure ammonium vanadate decomposed to $(NH_4)_2V_6O_{16}$ and $NH_4V_4O_{10}$ as an intermediate compound at 250 and 350 °C before the formation of V_2O_5 at 450 °C. CuO enhanced the formation of V_2O_5 at 300 °C. A series of copper vanadate phases were detected, $Cu_5V_2O_{10}$, $Cu_2V_2O_7$ and $Cu_3V_5O_4$, 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 $CuO–V_2O_5$ 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.

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 derivatographic curves of the component in the isolated state and of the multi-component system [8,9].

The solid-state chemistry of the ($M_xV_2O_5$) 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 ($V^{5+}–V^{4+}$). 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.

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2. Experimental

2.1. Materials

The starting materials were solids of basic copper carbonate, $CuCO_3$, $Cu(OH)_2$ and ammonium metavanadate, NH_4VO_3. 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 $CuO–V_2O_5$; 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 Dt-40 thermal analyzer. The sample was placed in platinum crucible (0.1 cm^3). 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 = 1.93 Å) at 30 kV and 10 mA with a scanning speed of 2° in 2θ min^{-1}.

The crystallite size of different phases present in the solids at 300 and 500 °C was calculated from Scherer equation [12]: $d = B\lambda/\beta \cos\theta$, where d is the average particle size, B the Scherer constant (0.89), λ the wavelength of X-ray beam, θ the diffraction angle of the investigated phase and $\boldsymbol{\beta}$ 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 Gs. Microwave power: 0.202637 W.

The catalytic activity of individual and mixed solids obtained at different calcination temperatures was determined using H_2O_2 decomposition in aqueous solution at 30, 40 and 50 °C using 0.5 ml volume of H_2O_2 of known concentration diluted to be 20 ml with distilled water. The mass of catalyst sample taken in each kinetic experiment was fixed at 10 mg for all samples. The reaction was followed up through a gasometric measurement of oxygen liberated at different time intervals till no further O_2 was liberated [13].

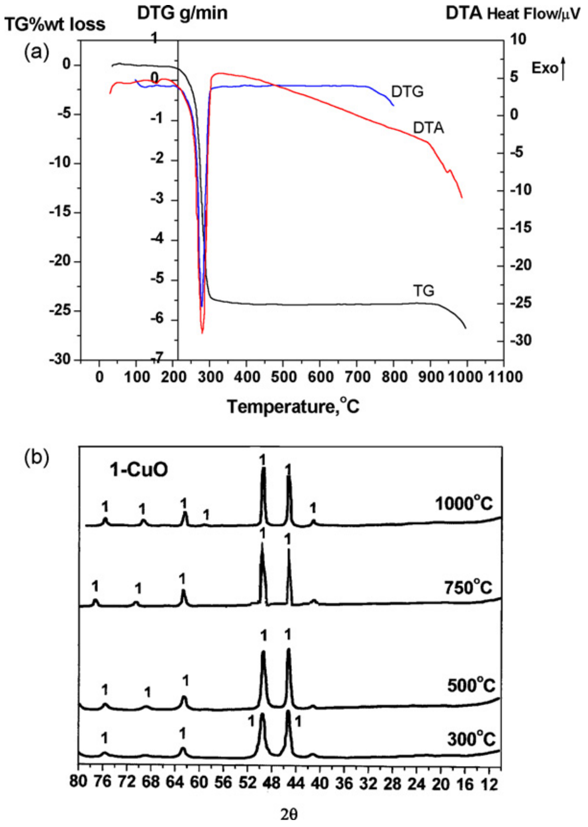

Fig. 1. (a) Thermal analysis (TG–DTG–DTA) of pure basic copper carbonate. (b) X-ray diffractograms of pure basic copper carbonate thermally treated at 300, 500, 750 and 1000 °C.

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 DTA-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 Cu_2O with total weight loss of 28%.

On the other hand, the X-ray diffractograms of copper basic 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 treatment temperature to 1000 °C without the detection of any diffraction lines of Cu_2O. The crystallite size 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.

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

Fig. 2a represents the (TG–DTA) curves of pure NH_4VO_3. 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, $(NH_4)_2V_6O_{16}$ and $NH_4V_4O_{10}$ with a constant weight losses of 12% and 16.5%, before the formation of V_2O_5 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 V_2O_5. 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]:

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O$$

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, $NH_4V_4O_{10}$, for pure solid preheated at 300 °C. Increasing the calcination temperature to 500 °C resulted in the detection of diffraction patterns of V_2O_5 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.