Journal of Analytical and Applied Pyrolysis 120 (2016) 207–214

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Exploration of the thermal decomposition of oxalates of copper and silver by experimental and computational methods

K. Sarada, K.R. Vijisha, K. Muraleedharan*

Department of Chemistry, University of Calicut, Calicut, 673635, India

ARTICLE INFO

Article history:
Received 2 April 2016
Received in revised form 5 May 2016
Accepted 5 May 2016
Available online 6 May 2016

Keywords:
Bond order
Bond length
Bond angle
Electron density topology
Thermal decomposition of copper and silver oxalates

ABSTRACT

Copper and silver oxalates have been synthesized and were characterized by IR and XRD. Thermal decomposition of the prepared oxalates has been studied experimentally using differential scanning calorimetric (DSC) and thermogravimetry (TG) and the decomposition products were characterized. Topological properties of electron density, bond orders, bond length and bond angle calculations were carried out in the light of the thermal decomposition pathway characteristic for these compounds with the help of density functional theory using LanL2DZ as basis set. All the computational studies were made using Gaussian09W simulation package. The obtained results shed some additional light on the origins of the complex pathway observed during the thermal decomposition process. Global reactive descriptors like vertical ionization potential, vertical electron affinity, electronegativity, electrophilicity, softness, hardness, etc., are calculated in order to analyze the extent of reactivity of the molecules considered. The obtained results from the experiments, support the conclusion that during the thermal decomposition process, copper oxalate decompose to Cu, Cu_2O/CuO nanoparticles and CO/CO_2, where as the silver oxalate decompose to Ag metal and CO_2, the silver metal on exposure to air is transformed to Ag_2O, which are in agreement with the theoretical analysis.

1. Introduction

Thermal decomposition of metal oxalates has been the subject of many researchers for more than a century [1–3]. According to earlier reports the thermal decomposition of copper oxalate is taking place through various pathways [4,5], of which the three main competing reactions are:

$CuC_2O_{4(s)}$:

a → $Cu_{(s)} + 2CO_{2(g)}$;
b → (½)$Cu_2O_{(s)}$ + (½)$CO_{(g)}$ + 1½ $CO_{2(g)}$
c → $CuO_{(s)} + CO_{(g)} + CO_{2(g)}$

Emmanual. et al. [6] tried to re-examine the thermal behavior of copper oxalate but the mechanism of thermal decomposition of copper oxalate was by no means got resolved. According to them the unexpected endothermic decomposition of copper oxalate cannot be explained unequivocally by the thermal, spectroscopic and X-ray methods [6]. Boldyrev [7] have been made an excellent review on the thermal decomposition of silver oxalate, in which so many decomposition paths were discussed, out of which, the formation of silver metal and evolution of carbon dioxide is most preferred. The lack of consistent description and explanation of the origin and thermal decomposition path of oxalates from the experimental results made us to think for the theoretical explanation of the same. The experimental findings can be rationalized through density functional theory (DFT)based computational analysis [8]. Density-functional theoretical investigation has been the subject of many researchers [9,10]. Diao et al. [11] have been performed a series of molecular dynamics simulations (MDSs) to study the thermal decomposition characteristics of epoxy resin, the agreement of the obtained results with available experimental observations provided useful insights into the complicated bulk thermal decomposition of organic materials under extreme conditions at the atomistic level. It seems reasonable to expect that the theoretical study of the fundamental features of electron density (topological analysis) and chemical bond (bond order, bond length, etc.) should in principle lead to the prediction of the decomposition ways of metal oxalates. Kolezyński et al. [12–18] recently carried out the theoretical analysis of electronic structure and bonding properties of many transition metal oxalates (including silver oxalate) which turned out to be a very promising and not only gave us additional insight into the thermal decomposition process in those oxalates but also helped to describe it as a series of consecutive bond breaking steps proceeding in theoretically predicted order. Their entire study was based on the topological analysis of electron density (Bader's Quantum Theory of Atoms in Molecules

* Corresponding author.
E-mail address: kmuralika@gmail.com (K. Muraleedharan).

http://dx.doi.org/10.1016/j.jaap.2016.05.007
0165-2370/

[19] formalism) obtained from first principles FP-LAPW calculations and structural and bonding properties-bond valence, bond strength, and stresses associated with deviation of given structure from ideal one (Brown's Bond Valence Method [20]). The objective of the present work is to investigate the thermal decomposition behavior of anhydrous copper and silver oxalates by experimental techniques and also by theoretical analysis of electronic structure and bonding properties based on the DFT method using Gaussian09W simulation package.

2. Materials and methods

2.1. Materials

AnalaR grade copper nitrate trihydrate ($CuNO_3{\cdot}3H_2O$), silver nitrate ($AgNO_3$), oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) all of Merck, India; assay ≥99.9% were used.

2.2. Experimental methodology

Solution with cation concentrations of Cu and Ag were co precipitated by adding 0.1 M oxalic acid solution with warming and stirring. The resultant solution was stirred for another 4 h. The reacted solution was kept for some time to settle the precipitate, then filtered off and washed several times with distilled water followed by ethyl alcohol and air dried in an oven kept at 40 °C and was used for characterization. The obtained precipitates of silver and copper oxalates were decomposed by keeping in a muffle furnace at 200 and 400 °C respectively for 4 h.

The X-ray diffraction (XRD) measurements of the samples were performed on a RIGAKU MINI FLEX-600 X-ray diffraction spectrophotometer using Cu Kα (1.5418A°) radiation.

The infra red (IR) spectrum of the samples in KBr pellet was recorded using a JASCO FT-IR-4100 instrument, which offers high sensitivity, maximum resolution (0.9 cm^{-1}) and high signal to noise ratio (22,000:1). The sample was compressed with KBr into pellet and analyzed as KBr disc from 400 to 4000 cm^{-1}.

The thermogravimetry (TG) and derivative thermogravimetry (DTG) were done on a T.A. thermal analyzer, model: TGA Q50 V20.2 Build 27 at a heating rate of 10° min^{-1}. The operational characteristics of the TG system are; atmosphere: flowing nitrogen, at a flow rate of 60 mL min^{-1}, sample mass: 10 mg, sample pan: silica. Duplicate run's were made under similar conditions and found that the data overlap with each other, indicating satisfactory reproducibility.

The differential scanning calorimetric (DSC) measurements of the samples was performed on a Mettler Toledo make(model: DSC822e) instrument. The operational characteristic of the DSC system are: atmosphere: flowing air at a flow rate of 20 mL min^{-1}; sample mass: 5 mg; sample holder: platinum. Samples were subjected to control heating, in the range 303–648 K at a heating rate of 10° min^{-1}.

2.3. Computational methodology

The theoretical analyses of electronic structure and bonding properties of anhydrous copper and silver oxalates have been done based on the DFT method. Density Functional Theory is a widely accepted computational tool because of its high degree of predicting power and accuracy [21]. The structures of copper and silver oxalates are optimized by DFT with LanL2DZ as basis set. The level of theory adopted was B3LYP, which consists of Becke's exchange functional [22] in conjunction with Lee-Yang-Parr correlation functional [23]. All the computational works were carried out through Gaussian 09 software package [24]. Natural Bond Order (NBO) analysis of these molecules enables to give a quantitative evaluation of electron density distribution. Global reactive descriptors like ionization potential, electron affinity, electronegativity, electrophilicity, softness, hardness, etc., are calculated in order to analyze the extent of reactivity of the molecules considered.

2.3.1. Natural bond order (NBO) analysis

NBO analysis is based on an approach of transforming multi electron wave functions of the molecules into localized form that corresponds to single-center (lone pair – LP) and two centered (natural bonding and antibonding orbitals – BD and BD* respectively) elements. It gives a deep insight into the intra and intermolecular orbital interaction in the molecules between filled donor and empty acceptor NBOs, which in turn will lead to the qualitative conclusion of donor-acceptor properties of substituents [25]. Each

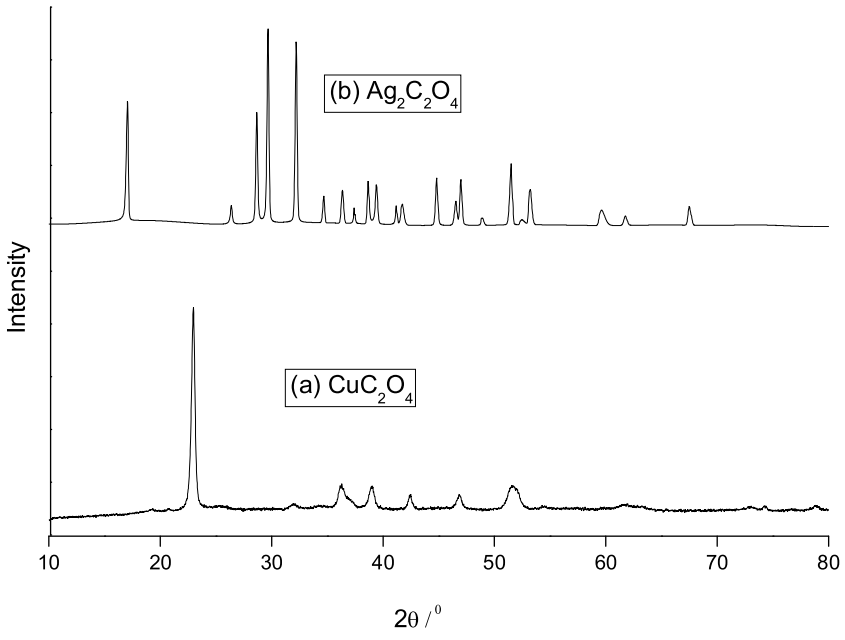

Fig. 1. XRD pattern of copper and silver oxalates.