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Comparison of the dehydration kinetics of solid state compounds of 2-methoxybenzylidenepyruvate with some divalent metal ions

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Experimental

2-methoxybenzylidenepyruvic acid (2-MeO-BP$^-$H$^+$) and its sodium salt, 2-methoxybenzylidenepyruvate (2-MeO-BP$^-$Na$^+$), were synthesized, purified and prepared, first the acid and then the salt, as described in literature [1]. All the complexes of the general formula $M^{m+}L_m$ nH_2O, where M are the divalent metal ions Fe, Co, Ni, Cu, Zn and L is the sodium salt. The solid-state compounds were prepared by dropwise adding the chlorides of the metal ions to the ligand solution (except for iron, where the sulphate was used) and this was done under continuous stirring until total precipitation was achieved. The precipitates were filtered and washed with water to totally eliminate the chloride (or sulphate) compounds and then dried at room temperature and stored until constant mass in a desiccator over anhydrous calcium chloride.

Kinetic evaluation of the dehydration steps were obtained using heating rates of 5, 10 and 20ºC min^{-1} from 30 to 500ºC. The curves were obtained using a SDT 2960 thermoanalyser system from TA Instruments Powered samples having a mass of 1 and 5mg (±0.05mg) were placed in an alumina crucible, under a nitrogen flow of 100 mL min^{-1}.

This is compound also was examined using Scanning Electron Microscopy (SEM). The particles were sputtercoated with a thin and uniform layer of gold using a vacuum evaporator and then examined using a JEOL Scanning Microscope, model JSM-T-330A at an accelerating voltage of 20 kV.

Results and discussion

In a previous work, these were characterized by simultaneous TG-DTA and DSC curves (in dynamic air atmosphere), infrared spectroscopy and X-ray diffractometry [2]. This compounds are in agreement with the stoichiometry $M{:}L_2$ nH_2O where M represents the bivalent metal ions, L is the ligand and n is the number of water molecules.

The kinetic parameters of dehydration of these compounds were evaluated from the TG curves shown in the Figures 1 and 2.

For the cobalt, nickel and zinc compounds (Figure 1), the TG curves to first mass loss seen between 30 and 110ºC shown a pattern of dehydration and for the copper (130ºC) and iron (150ºC) compounds (Fig. 2), these correspond to another dehydration pattern. The initial temperature of thermal decomposition occurs for cobalt (185ºC), nickel (240ºC) and zinc (210ºC); while for iron and copper occurs at 130ºC and 150ºC, respectively. The thermal decomposition in all the TG curves occurs in more than one consecutive step without the formation of stable intermediates or the respective oxides.

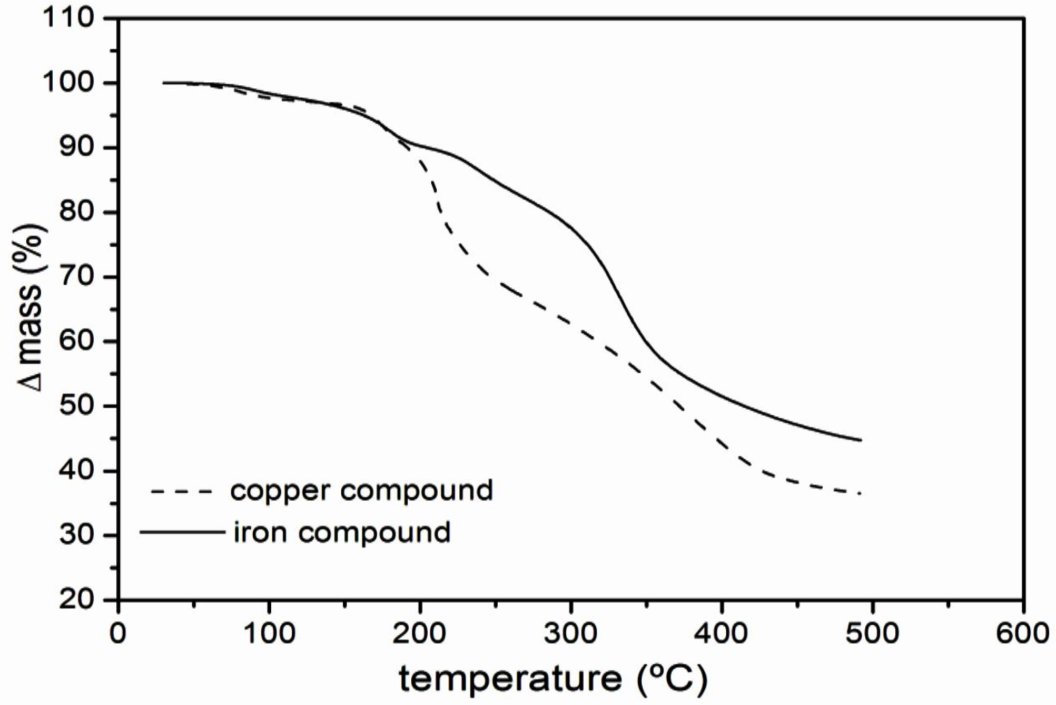

Figure 2. TG curves of the sodium salt, copper, iron and ligand compounds, with mass sample of 1mg, at heating rate of 10ºC min^{-1} in nitrogen atmosphere.

The kinetic parameters of the data was obtained using the isoconversional method of Flynn, Wall and Ozawa (FWO) because it is commonly used to avoid the kinetic model [11,12,13]. This method is based on fixed values of the degree of conversion (α) obtained from the experiments at different heating rates (β):

$$\alpha_t = \frac{(C_t - C_0)}{(C_\infty - C_0)} \quad (1)$$

where C represents the reagent concentration, as well as other physical properties which are represented in the TG experiment. The subscript corresponds to the elapsed time, *t*, where the initial time is *t* = 0 and the final time is *t* = α.

The dependence of α as a function of time can be expressed as the following differential equation [14]:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \quad (2)$$

where k(T) is the temperature-dependent rate constant and f(α) is a function that represents the reaction model. The k(T) usually employs the Arrheinius equation [15]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (3)$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

For dynamic data obtained at a constant heating rate, β = dT/dt, this new term is inserted in the Eq. (3) to obtain the transformation [11]:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\beta R}p(x) \quad (4)$$

Thus, the non isothermal kinetics have resolved the major problem of the isothermal exper-

The activation energy (E_a) versus conversion degree (α) values for the dehydration are shown in the Figures 3 and 4.

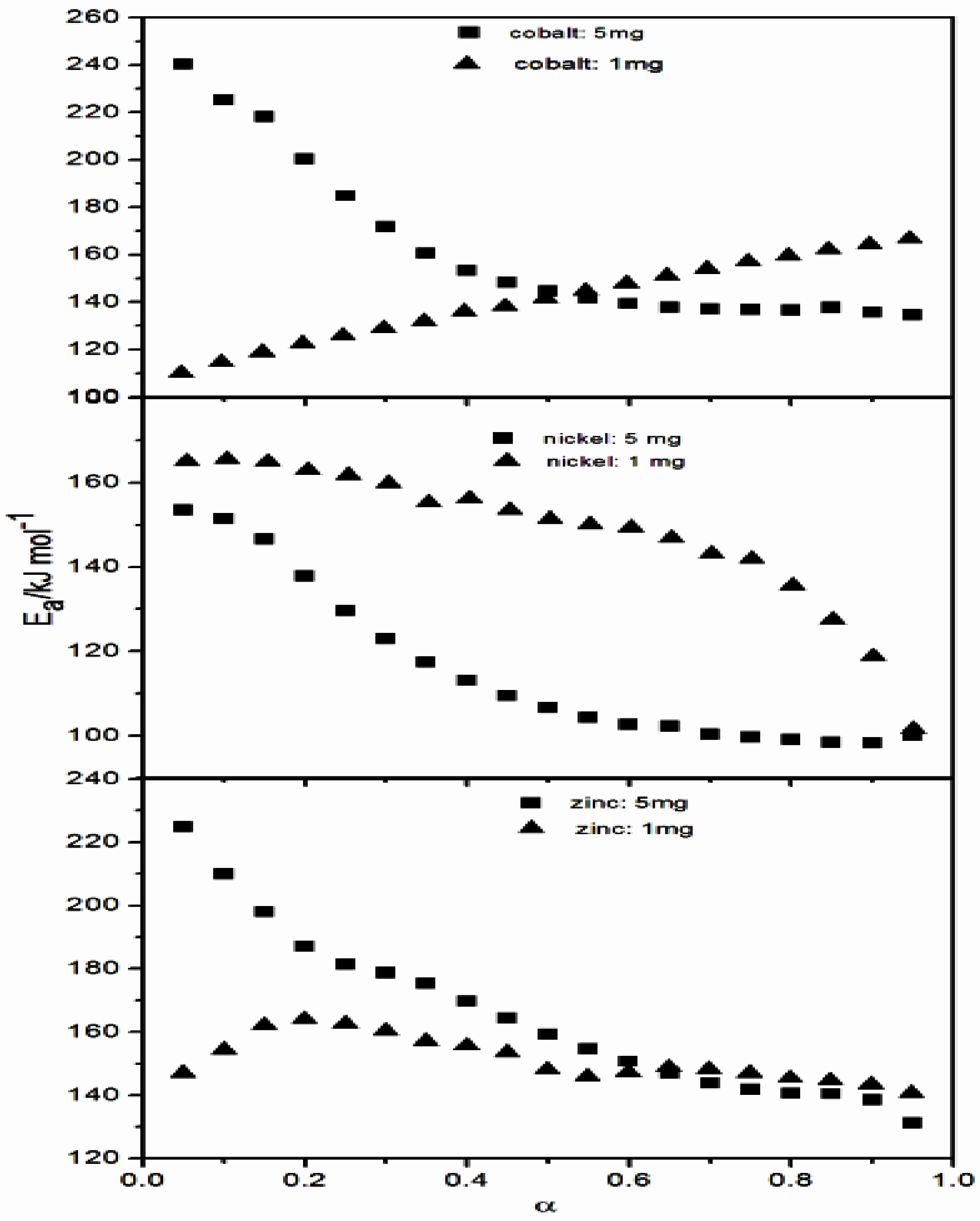

Figure 3. The calculated Ea/kJ mol-1 as a function of α for the dehydration stage of the cobalt, nickel and zinc compounds.

the presence or not of cover on the crucible, etc [20-22]. Furthermore, it is clear that the values of activation energy for first dehydration step are variable, which indicate that can be regarded as single step reaction. Additionally, the particle size or non-homogeneous particles of each compound can also alter the kinetic behavior. Figures 5 to 8 show SEM images of particles of the cobalt and copper compounds. For the cobalt compound, can be seen different sizes of the particles before and after the dehydration. This was attributed to destruction of the structure and subsequent contraction of the sample mass. For the copper compound, can be seen that there was a contraction in the volume without destroy the structure. Thus, the activation energy indicates that only the thermal conductivity alters the kinetic behavior.

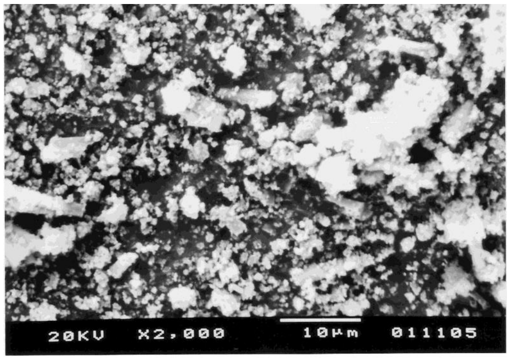

Figure 5. SEM hydrated cobalt compound

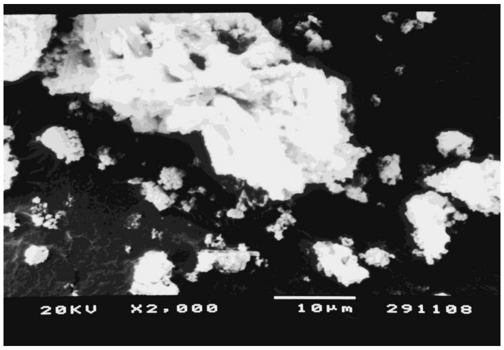

Figure 6. SEM dehydrated cobalt compound

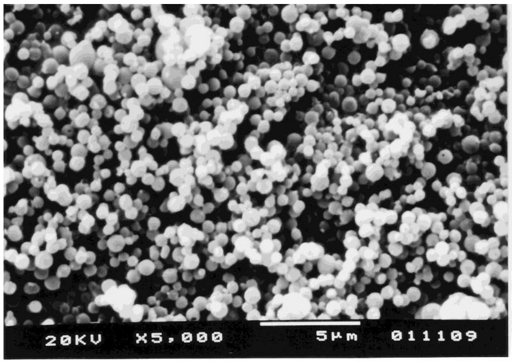

Figure 7. SEM hydrated cooper compound.

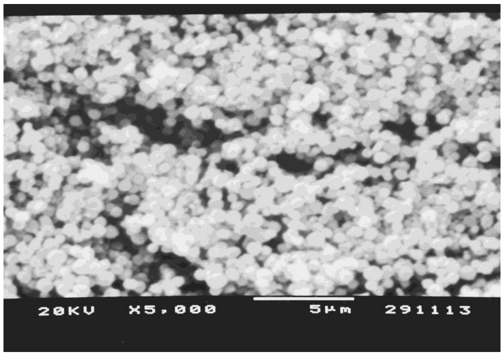

Figure 8. SEM dehydrated copper compound

From the information obtained, we can use the values of the activation energy and the pre-exponential factor to make the following correlation [23-25]:

$$\ln A = a + bE$$

where a and b are the compensation constants. The average values found for the plots of the activation energy and pre-exponential factor are commonly called of kinetic compensation effect (KCE). The existence of the "kinetic compensation effect" has been observed in literature for several groups of heterogeneous reactions. The linear relationship between lnA and E_a for the dehydration reactions and thermal decomposition allows us to group them according to their similarities [23,26].

For the dehydration, as shown in Figure 9, evidence for the KCE was seen, but there was not relationship between the numbers of water mole-

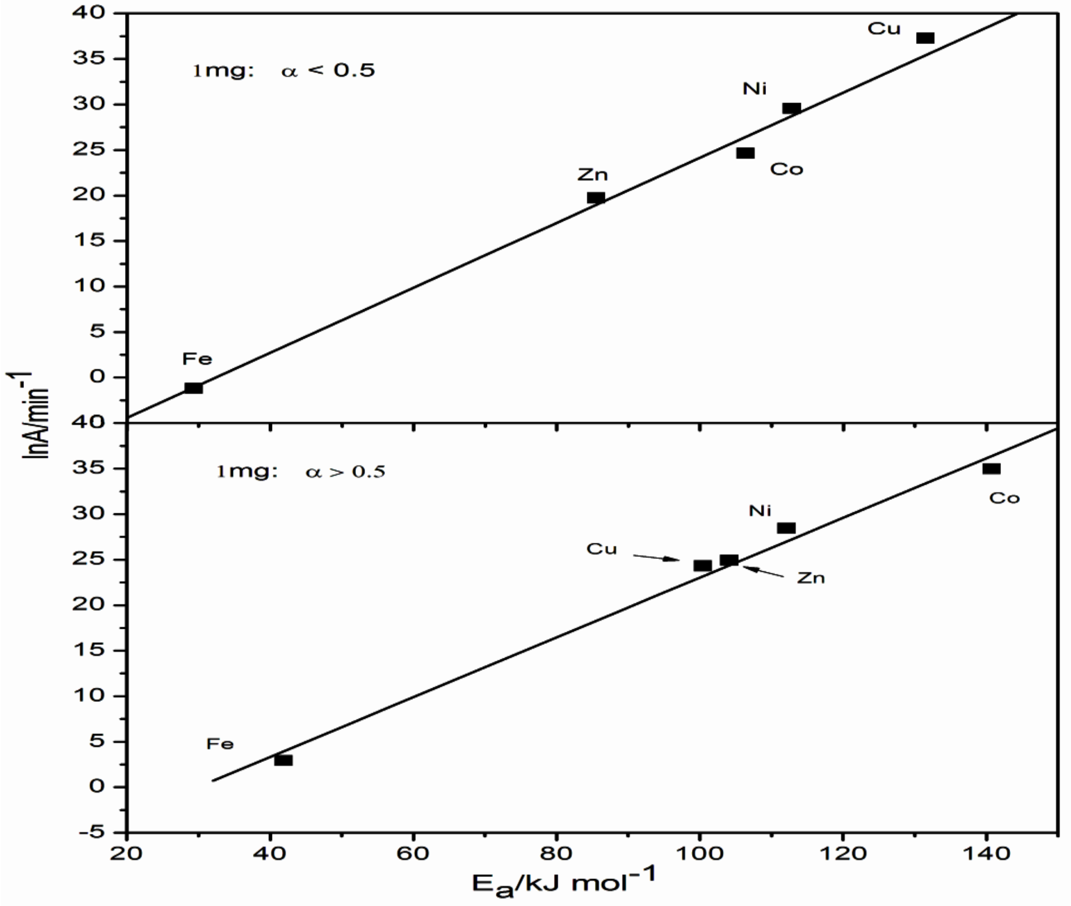

Figure 10. Linear plot of ln A/min^{-1} versus Ea/kJ mol^{-1} for the dehydration reaction with mass sample of 1mg in two intervals of conversion degree.

Abstract: Divalent metal complexes of ligand 2-methoxybenzylidenepyruvate with Fe, Co, Ni, Cu and Zn as well as sodium salt were synthesized and investigated in the solid state. TG curves of these compounds were obtained with masses sample of 1 and 5mg under nitrogen atmosphere. Different heating rates were used to characterize and study these compounds from the kinetic point of view. The activation energy and pre-exponential factor were obtained applying the Wall-Flynn-Ozawa method to the TG curves. The obtained data were evaluated and the values of activation energy (E_a / kJ mol^{-1}) was plotted in function of the conversion degree (α). The results show that due to mass sample, different activation energies were obtained. The results are discussed mainly taking into account the linear dependence between the activation energy and the pre exponential factor, where was verified the effect of kinetic compensation (KCE) and possible linear relations between the dehydrations steps of these compounds.

Keywords: bivalent metal ions, 2-methoxybenzylidenepyruvate, non-isothermal kinetics, dehydration

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