

Intercalation compounds of γ -zirconium and γ -titanium phosphates Kinetic study of dehydration and decomposition processes for 2,9-dimethyl-1,10-phenanthroline and its intercalated copper complex materials

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Abstract

γ -Zirconium and γ -titanium phosphates containing organic diamine 2,9-dimethyl-1,10-phenanthroline and its in situ formed copper complex were studied by thermal analysis and physical measurements. All the derived materials show a layered structure and their interlayer distance is increased with respect to that of their precursors. Melting, simultaneous vaporization and oxidation, as well as a decomposition process take place in the pure diamine. After dehydration, all the intercalation materials undergo a two-step decomposition. The presence of the formed copper complex between the layers of the two ion-exchangers considered shows a destabilizing effect with respect to the intercalated diamine materials, resulting in a decrease of the decomposition temperatures and the activation energy of decomposition. The application of the isoconversional Ozawa–Flynn–Wall method substantially confirms the obtained results.

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1. Introduction

Layered inorganic ion-exchangers with a non rigid structure such as the acid phosphates of tetravalent metals ($\text{Me(IV)(HPO}_4)_2 \cdot n\text{H}_2\text{O}$; $\text{Me} = \text{Zr, Ti, Sn}$; $n = 1, 2, \dots$) are able to exchange transition metal ions [1] and to intercalate organic molecules [2]. A coordination compound can be directly inserted as a pre-formed complex or its formation in situ may be favoured by an ion-exchanged transition metal ion and a ligand previously intercalated between the layers of the material [3]. Its ion-exchange capacity and the ability to intercalate potential catalytic species along with the chemical and thermal stability make this class of organic–inorganic composite materials useful in heterogeneous catalysis [4]. On the other hand, the importance of the synthesized and studied materials is that copper

compounds are increasingly employed in various homogeneous catalytic processes. However, the immobilization of these compounds by anchoring them on insoluble matrices is certainly of great interest to minimize the loss of metal and facilitate the separation of the catalyst from the reaction mixture.

The gamma phases of zirconium phosphate, $\gamma\text{-Zr(PO}_4\text{)(H}_2\text{PO}_4\text{)} \cdot 2\text{H}_2\text{O}$, ($\gamma\text{-ZrP}$) and titanium phosphate, $\gamma\text{-Ti(PO}_4\text{)(H}_2\text{PO}_4\text{)} \cdot 2\text{H}_2\text{O}$, ($\gamma\text{-TiP}$) may be considered among the most studied inorganic ion-exchanger materials with a layered structure [5,6]. The organic diamine 2,9-dimethyl-1,10-phenanthroline (dmp) is able to be intercalated between the layers of $\gamma\text{-ZrP}$ and $\gamma\text{-TiP}$ to give the intercalated phases denoted as $\gamma\text{-ZrPdmp}$ and $\gamma\text{-TiPdmp}$. These materials subsequently exchange copper ions giving dmpCu complex formed in situ ($\gamma\text{-ZrPdmpCu}$ and $\gamma\text{-TiPdmpCu}$) (Fig. 1).

As a follow-up of our previous study [6], the present investigation aims at showing the influence of the ion-exchangers considered on the thermal stability of the dmpCu complex and to study the dehydration and decomposition processes of

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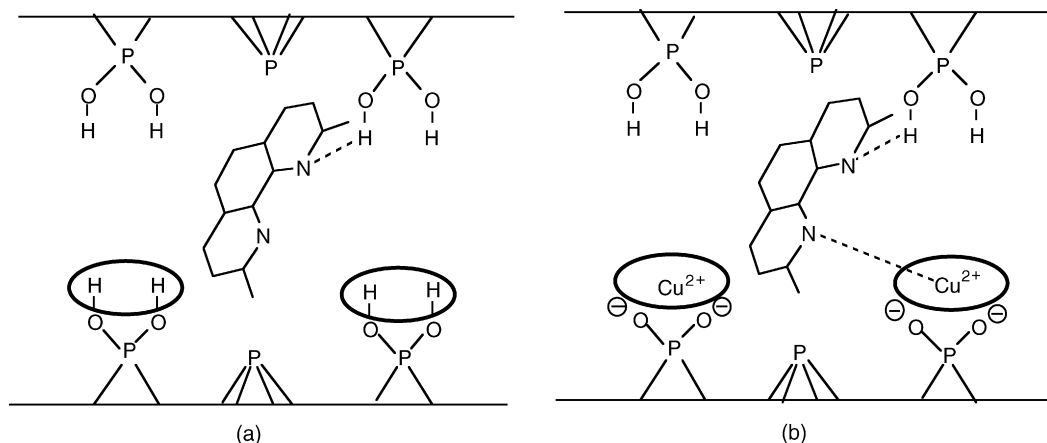


Fig. 1. Possible arrangements of dmp (a) and dmpCu complex (b) between the layers of the γ -ZrP exchanger.

all the considered materials. Moreover, even if the thermal behaviour of γ -ZrPdmpCu was already examined in an earlier study [7], to the best of our knowledge no information is available on the decomposition kinetics of dmp intercalated as such or as a complex in these materials. The mechanisms of these processes were hypothesized on the basis of the simultaneous TG/DTG/DTA techniques, and the activation energy was determined by means of two model-free kinetic methods, the iso-conversional Ozawa–Flynn–Wall and the single point Kissinger method.

2. Theory

Kinetic investigations on solid-state reactions are usually described by the following kinetic equation [8,9]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t is the time, T the temperature, α the extent of conversion and $f(\alpha)$ is the reaction model associated to a particular reaction mechanism. By expliciting the temperature dependence of $k(T)$ through the Arrhenius equation, one obtains

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (2)$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant. For nonisothermal experiments performed at constant heating rates β , the reaction rate $d\alpha/dt$ in Eq. (2) is replaced with $\beta \cdot d\alpha/dT$, giving

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

Approaches based on fitting of kinetic data to assumed reaction models $f(\alpha)$ are denoted as model-fitting methods [9,10]. Selection of the most suitable $f(\alpha)$ reaction model from the best linear fit (assumed linear a priori) can be misleading. In fact, due to the fact that in a single nonisothermal experiment temperature and extent of conversion are varied simultaneously, several $f(\alpha)$ models can fit data with Arrhenius parameters that can vary

noticeably [11,12]. This problem is solved in the model-free isoconversional methods that allow for estimating the activation energy as a function of α without choosing the reaction model using multiple heating rate experiments.

The basic assumption of these methods is that the reaction rate at constant extent of conversion α is only a function of the temperature [13]. Hence, constant E values can be expected in the case of single stage decompositions, while for multi-step processes E varies with α due to the variation in the relative contributions of single steps to the overall reaction rate [14].

According to the Ozawa–Flynn–Wall (OFW) method [15,16], which is based on an integral form of Eq. (1), for a set of nonisothermal TG experiments carried out at different constant heating rates β , the activation energy at any particular value of α is determined by the following equation:

$$(\ln \beta)_\alpha \cong \ln\left(\frac{AE}{R}\right)_\alpha - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E}{RT}\right)_\alpha \quad (4)$$

from the slope of the straight line obtained by plotting $\ln \beta$ versus $1/T$. Errors may be introduced into the calculation of activation energy from Eq. (4) by the fact that Doyle's linear approximation:

$$\ln p(x) \cong -5.3305 - 1.052x \quad (5)$$

where $x = E/RT$, is valid only in the range $20 \leq x \leq 60$. Moreover, some authors proposed [17] corrections of the temperature integral $p(x)$ due to non-linearity of Eq. (5).

If the maximum of the reaction rate is achieved at the maximum peak of a single heating rate TG/DSC experiment ($d(d\alpha/dt)/dt = 0$ for $T(t) = T_m$), the peak temperature T_m is a function of the heating rate through the Kissinger equation [18]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{RT_m} + \ln\left(\frac{AR}{E}\right) \quad (6)$$

This “model-free” kinetic method can be applied without any approximation, is valid only for the maximum peak and the plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ gives a straight line with a slope equal to $-E/R$.

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