Kinetic analysis of the oxidative decomposition in γ-zirconium and γ-titanium phosphate intercalation compounds
The case of 2,2′-bipyridyl and its copper complex formed *in situ*

Stefano Vecchio [a,*], Romolo Di Rocco [b], Carla Ferragina [b]

[a] *Department of Chemical Engineering (I.C.M.A), University of Rome "La Sapienza", via del Castro Laurenziano 7, 00161 Rome, Italy*
[b] *CNR, Istituto di Metodologie Inorganiche e dei Plasmi, via Salaria km. 29.300, 00016 Monterotondo, Rome, Italy*

Abstract

The thermal behaviour of the heterocyclic compound 2,2′-bipyridyl and its copper complex formed *in situ*, both intercalated between the layers of γ-zirconium and γ-titanium phosphates was studied by simultaneous thermogravimetry and differential scanning calorimetry techniques using non-isothermal constant heating rate conditions up to 873 K under a stream of air. In all the obtained intercalation materials, which are found to be stable up to 600 K, the ligand shows an oxidative decomposition practically in only one step. Model-free isoconversional method of Ozawa–Flynn–Wall, applied to the vaporization of pure 2,2′-bipyridyl and to the oxidative decomposition step occurring in each intercalation material examined, yields practically constant activation energies for values of the fraction decomposed $\alpha \leq 0.7$. The activation energies calculated using the best fit between calculated and theoretical $g(\alpha)$ models do not differ significantly from the corresponding mean E values selected using the isoconversional OFW method in the range $\alpha \leq 0.7$. Activation energies derived by the Kissinger method show a good agreement with the mean values derived by the former method, and the Arrhenius rate constants determined using also the pre-exponential factor values enable to conclude that the bipyCu intercalation materials show a destabilizing effect with respect to the corresponding bipy intercalation materials (negligible difference in the oxidative decomposition temperatures, but a significant difference in the rate constant values: at least one order of magnitude).
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1. Introduction

Acid phosphates of tetravalent metals such as Zr, Ti and Sn are insoluble ion-exchangers that can be prepared in crystalline forms with nonrigid layered structures. The most studied among these materials, γ-zirconium and γ-titanium phosphates (γ-ZrP, γ-TiP) [1–3], are well known to exchange metal ions [4,5], to intercalate organic bases [6,7] and to support non-polar molecules [8,9]. The intercalation compounds that were obtained by intercalating polar organic bases easily exchange transition metal ions that are subsequently coordinated to the base through the layers, giving rise to complexes formed *in situ* between the layers of the host matrices. In the present study,

as a follow-up of our previous studies [10,11], γ-ZrP and γ-TiP were intercalated with the organic base 2,2′-bipyridyl (bipy) and denoted as γ-ZrPbipy, γ-TiPbipy. The two obtained materials were subsequently exchanged with copper ions to give complex formed *in situ* (γ-ZrPbipyCu, γ-TiPbipyCu). These materials were prepared with a particular view to obtain either catalysts or catalyst precursors to be used in heterogeneous catalysis by complexes usually utilized in the homogeneous catalysis [12–14]. The present study is devoted to characterize the thermal oxidative decomposition of these intercalation materials using different kinetic methods and provide reliable Arrhenius parameters and a suitable model function for each process studied. On the other hand, to the best of our knowledge, no relevant information are available in literature on the oxidative decomposition kinetics of bipy not intercalated or intercalated (as such or as a copper complex) between the layers of these ion-exchangers.

2. Experimental and method

2.1. Chemicals

The copper acetate, zirconyl chloride, titanium oxide, phosphoric acid and 2,2′-bipyridyl were supplied by Aldrich (reagent grade) and used without further purification.

2.2. Materials

The precursors (γ-ZrP and γ-TiP), the intercalation compounds obtained with bipy (γ-ZrPbipy and γ-TiPbipy) and the copper complexes formed *in situ* (γ-ZrPbipyCu and γ-TiPbipyCu) were prepared as reported in literatures ([2,3] and [15,16], respectively). Intercalation of bipy and formation of the bipyCu complex between the layers of the exchangers evidenced by X-ray photoelectron spectroscopic measurements in [17] are outlined in Fig. 1 for γ-ZrP as an example.

2.3. Physical measurements and chemical analysis

Copper ions were determined in the supernatant solutions, before and after contact with the exchangers with a GBC 903 A.A. spectrophotometer. Phosphates were determined colorimetrically [18]. X-ray powder diffraction (XRPD) was used to study phase changes in the materials by monitoring the reflection and its armonics. A Philips diffractometer (model PW 1130/00) was used with Ni-filtered Cu Kα radiation (λ = 1.541 Å).

2.4. Thermal measurements

Water and the bipy contents and the thermal behaviour of the tested materials as well as of pure bipy were determined with a simultaneous TG/DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 10 K min^{-1} calcined up to 1373 K to constant weight in an airflow. The TG and DSC experimental measurements were carried out on a simultaneous Stanton Redcroft 625 thermoanalyzer, connected to 386 IBM-compatible personal computer. Thermodynamic quantities were calculated using the Stanton Redcroft Data Acquisition System, Trace 2, version 4. Temperature and heat flow rate scales were calibrated with very pure standards (indium, lead, tin, zinc), whose melting temperatures and enthalpies are well known [19]. Samples of 6–8 mg were weighed into Al pans in an argon-filled dry box to avoid a possible sample degradation, and then in the thermoanalyzer, where the purge air stream fluxed to continuously remove the gases given off during the thermal heating process experiment. As far as the thermal analysis study is concerned, three TG/DSC experiments were made for each material at 8 K min^{-1} using fresh samples only and a good precision of experimental data was obtained (<1%). On the other hand, for the kinetic analysis the TG/DSC measurements have been carried out at different heating rates (2, 4, 6 and 8 K min^{-1}) up to 873 K under a 100 ml min^{-1} stream of air.

3. Theory

Kinetics of solid-state reactions is usually described by the following basic equation:

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

where α is the fraction decomposed defined as $\alpha = (1/Q_{tot})\int_0^f (dQ/dt)dt$ (being Q_{tot} and dQ/dt the overall heat of reaction and the heat flux, respectively), $f(\alpha)$ the model function, which assumes different mathematical forms depending on the reaction mechanism [20] and $k(T)$ is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius equation:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where E is the activation energy, A the pre-exponential factor, R the gas constant and T is the absolute temperature. Moreover, taking into account that under non-isothermal condition the heating rate $\beta = dT/dt$, where t is the time, by combining Eqs. (1) and (2), it results

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

Most of the methods that describe the kinetics of reactions in solids use Eq. (3) as well as several approximation of its integral
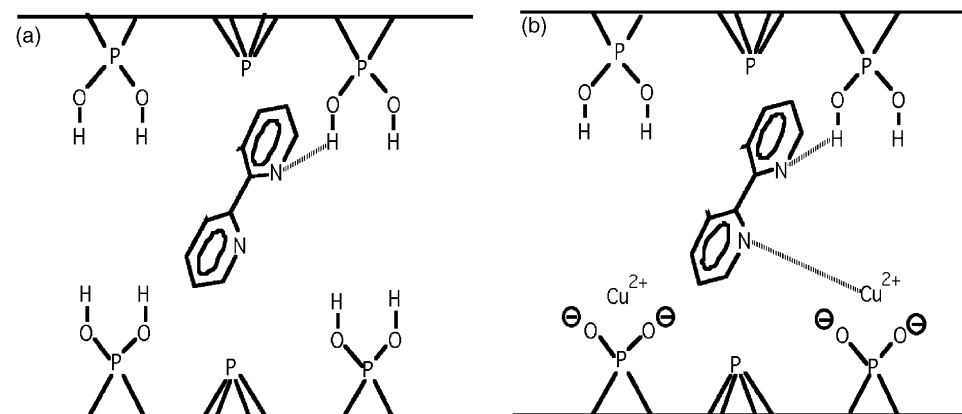

Fig. 1. Possible arrangements of bipy (a) and bipyCu complex (b) between the layers of the γ-ZrP exchanger.