

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

Stefano Vecchio^{a,*}, Romolo Di Rocco^b, Carla Ferragina^b

^a *Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia, Università di Roma "La Sapienza",
Via del Castro Laurenziano 7, 00161 Roma, Italy*

^b *CNR, Istituto di Metodologie Inorganiche e dei Plasmi, via Salaria km. 29.300, 00016 Monterotondo, Roma, Italy*

Received 11 November 2005; received in revised form 23 December 2005; accepted 24 December 2005
Available online 21 February 2006

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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Keywords: Ion-exchanger; Intercalation compounds; Thermal behaviour; X-ray powder diffraction; Kissinger method

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

* Corresponding author. Tel.: +39 06 49766906; fax: +39 06 49766749.
E-mail address: stefano.vecchio@uniroma1.it (S. Vecchio).

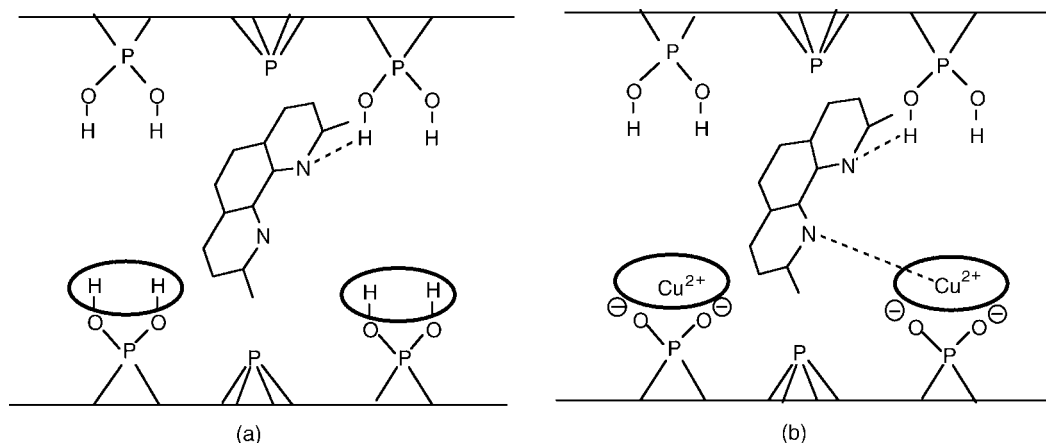


Fig. 1. Possible arrangements of dmp (a) and dmpCu complex (b) between the layers of the γ -ZrP exchanger.

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 $-E/R$.

3. Experimental

3.1. Chemicals and materials

The copper acetate, zirconyl chloride, titanium oxide, phosphoric acid and 2,9-dimethyl-1,10-phenanthroline were purchased reagent grade from Aldrich and used without further purification. γ -ZrP, γ -TiP and their intercalation compounds were prepared as reported in literature [6,19–22].

3.2. Thermal analysis measurements

Water and the dmp contents as well as the thermal behaviour of the studied materials were determined using a Stanton Redcroft 1500 simultaneous TG/DTA thermoanalyzer (STA 1500), Pt crucibles, heating rate 10 K min^{-1} , calcined up to 1737 K to constant weight in an airflow (100 ml min^{-1}). Three runs were made for each material in order to test the reproducibility of the thermal analysis measurements, and no appreciable differences could be found among them. The kinetic evaluation of dehydration and decomposition processes was done with heating rates of 2, 4, 6 and 8 K min^{-1} for the intercalated materials. The melting and vaporization enthalpy as well as the activation energy of vaporization for the pure dmp were determined using a Stanton Redcroft 625 simultaneous TG/DSC thermoanalyzer (STA 625) connected to a 386 IBM-compatible personal computer, under the same above-mentioned heating rates and airflow. Thermodynamic quantities were calculated with the Stanton Redcroft Data Acquisition System, Trace 2, Version 4. The calibration of the STA 625 thermoanalyzer was performed with very pure standards. To this end, indium and benzoic acid were used in the present study as their melting temperatures and enthalpies are well known. Five to seven milligrams of samples were weighed into aluminium pans in an argon-filled dry box and then in the thermoanalyzer, where the purge air stream fluxed to continuously remove the gases given off during the thermal heating process experiment.

3.3. 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 [23]. X-ray powder diffraction (XRPD) was used to study phase changes in the materials by monitoring the reflection and its harmonics. The XRPD measurements were performed with a Philips diffractometer (model PW 1130/00) with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$).

4. Results and discussion

4.1. Materials

The proposed chemical formulas for the examined materials are summarized in Table 1 [6,22].

Table 1
Chemical composition of the examined materials

Materials	Chemical composition	Interlayer distance, d (\AA)
γ -ZrPdmp	$\gamma\text{-Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{dmp}_{0.48}\cdot 1.85\text{H}_2\text{O}$	19.40
γ -ZrPdmpCu	$\gamma\text{-Zr}(\text{PO}_4)(\text{H}_{1.38}\text{PO}_4)\text{Cu}_{0.31}\text{dmp}_{0.41}\cdot 1.30\text{H}_2\text{O}$	19.40
γ -TiPdmp	$\gamma\text{-Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)\text{dmp}_{0.33}\cdot 2.20\text{H}_2\text{O}$	17.00
γ -TiPdmpCu	$\gamma\text{-Ti}(\text{PO}_4)(\text{H}_{1.34}\text{PO}_4)\text{Cu}_{0.33}\text{dmp}_{0.31}\cdot 2.45\text{H}_2\text{O}$	17.00

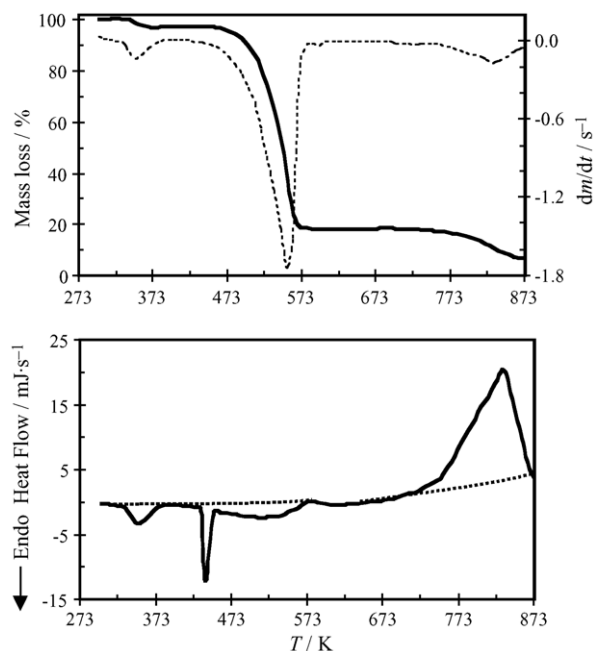


Fig. 2. TG, DTG and DSC curves of dmp at 8 K min^{-1} under a stream of air.

4.2. Thermal and kinetic analysis

4.2.1. dmp

TG/DTG and DSC curves of dmp are shown in Fig. 2. Three endothermic DSC peaks are shown due to dehydration, melting and vaporization of dmp (around 340, 430 and 550 K, respectively). In the temperature range 650–873 K a noticeable exothermic effect associated to a single step of mass loss due to decomposition takes place. ΔH_{fus} and ΔH_{vap} values of dmp are given in Table 2 at different heating rates. No actual dependence of ΔH_{fus} and ΔH_{vap} values on β can be observed. Activation energies of dmp vaporization calculated by the OFW method are given in Table 3. Practically, constant E values between 72 and 82 kJ mol^{-1} were found (changes lie within the estimated errors). According to these results $x = E/RT$ is close to 20, which is the lower limit to apply Doyle's approximation. The obtained

Table 2
Melting and vaporization enthalpies of dmp for different heating rates

β (K min^{-1})	ΔH_{fus} (kJ mol^{-1})	ΔH_{vap} (kJ mol^{-1})
2	16.0 ± 0.7	28 ± 4
4	17.5 ± 0.7	30 ± 3
6	16.7 ± 0.4	29 ± 3
8	17.2 ± 0.5	30 ± 4

Table 3

E dependencies on the degree of conversion according to the OFW method for vaporization of dmp

α	E (kJ mol ⁻¹)	α	E (kJ mol ⁻¹)
0.05	72 ± 5	0.55	78 ± 3
0.10	75 ± 5	0.60	81 ± 3
0.15	77 ± 6	0.65	80 ± 3
0.20	73 ± 3	0.70	81 ± 3
0.25	74 ± 3	0.75	81 ± 3
0.30	75 ± 3	0.80	81 ± 3
0.35	77 ± 3	0.85	82 ± 3
0.40	75 ± 2	0.90	80 ± 1
0.45	77 ± 2	0.95	78 ± 1
0.50	78 ± 3		

Table 4

E dependencies on the degree of conversion according to the OFW method for decomposition of dmp

α	E (kJ mol ⁻¹)	α	E (kJ mol ⁻¹)
0.05	115 ± 6	0.55	136 ± 3
0.10	126 ± 5	0.60	135 ± 3
0.15	135 ± 6	0.65	131 ± 2
0.20	139 ± 5	0.70	129 ± 2
0.25	140 ± 4	0.75	128 ± 2
0.30	142 ± 3	0.80	126 ± 3
0.35	141 ± 3	0.85	122 ± 3
0.40	140 ± 2	0.90	116 ± 4
0.45	141 ± 2	0.95	108 ± 4
0.50	138 ± 3		

ΔH_{vap} values (Table 2) are quite lower than the corresponding E_a values, probably due to a superimposition of the endothermic vaporization and an exothermic oxidation process at ~550 K (Table 3). Activation energy of decomposition for dmp (Table 4) slightly varies in the range 113–142 kJ mol⁻¹ even if it remains quite constant within the experimental error (between 140 and 147 kJ mol⁻¹) in the range 0.15 < α < 0.60.

4.2.2. γ -ZrPdmp and γ -ZrPdmpCu

From TG/DTG/DTA curves (Figs. 3 and 4), it can be seen that multi-step dehydration processes took place up to 493 K, due to the presence of both coordination and lattice water. For γ -ZrPdmp, a noticeable loss of water accompanied by a strong endothermic DTA peak is shown up to 350 K. Dehydration of γ -ZrPdmpCu is revealed up to 473 K either by the presence of several small DTG peaks corresponding to some consecutive steps of mass loss recorded in the TG curve and only two small endothermic DTA peaks. The slowest activation energy of dehydration for γ -ZrPdmp is found for the first step (Table 5),

Table 5

Activation energies (kJ mol⁻¹) obtained from Kissinger method

Materials	Dehydration			Decomposition	
	Step 1	Step 2	Step 3	Step 1	Step 2
γ -ZrPdmp	62	183	70	182	104
γ -ZrPdmpCu	177	153	–	139	–

Uncertainty associated to activation energies is always less than 10%.

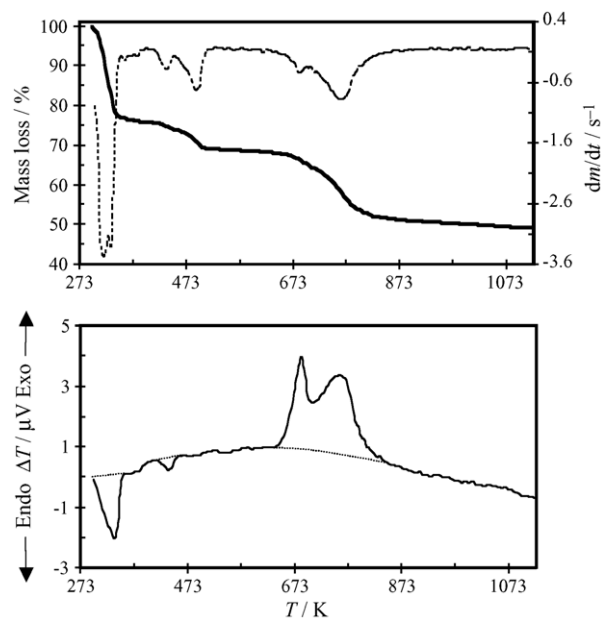


Fig. 3. TG, DTG and DTA curves of γ -ZrPdmp at 8 K min⁻¹ under a stream of air.

thus confirming that mainly water is weakly linked, as it can be concluded from the TG/DTA measurements. The second step shows noticeably higher E values, comparable with those of the dehydration processes of γ -ZrPdmpCu. Moreover, the ligand decomposition occurs in both the samples in two steps between 550 and 850 K. In this range the water loss derived from the condensation of the POH groups to give pyrophosphate groups is also present [24]. The activation energies of the two decomposition steps for γ -ZrPdmp are quite different: the second step exhibits the lowest E value (Table 5) and the sharpest mass loss (Fig. 3) even though the intensity of the two exothermic DTA

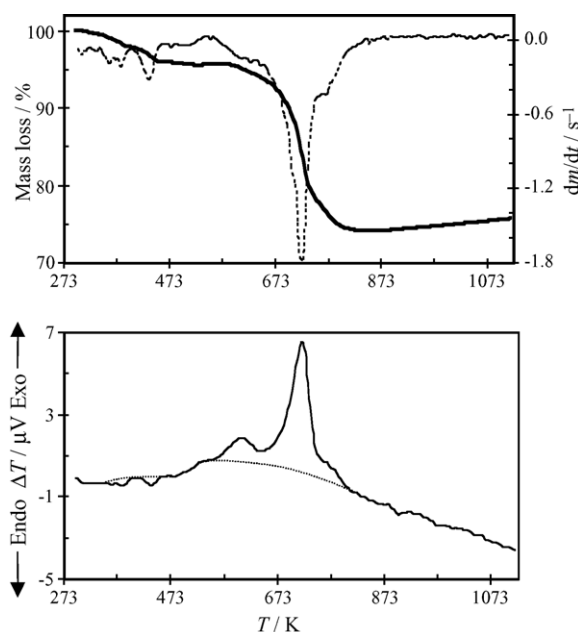


Fig. 4. TG, DTG and DTA curves of γ -ZrPdmpCu at 8 K min⁻¹ under a stream of air.

peaks may be considered comparable. However, the first decomposition step associated with the release of the more weakly linked dmp seems to be the rate determining step. After this step, the release of the remaining moieties of the ligand is accelerated, probably due to a rearrangement of the residual dmp between the layers.

From the two-stage decomposition steps of γ -ZrPdmpCu only one E value of 139 kJ mol^{-1} was found with the Kissinger method (Table 5), probably ascribed to the highest exothermic effect recorded in the corresponding DTA curve between 650 and 760 K (Fig. 4). These results indicate that the dmp in γ -ZrP has an appreciable thermal stability, due to a ligand–matrix interaction. In addition, the presence of Cu accelerates the thermal release of the ligand (about 100 K lower than in γ -ZrPdmp) [3a,25,26].

4.2.3. γ -TiPdmp and γ -TiPdmpCu

From TG/DTG/DTA curves (Figs. 5 and 6), it can be seen that only one well-defined dehydration step takes place up to 573 K for both the materials. In spite of the fact that several mass losses occurred up to 480 K only one endothermic DTA peak is shown at about 330 K for both materials. Ligand decomposition occurs in two (γ -TiPdmpCu) or three steps (γ -TiPdmp) between 573 and 1023 K. In this range the water loss derived from the condensation of the POH groups giving pyrophosphate groups is also present. γ -TiPdmpCu shows a peak related to the phase transition of layered pyrophosphate to cubic pyrophosphate [24] at 943 K, while for γ -TiPdmp this peak is probably concealed by the superimposition of that corresponding to the third ligand decomposition step at about 1073 K. It is evident that the presence of Cu accelerates the decomposition process occurring at about 573 and 673 K instead of 660, 750 and 1073 K.

In Table 6, it can be seen that the presence of the dmpCu complex between the layer of γ -TiPdmpCu noticeably decreases the

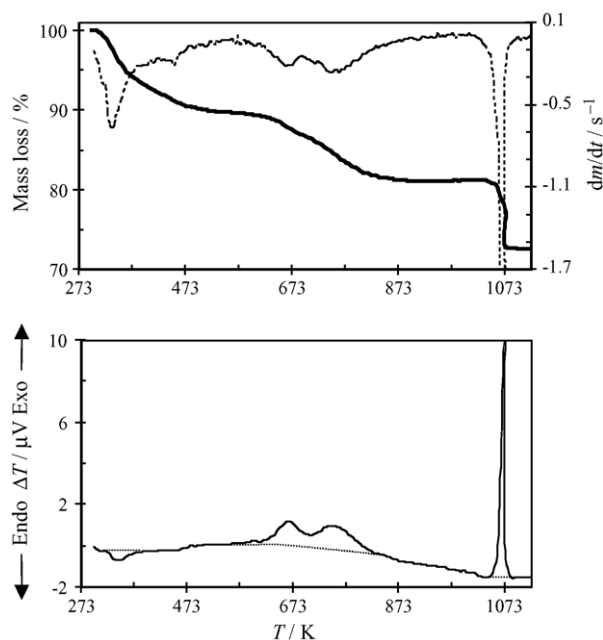


Fig. 5. TG, DTG and DTA curves of γ -TiPdmp at 8 K min^{-1} under a stream of air.

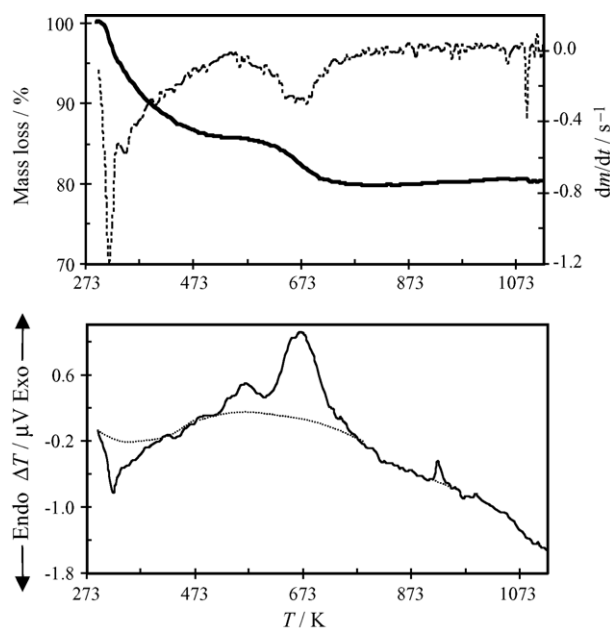


Fig. 6. TG, DTG and DTA curves of γ -TiPdmpCu at 8 K min^{-1} under a stream of air.

rate of dehydration compared with that of γ -TiPdmp. Activation energy of the third decomposition step of γ -TiPdmp is very high compared with those of the other decomposition steps (rate determining step).

For the decomposition step of γ -TiPdmpCu a single value of 138 kJ mol^{-1} is found, which is comparable with that of decomposition for γ -ZrPdmpCu. Therefore, as already found for γ -ZrPdmp and γ -ZrPdmpCu, the thermal stability of dmp is higher when it is intercalated as such or as a copper complex inside the cavities of γ -TiP.

4.2.4. E -dependencies for decomposition processes of intercalated materials

The dependencies of activation energy on the extent of conversion using the isoconversional OFW method are given for the decomposition processes only in Fig. 7. The examined materials show practically constant E values in the range $0.2 < \alpha < 0.8$, except for an increase from 162 to 250 kJ mol^{-1} for γ -TiPdmp (Fig. 7, plot c) and a slight decreasing trend for γ -TiPdmpCu (Fig. 7, plot d) with E values ranging from 140 to 121 kJ mol^{-1} . Even if E values may be considered practically constant for decomposition step of γ -ZrPdmpCu (in agreement with the results of the Kissinger method), two values are actually determined, about 145 kJ mol^{-1} in the range $0.2 < \alpha < 0.35$ and 139 kJ mol^{-1} in the range $0.4 < \alpha < 0.8$, which are caused by

Table 6
Activation energies (kJ mol^{-1}) obtained from Kissinger method

Materials	Dehydration	Decomposition		Oxidation
		Step 1	Step 2	
γ -TiPdmp	82	185	144	334
γ -TiPdmpCu	152	138	–	–

Uncertainty associated to activation energies is always less than 10%.

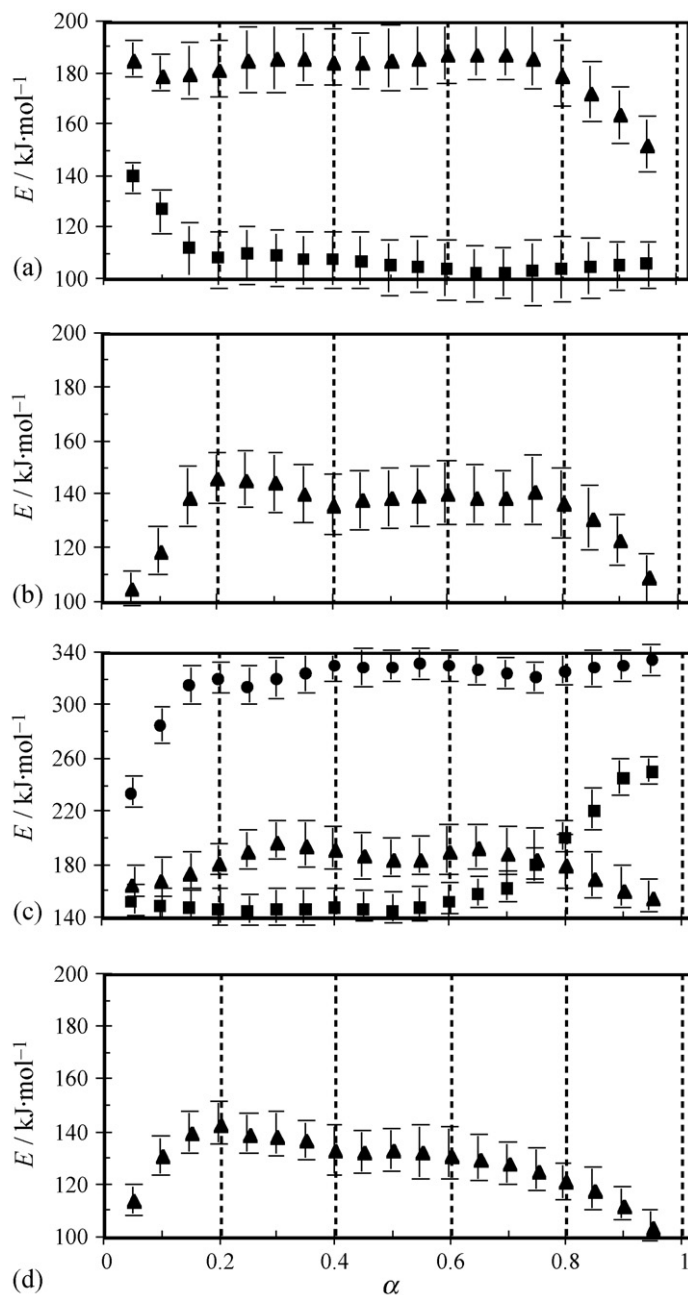


Fig. 7. Dependencies of the activation energy on the extent of conversion (OFW method) for the first (black triangles), the second (black squares) and the third (black circles) decomposition processes of: γ -ZrPdmp (a), γ -ZrPdmpCu (b), γ -TiPdmp (c) and γ -TiPdmpCu (d).

the two exothermic effects recorded in the corresponding DSC curves (Fig. 4). Moreover, a substantial agreement is observed between these values and those obtained by the Kissinger method. Although decreasing or increasing trends are found for $\alpha < 0.2$ and $\alpha > 0.8$, we think that this behaviour is usually a computational artifact due to the transition from one mass loss to another, which occurs consecutively [27].

4.3. XRPD

Fig. 8 shows the XRPD patterns of intercalated materials in which a layered and well-crystallized structure is present. As far as the dmp materials are concerned a noticeable increase of

interlayer distance d is observed, if compared to those of their precursors γ -ZrP (from 12.30 to 19.40 Å) and γ -TiP (from 11.60 to 17.00 Å). Usually, the interlayer distance of the obtained intercalated complexes increases with the complex formation [28], thus indicating that the ligand modifies its interlayer orientation when it gives rise to the coordination. In this case, the dmpCu materials maintain the same d as that of its direct precursors, but their diffractograms are different. The complex formation, however, takes place as confirmed by their electronic and ESR spectra [21,22]. The d of the dmp materials compared with that of the analogue phen materials [6] shows evident differences for the γ -ZrP derivatives: an increase of about 1 Å is present for γ -ZrPdmp compared with γ -ZrPphen and only one d reflection

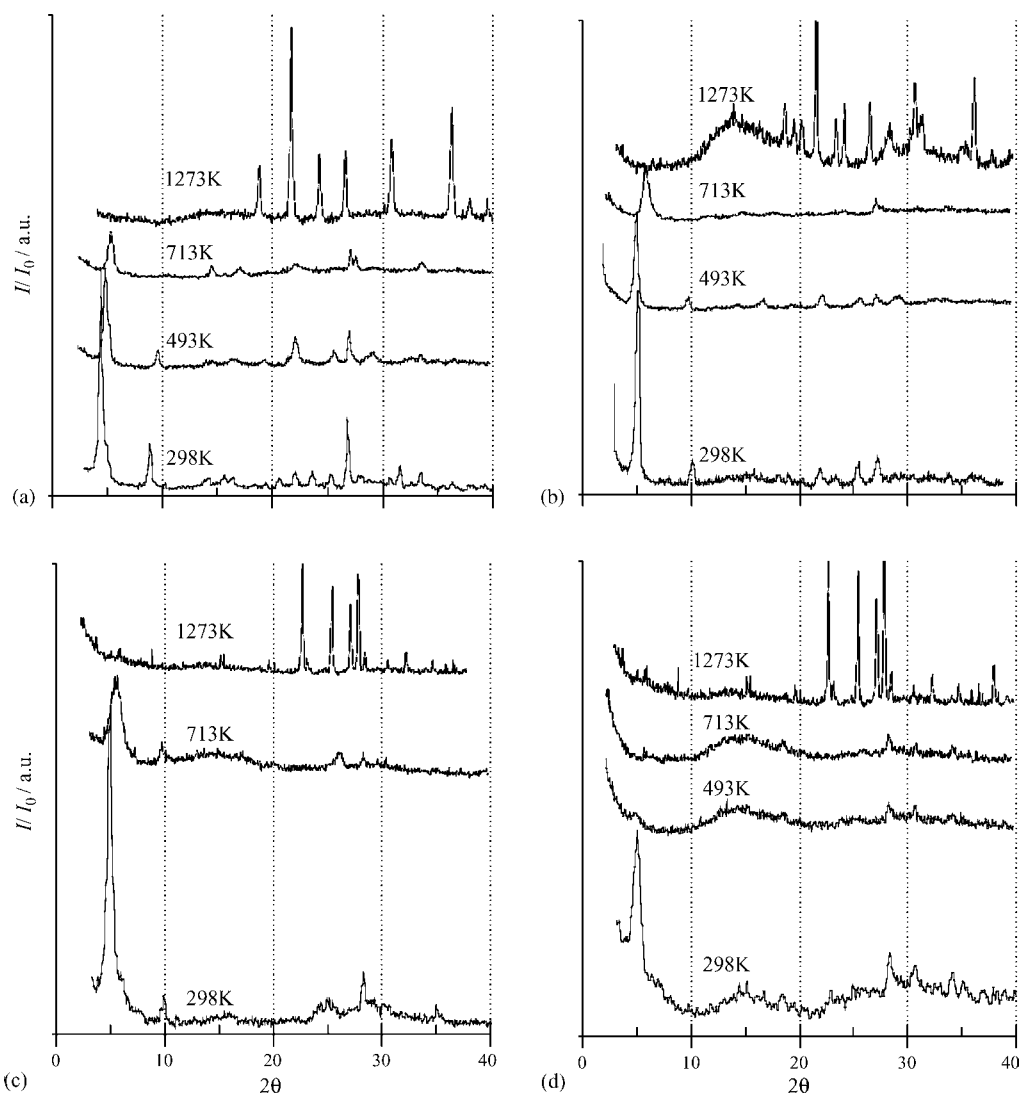


Fig. 8. XRPD pattern recorded on samples treated at selected temperatures: (a) γ -ZrPdmp, (b) γ -ZrPdmpCu, (c) γ -TiPdmp and (d) γ -TiPdmpCu.

for γ -ZrPdmpCu. These results can be ascribed to a less tilted orientation of the ligand between the γ -ZrP layers and a greater affinity to give dmpCu complexes.

On all the obtained samples treated at selected high temperatures, the XRPD measurements were also performed to determine their behaviour and stability. For the dmp materials, after dehydration at 493 K, the diffractograms do not change appreciably (only a little decrease of relative intensity is found). At 873 K, γ -TiPdmp is quite amorphous (due to a partial decomposition of the ligand). At 1273 K cubic-pyrophosphate phase are found. For materials containing dmpCu, at 493 and 873 K the diffractograms are very similar to these of precursors γ -ZrPdmp and γ -TiPdmp. Copper double phosphates of Ti and Zr are found at 1273 K.

5. Conclusions

Taking into account all the presented results, the following remarks can be drawn:

- (1) Simultaneous vaporization and oxidation followed by decomposition of dmp are described by single steps of mass loss up to 873 K. Negligible change in E values are found for the former process. Vaporization enthalpies derived from DSC experiments are noticeably lower than the corresponding E values, because of a balance of endothermic and exothermic effect (vaporization and oxidation, respectively), being the latter predominant. Decomposition of dmp shows slight increasing and decreasing trend for $\alpha < 0.15$ and $\alpha > 0.60$, respectively, thus revealing the complex nature of the dmp decomposition process.
- (2) Thermal analysis measurements carried out on the intercalation compounds evidenced that ligand decomposition occurs in two well-defined steps between 550 and 873 K. A third step takes place in γ -TiPdmp between 1040 and 1080 K, ascribed to the oxidation of a carbonaceous residue. As far as the Cu materials are concerned the ligand decomposition takes place at lower temperature (between 30 and 100 K) with respect to their precursors.

- (3) Comparable E values are found for the first decomposition step of γ -ZrPdmp (182 kJ mol^{-1}) and γ -TiPdmp (185 kJ mol^{-1}) as well as for γ -ZrPdmpCu (139 kJ mol^{-1}) compared with that of γ -TiPdmpCu (138 kJ mol^{-1}). In addition, from these results it can be seen that E values for the single step decomposition of γ -ZrPdmpCu and γ -TiPdmpCu are lower than those of the first decomposition step of γ -ZrPdmp and γ -TiPdmp. The activation energy for the oxidation occurring in γ -TiPdmp at high temperatures is very high (334 kJ mol^{-1}).
- (4) Activation energies of the two-step decomposition for the intercalation materials as well as for the oxidation in γ -TiPdmp obtained by OFW method essentially agree with those derived from the Kissinger method in the range $0.2 < \alpha < 0.8$, although the exceptions we found confirm the multi-step nature of the examined decomposition processes.
- (5) XRPD spectra indicate well crystalline and layered structures, which are maintained up to about 700 K.

As a result of the present kinetic study it is possible to affirm that the decomposition of dmp is faster when the Cu is present. The hosting matrix does not noticeably influence the dmp decomposition. Moreover, from the isoconversional method a certain dependence of E on α is shown, thus concluding that this process follows multi-step kinetics for all the examined materials and confirming the results obtained in the previous paper [6] for both phen and phenCu complex.

Acknowledgements

Authors are grateful to the National Research Council of Italy (CNR) and the Italian M.U.R.S.T. for their financial support.

References

- [1] A. Clearfield, in: A. Clearfield (Ed.), *Inorganic Ion-Exchange Materials*, CRC Press, Boca Raton, 1982, pp. 20–32.
- [2] C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, A.A.G. Tomlinson, *J. Chem. Soc.; Chem. Commun.* 15 (1984) 1204.
- [3] (a) C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, A.A.G. Tomlinson, *J. Phys. Chem.* 89 (1985) 4762;
(b) C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, A.A.G. Tomlinson, *J. Chem. Soc. Dalton Trans.* 2 (1986) 265;
- (c) C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, A.A.G. Tomlinson, *Mat. Res. Bull.* 22 (1987) 29.
- [4] (a) P. Giannoccaro, S. Doronzo, C. Ferragina, *Heterogeneous Catalysis and Fine Chemicals IV*, Elsevier Science, New York, 1997;
(b) P. Giannoccaro, E. De Giglio, M. Gargano, M. Aresta, C. Ferragina, *J. Mol. Catal. A* 157 (1–2) (2000) 131.
- [5] A. Norlund Christiansen, E. Krogh-Anderson, I.G. Krogh-Andersen, G. Alberti, M. Nielsen, M.S. Lehmann, *Acta Chem. Scand.* 44 (1990) 865.
- [6] S. Vecchio, R. Di Rocco, C. Ferragina, S. Materazzi, *Thermochim. Acta* 435 (2005) 181.
- [7] C. Ferragina, A. La Ginestra, M.A. Massucci, P. Cafarelli, R. Di Rocco, *J. Therm. Anal.* 41 (1994) 1469.
- [8] S. Vyazovkin, C.A. Wight, *J. Phys. Chem. A* 101 (1997) 8279.
- [9] M.E. Brown, D. Dollimore, A.K. Galwey, *Reactions in the solid state*, in: *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1980.
- [10] J. Sestak, *Thermophysical properties of solids*, in: *Comprehensive Analytical Chemistry*, Elsevier, Amsterdam, 1984.
- [11] S. Vyazovkin, C.A. Wight, *Anal. Chem.* 72 (2000) 3171.
- [12] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, *Thermochim. Acta* 355 (2000) 125.
- [13] S. Vyazovkin, *Thermochim. Acta* 355 (2000) 155.
- [14] S. Vyazovkin, N. Sbirrazzuoli, *Macromol. Chem. Phys.* 200 (1999) 2294.
- [15] T. Ozawa, *Bull. Chem. Soc. Jpn.* 38 (1965) 1881.
- [16] J.H. Flynn, L.A. Wall, *J. Res. Natl. Bur. Stand. A Phys. Chem.* 70A (1966) 487.
- [17] N. Sbirrazzuoli, Y. Girault, L. Elègant, *Thermochim. Acta* 293 (1997) 25.
- [18] (a) H.E. Kissinger, *Anal. Chem.* 29 (1957) 1702;
(b) H.E. Kissinger, *J. Res. Natl. Bur. Stand.* 57 (1956) 217.
- [19] S. Yamanaka, M. Tanaka, *J. Inorg. Nucl. Chem.* 41 (1979) 45.
- [20] S. Allulli, C. Ferragina, A. La Ginestra, M.A. Massucci, N. Tomassini, *J. Inorg. Nucl. Chem.* 39 (1977) 1043.
- [21] C. Ferragina, M.A. Massucci, A.A.G. Tomlinson, *J. Chem. Soc. Dalton Trans.* (1990) 1191.
- [22] C. Ferragina, A. La Ginestra, M.A. Massucci, P. Cafarelli, P. Patrono, A.A.G. Tomlinson, in: P.A. Williams, M.J. Hudson (Eds.), *Recent Developments in Ion Exchange*, vol. 2, Elsevier Applied Science, London/New York, 1990, pp. 103–108.
- [23] G. Alberti, U. Costantino, E. Torracca, *J. Inorg. Nucl. Chem.* 28 (1966) 225.
- [24] U. Costantino, A. La Ginestra, *Thermochim. Acta* 58 (1982) 179.
- [25] C. Ferragina, P. Cafarelli, R. di Rocco, *Mater. Res. Bull.* 33 (1998) 1635.
- [26] C. Ferragina, P. Cafarelli, *J. Therm. Anal. Calorim.* 53 (1998) 189.
- [27] T. Sell, S. Vyazovkin, C.A. Wight, *Combust. Flame* 119 (1999) 174.
- [28] C. Ferragina, A. Frezza, A. La Ginestra, M.A. Massucci, P. Patrono, in: M., Occelli, H., Robson (Eds.), *Expanded Clays and Other Microporous Solids*, New York 1992, pp. 263–281.