Journal of Solid State Chemistry **145,** 649–654 (1999)
Article ID jssc.1999.8276, available online at http://www.idealibrary.com on IDEAL®

Enthalpy of Interaction and Activation Energy for Thermal Degradation of Modified Forms of Lamellar Titanium Hydrogenphosphate

Liliane M. Nunes and Claudio Airoldi

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, São Paulo, Brazil

and

Robson F. de Farias[1]

Departamento de Química, Universidade Federal de Roraima, 69310-270 Boa Vista, Roraima, Brazil

Received December 3, 1998; revised March 9, 1999; accepted March 13, 1999

Crystalline alpha titanium hydrogenphosphate (TPH), the derivatives of potassium (TPK), calcium (TPCa), barium (TPBa), lanthanum (TPLa), and the intercalated forms of *n*-butylamine (TPBA) and pyridine (TPPy) were prepared. Thermodynamics of ionic exchange and intercalation processes were performed through calorimetric titration. The enthalpic values for potassium, calcium, barium, and lanthanum gave: -0.54 ± 0.04; 5.82 ± 0.24; 1.11 ± 0.09, and 5.85 ± 0.13 kJ mol^{-1}, respectively. For the intercalation with butylamine and pyridine the values -42.5 ± 0.15 and -66.76 ± 1.10 kJ mol^{-1} were obtained. The nonisolthermal Coats–Redfern method was used to calculate the kinetical parameters for thermal degradation of all matrices through thermogravimetric data. The matrices presented two or three mass loss steps. The activation energy (E_a) values for the condensation of the OH groups are 67, 155, 124, 147, 117, 318, and 477 kJ mol^{-1} for TPH, TPK, TPCa, TPBa, TPLa, TPBA, and TPPy, respectively. The plot of the enthalpic values as function of E_a gave a linear relationship, expressed by the equation: $\Delta_{int}H^0_m = -0.212 \times E_a + 31.070$, which correlated the thermochemical and kinetical parameters. © 1999 Academic Press

Key Words: **α-titanium hydrogenphosphate; thermal degradation; interaction enthalpy; ionic exchange.**

INTRODUCTION

Inorganic ionic exchangers continue to develop a wide use in many analytical applications, taking into account the best selectivity and a high specificity, which are the main properties explored for a desired cation. For this purpose, the utility is derived for chromatographic separations, in which a pronounced exchange capacity is expected (1, 2). Other possible applications are in catalysts studies (3), ionic conductors (4), renal dialysis (5), and water softening (6). In these cases the usefulness is connected to some modification in their optic and electronic properties (6, 7).

Crystalline titanium hydrogenphosphate in alpha form, α-Ti(HPO$_4$)$_2 \cdot$ H$_2$O, (α-TPH), has an interlayer distance of 760 pm. This compound belongs to a special class of lamellar materials and presents an interesting behavior as an ionic exchanger. On the other hand, it is largely applied as an excellent matrix for an intercalation process (8). A great deal of studies on this ionic exchanger referred mainly to structural features, but thermodynamic data for the ionic exchange reactions are rare. For other similar compounds such as γ-titanium (γ-TPH) and α-zirconium (α-ZrPH) hydrogenphosphates, some thermodynamic values were obtained. The main objective in these investigations is focused on alkaline metals used to obtain ionic-exchange isotherms at different temperatures (7, 9–11). The same exchange process was followed by calorimetric determinations with amorphous or crystalline α-titanium or α-zirconium hydrogenphosphate (12, 16). In addition, the ionic exchange behavior of those materials has been studied with a complete series of alkaline metals, with the matrices α-TPH, α-ZrPH, and γ-TPH (7, 9, 10, 17, 18). However, any data is reported to modified matrices, such as those containing lanthanum or *n*-butylamine.

The aim of this publication is to investigate the relationship between thermochemical data of the enthalpies of exchange or intercalation obtained through calorimetric titration and the kinetic parameters for the thermal

---

[1] Present address: Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970, Campinas, São Paulo, Brasil. E-mail: rffarias@iqm.unicamp.br.

degradation. These last parameters were calculated from nonisothermal thermogravimetric data for a series of modified matrices derived from α-titanium hydorgenphosphate.

EXPERIMENTAL

All chemicals are reagent grade. α-TPH was obtained by reacting 0.126 moles of titanium trichloride 15% with 0.50 moles of phosphoric acid 85% for four days, in a polyethylene flask, at 333 K with periodical stirring (19). The solid was separated by centrifugation and washed with bidistilled water until the washing part reached the range of pH 3.5 to 4.0. Then, the final product was dried at 313 K for several hours.

Crystalline alpha titanium hydrogenphosphate derivatives of potassium (TPK), calcium (TPCa), barium (TPBa), lanthanum (TPLa), and the intercalated forms of *n*-butylamine (TPBA) and pyridine (TPPy) were obtained by using a batch method. In this process, the crystalline lamellar solid α-TPH was directly left in contact with the agent solution for 4 h to exchange the desired species at 298 K. The intercalation of pyridine (py) and *n*-butylamine (BA) was performed by using the same process, and the products TPPy and TPBA were isolated after 12 and 24 h, respectively. The modified phosphates were dried for 24 h at 313 K and then analyzed.

The degree of exchange to produce potassium and calcium matrices was determined through the cation concentration of the supernatant after exchanging, by using flame photometry of the exchanged cation in solution (20). The amount of exchanged cations (n_f) was determined through the relationship $(n_i - n_s)/m$, where n_i is the initial number of moles of cation in solution, n_s is the number of moles of cation in equilibrium with the solid phase after the exchange process, and m is the mass of the exchanger used. For modified barium and lanthanum matrices, the percentage of cation exchanged was determined through complexometric titration with EDTA (21). The amount of intercalated *n*-butylamine and pyridine was determined by direct titration through at least three samples of the supernatant with standard hydrochloric acid solution.

All the obtained materials were characterized by using the following techniques: (i) thermogravimetry (TG) in a DuPont apparatus, model 1090B, under argon atmosphere, with a heating rate of 0.083 K s^{-1}, (ii) X-ray diffraction pattern using Cu$K\alpha$ radiation in Shimadzu model XD3A instrument, (iii) infrared spectra in a BOMEM equipment, as KBr pellets, and (iv)^{31}P NMR CP MAS spectra of solid samples using a AC 300/P Bruker instrument to 121 MHz at room temperature.

The calorimetric titrations were performed in a differential isothermic microcalorimetric system LKB 2277. In a stainless steel ampule about 20.0 mg of the exchanger was suspended in 2.0 cm^3 of bidistilled water. The system was stirred with a gold helix and thermostated at 298.15 ± 0.02 K. After stabilization of the base line, the apparatus was standardized and a microsyringe was coupled to the system. The microsyringe was connected to a stainless steel needle and through it increments of the metallic ion solution were added to the suspension. The thermal effect caused by the reaction was recorded after each addition. The same procedure was used to follow the thermal effect of the exchanger and the titrand solution in water. The calorimetric study of the intercalated *n*-butylamine was performed by using an ampule break technique (22).

The kinetic parameters for the thermal degradation of the unmodified and modified matrices were calculated by using the obtained thermogravimetric data, through the nonisothermal Coats–Redfern method (23).

RESULTS AND DISCUSSION

X-ray diffraction patterns for the intercalated matrices TPBA and TPPy exhibit distinct interlamellar distances as illustrated in Fig. 1. For example, the precursor presented an interlamellar distance of 756 pm, which is characteristic for this compound (8, 24). On the other hand, a dramatic increase in interlayer distance was observed for TPBA at

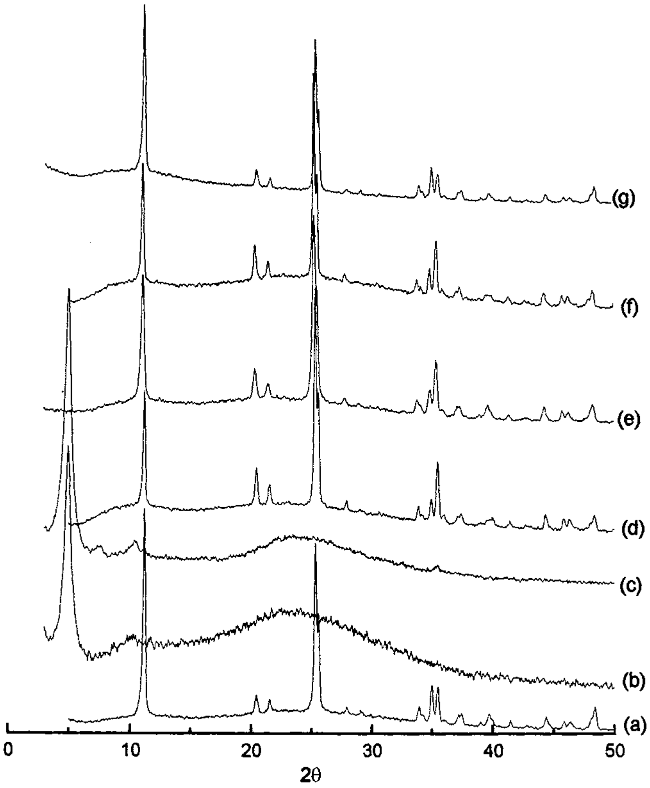


FIG. 1. X-ray diffraction patterns of the matrices: (a) TPH, (b) TPBA, (c) TPPy, (d) TPK, (e) TPCa, (f) TPBa, and (g) TPLa.

TABLE 1

Enthalpy of Exchange or Intercalation $\Delta_{int}H^{\theta}_{m}$/kJ mol^{-1} for Alpha Titanium Hydrogenphosphate Derivates of Potassium (TPK), Calcium (TPCa), Barium (TPBa), Lanthanum (TPLa), *n*-Butylamine (TPBA), and Pyridine (TPPy) at 298.15 K

Matrix	$\Delta_{int}H^{\theta}_{m}$/kJ mol^{-1}
TPK	-0.54 ± 0.04
TPCa	5.82 ± 0.24
TPBa	1.11 ± 0.09
TPLa	5.85 ± 0.13
TPBA	-42.50 ± 0.15
TPPy	-66.76 ± 1.10

1839 pm, which is caused by the insertion of the amine molecule. This value evidenced the intercalation of the *n*-butylamine into the gallery space of the crystalline TPH support (12). The infrared and ^{31}P NMR CP MAS results obtained are in total agreement with previous synthesis (8, 12, 24) and confirms the identity of all these materials.

The exchange enthalphy for TPK, TPCa, TPBa, and TPLa matrices and the intercalation enthalpic results for TPBA and TPPy are presented in Table 1. The thermogravimetric curve for the unmodified matrix is presented in Fig. 2. TG curves for the modified matrices are presented in Figs. 3a–3f, and the calculated kinetic parameters are summarized in Table 2, where E_a is the activation energy and A is the pre-exponential or frequency factor. The subscripts 1, 2, and 3 represent the first, second, and third mass loss steps, respectively. For all mass loss processes, the order of reaction, n, was assumed as equal to 1. This value provided the best correlation, factor, r, which always gave values above 0.99 for all steps of calculation. The temperature range (K) corresponding to each thermal process considered for the calculations were: 453–533 and 673–798 for TPH; 453–493 and 648–674 for TPK; 773–824, 448–523, and 705–783 for TPCa; 473–533, 623–673, and 773–838 for TPBa; 463–533, 624–689, and 743–819 for TPLa; 325–354, 501–573, and 998–1048 for TPBA; 328–373, 483–573, and 1043–1103 for TPPy.

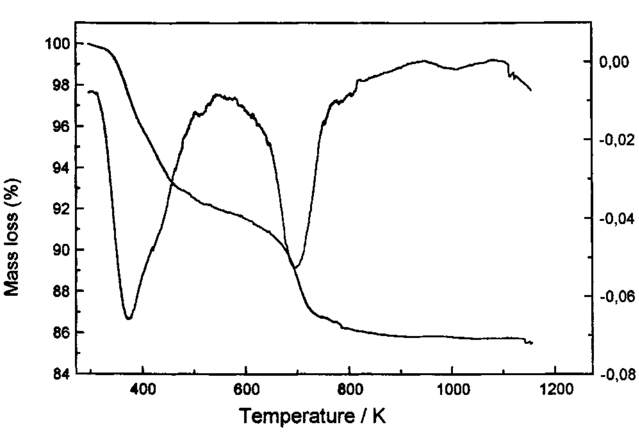
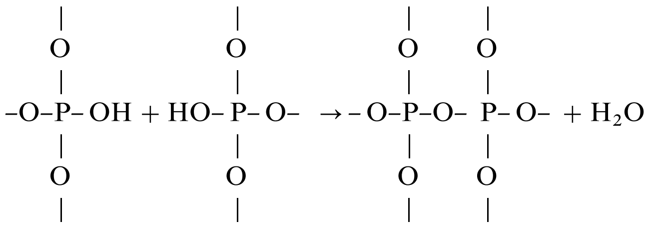


FIG. 2. Thermogravimetric curve for the TPH matrix obtained under argon atmosphere.

The thermogravimetic curves of TPH and TPCa presented only two stages of decomposition. The first one is due to the release of water of hydration and the second one is due to the condensation of two OH groups of the matrix to form one mole of water to give a pirophosphate, as is schematicaly represented below.



$$-O-P-OH + HO-P-O- \rightarrow -O-P-O-P-O- + H_2O$$

For TPK, TPBa, and TPLa matrices, the mass loss due to the condensation of OH groups occurs in two steps differing from TPBA and TPPy, where three mass loss steps were observed. The second one is due to the release of the organic moiety; the first and the third steps are related to the same process observed for the original precursor.

The first feature to be noticed from the thermogravimetric curves is related to the first mass loss step, which is due to the release of water of hydration. For TPH TPCa, and TPLa, very close temperature values are obsered: 315, 329, and 318 K, respectively. On the other hand, for TPK and TPBa, higher values, 415 and 430 K, are observed. Lower temperature values are observed for TPBA and TPPy, which are 304 and 308 K, respectively. This phenomenon could be attributed mainly to the fact that, for TPBA and TPPy, the acidic sites of the matrices are interacting directly to the neutral molecules with a total amount of intercalated organic molecules of 4.07 and 3.50 mmol g^{-1} for TPBA and TPPy, respectively. Consequently, there are not available groups to form hydrogen bonding to water molecules.

For TPK, TPCa, TPBa, and TPLa matrices the cations bonded to the matrices can interact with the water molecules within the lamella. However, the amount of exchanged protons were higher to TPK (0.90 mmol g^{-1}) and TPBa (0.72 mmol g^{-1}) than for the other matrices. For example, TPCa and TPLa presented 0.58 and 0.070 mmol g^{-1}, respectively. The lower exchanged amount for this last matrix could be understood as a consequence of the larger hydration shell of the La^{3+} ion, which makes the diffusion of the ions into the matrix galleries difficult.

As can be observed, from the increased thermal stability of the exchanged matrices, the physisorbed water molecules interact most strongly with the exchanged cation. The strength of this interaction, at least apparently, remains the same for TPCa and TPLa when compared with the

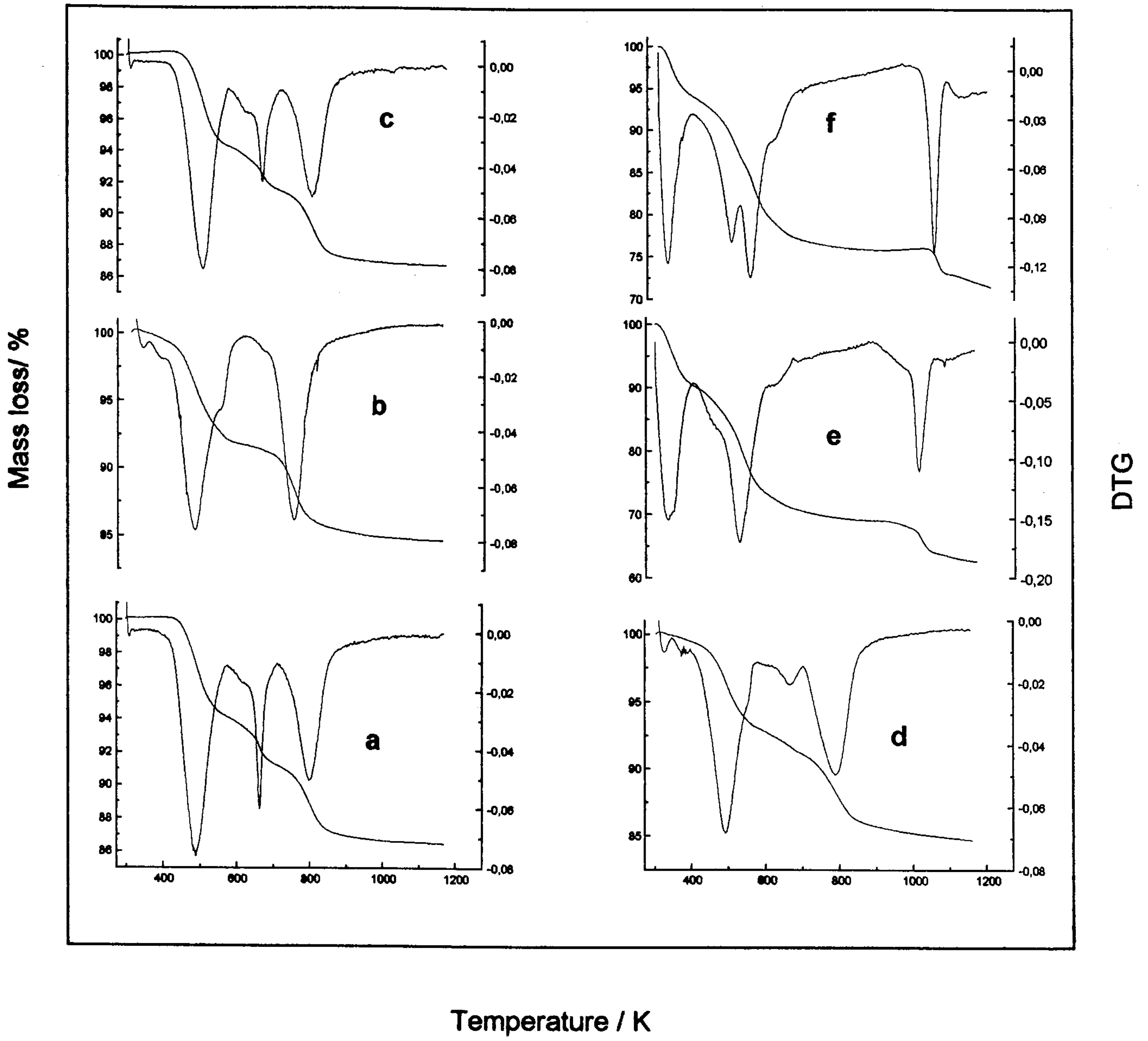


FIG. 3. Thermogravimetric curves for the TPK (a), TPCa (b), TPBa (c), TPLa (d), TPBA (e), and TPPy (f) matrices obtained under argon atmosphere.

nonexchanged matrix. This is reasonable since the total amount of exchanged cation is the smallest. However, for TPK and TPBa, the total amount of exchanged cations has a significantly increasing value due to the interaction with the physisorbed water molecules. As a consequence, the thermal stability is increased. The organic molecules intercalated exhibit a very large volume when compared with the metal cations, and then, the steric hindrance of the organic molecules makes the interaction of the water molecules with the available protons difficult.

The activation energy values for the first mass loss step, E_{a1}, are of the same order for TPH, TPCa, TPLa, TPBA, and TPPy, whereas it is almost twice this medium value for TPK and TPBa. For the intercalated matrices TPBA and TPPy, the energy necessary to promote the diffusion of the water molecules from outside to the lamellar galleries is obstructed by the steric hindrance of the organic molecules. This fact caused an increase of the activation energy values, in spite of the weaker interaction of water molecules with acidic sites for TPH, TPCa, and TPLa matrices that occurred. The highest values calculated to TPK and TPBa could be explained as a consequence of the increase in the metal cation radius from TPH to TPK and also from TPCa to TPBa. Thus, in both cases, a decrease of the hardness of the

TABLE 2

Activation Energy (E_a) and the Corresponding Frequency Factor (A) for the Thermal Degradation, as Obtained by Thermogravimetric Data for Alpha Titanium Hydrogenphosphate (TPH) and the Derivates of Potassium (TPK), Calcium (TPCa), Barium (TPBa), Lanthanum (TPLa), *n*-Butylamine (TPBA), and Pyridine (TPPy) matrices

	Matrix						
	TPH	TPK	TPCa	TPBa	TPLa	TPBA	TPPy
E_{a1}	41	81	39	72	44	46	44
A_1	3.29×10^3	1.00	2.2×10^3	10^4	6.5×10^3	2.1×10^6	1.3×10^6
E_{a2}	67	150	124	95	85	40	33
A_2	4.9×10^3	2.5×10^{11}	10^8	7.2×10^6	1.3×10^6	834.3	138.8
E_{a3}	—	155	—	147	117	318	477
A_3	—	2.4×10^9	—	6.4×10^8	7.0×10^6	4.5×10^{15}	3.9×10^{22}

cation leads to a stronger interaction with water molecules. The higher E_{a1} values for TPK and TPBa are in agreement with the sequence of the thermal stability.

For TPK, TPBa, and TPLa the condensation of OH groups occurred in two steps, differing from the single step for TPH. This feature could be explained keeping in mind that, for TPK, TPBa, and TPLa matrices, some OH groups remain close together, as proposed for TPH, and consequently are condensed first. In this direction, OH groups that are so far from M^{2+} or M^{3+} cations condense at higher temperatures, since the diffusion process is most difficult for this kind of matrices.

The activation energy for last mass loss step, which is due to the condensation of the OH groups, gave the value of 67 kJ mol^{-1} for TPH and is larger for all other matrices. This phenomenon could be understood if it is also remembered that, for TPH, the hydroxyl groups are much closer than in other matrices and the condensation process can take place easier in adjacent TPH layers. The largest values for TPBA and TPPy support this explanation, since the organic molecules obstruct the diffusion process of the OH groups on the matrices, which results in greater activation energy values. For both matrices, TPBA and TPPy, the last observed mass loss step is due to the release of structural water, which originated from the decomposition of phosphate groups, to give pyrophosphate as a final stage.

E_{a2} values for TPBA and TPPy are related to the release of the organic moiety and connected to a sterical explanation. The largest buthylamine molecules must diffuse slowly to the outside of the lamellar matrix galleries. This proposed model has, as a consequence, a large value for the activation energy.

The values of the enthalpies of interaction, $\Delta_{\text{int}}H^{\theta}_{\text{m}}$, presented in Table 1, can be compared with the activation energy values associated to the OH condensation. It is observed that most exothermic $\Delta_{\text{int}}H^{\theta}_{\text{m}}$ values correspond to larger E_a values. $\Delta_{\text{int}}H^{\theta}_{\text{m}}$ as a function of E_a values plot gave a linear relationship, as observed in Fig. 4. It is worth noting the fact that due to the similarity in thermal behavior presented by TPH and ZrPH (25), all intermediary products formed during the thermal decomposition of the pure or modified matrices are crystalline in nature.

As reported before (26), the condensation of the OH groups of the TPH lamellar matrix leads to the formation of the corresponding pyrophosphate. Certainly, the most exothermic values of $\Delta_{\text{int}}H^{\theta}_{\text{m}}$ correspond to the most stable modified matrix formed. Thus, the proportional increase observed in the E_a values can be understood as a consequence of the increase in the thermodynamic difficulty to form the pyrophosphate compound.

From the obtained data, the correlation can be established by means of the equation: $\Delta_{\text{int}}H^{\theta}_{\text{m}} = -0.212 \times E_a + 31.070$, which clearly proves that, for the solid samples studied, there is a close relationship between the thermodynamic parameters and the kinetic for the thermal degradation processes.

CONCLUSION

The obtained results showed that the thermoanalytical techniques are of great importance to understand the chemical behavior of lamellar solid matrices. Furthermore, the calorimetric data and activation energy for the thermal degradation, as obtained by a nonisothermal thermogravimetric curve, are very close in relationship. Thus, thermokinetic and calorimetric data are necessary for a full study of these kind of matrices.

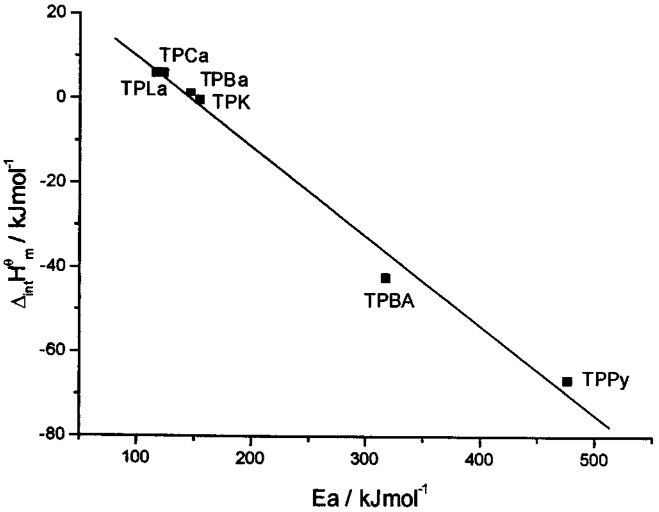


FIG. 4. Enthalpy of exchange or intercalation $\Delta_{\text{int}}H^{\theta}_{\text{m}}$ as a function of the activation energy, E_a, for TPK, TPCa, TPBa, TPLa, TPBA, and TPPy matrices.

ACKNOWLEDGMENTS

The authors are indebted to CAPES and CNPq for fellowships and FAPESP for financial support.

REFERENCES

1. A. Airoldi and S. Roca, *J. Mater. Chem.* **6,** 1963 (1996).
2. H. Kaneto, A. Abe, T. Tsuji, and Y. Tamaura, *Chromatographia* **35,** 193 (1993).
3. A. Clearfield. and D. S. Thakur, *Appl. Catal.* **26,** 1 (1986).
4. E. Ruiz-Hitzky, *Adv. Mater.* **5,** 334 (1993).
5. M. Saúrez, M. L. Rodríguez, R. Llavona, J. R. García, and J. Rodríguez, *Thermochim. Acta* **249,** 367 (1995).
6. M. Ogawa and K. Kuroda, *Chem. Rev.* **95,** 399 (1995).
7. A. L. Blumenfeld, A. S. Golub, G. Protsenko, Y. N. Novikov, M. Casciola, and U. Costantino, *Solid State Ionics* **68,** 105 (1994).
8. A. Clearfield, "Inorganic Ion Exchange Materials," CRC Press, Boca Raton, FL, 1982.
9. C. Trobajo, M. Suárez, T. Llavona, J. R. García, and J. Rodríguez, *Thermochim. Acta* **186,** 253 (1991).
10. R. Llavona, M. Suárez, J. R. García, and J. Rodríguez, *Inorg. Chem.* **28,** 2863 (1989).
11. L. Kullberg and A. Clearfield, *J. Phys. Chem.* **85,** 1585 (1981).
12. S. Roca and C. Airoldi, *Thermochim. Acta* **284,** 289 (1996).
13. S. Roca and C. Airoldi, *J. Chem. Soc., Dalton Trans.* 2517 (1997).
14. A. Clearfield and L. H. Kullberg, *J. Phys. Chem.* **78,** 152 (1974).
15. L. Kullberg and A. Clearfield, *J. Phys. Chem.* **84,** 165 (1980).
16. M. Suárez, J. R. García, and J. Rodríguez, *J. Phys. Chem.* **88,** 157 (1984).
17. M. A. Salvadó, P. Pertierra, S. García-Granda, M. Suárez, M. L. Rodríguez, R. Llavona, J. R. García, and J. Rodríguez, *J. Mater. Chem.* **6,** 415 (1996).
18. E. González, R. Llavona, J. R. García and J. Rodríguez, *J. Chem. Soc., Dalton Trans.* 829 (1989).
19. A. Bortun, E. Jaímez, R. Llavona, J. R. García, and J. Rodríguez, *Mater. Res. Bull.* **30,** 413 (1995).
20. G. W. Ewing, "Instrumental Methods of Chemical Analysis," 4th ed. McGraw-Hill, New York, 1975.
21. H. A. Flaschka, "EDTA Titrations," Pergamon Press, London, 1964.
22. C. Airoldi and S. F. Oliveira, *Struct. Chem.* **2,** 41 (1991).
23. A. W. Coats and J. P. Redfern, *Nature* **201,** 68 (1964).
24. V. Vesely and Pekárek, *Talanta* **19,** 219 (1972).
25. L. Szirtes, S. K. Shakshooki, A. M. Szeleczky, and A. O. Rajeh, *J. Thermal Anal.* **51,** 503 (1998).
26. G. Alberti and T. Bein (Eds.), "Comprehensive Supramolecular Chemistry," Vol. 7. Pergamon Press, New York, 1996.