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γ-ZIRCONIUM AND γ-TITANIUM PHOSPHATES PLATINUM INTERCALATION COMPOUND

Preparation, characterization and thermal behaviour

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Abstract

Inorganic ion-exchangers with a layered structure such as γ-zirconium and γ-titanium phosphates, intercalated with organic diamines, are able to exchange Pt^{2+} ions to give new intercalation compounds that can be utilized in heterogeneous catalysis. The experiments performed at different temperatures (25 and 45°C), show different ion uptakes, greater at 45°C and for the materials derived from γ-zirconium phosphate. After platinum exchange, all the materials show an amorphization in the XRD if compared with their precursors. The thermal behaviour of the platinum materials is specific, depending on the exchanger used and the ligand inside the exchanger. Pt^{2+} ion has a catalytic effect on ligand elimination in the γ-zirconium phosphate platinum compounds, but not in those derived from γ-titanium. All the obtained yellow materials show a small step in the TG curves and simultaneously we have the $Pt^{2+}\rightarrow Pt^0$ reduction: this is confirmed by XRD registered at the temperatures of the thermal effect, showing peaks at d_{hkl}=2.27 and 1.95 Å.

Keywords: intercalation compounds, ion-exchangers, platinum complexes

Introduction

Transition metal ion compounds are usually employed in homogeneous catalysis. The increasing interest in using them by anchoring these materials to insoluble matrices have still to be studied. Layered inorganic ion-exchangers with a non-rigid structure, such as α- [1, 2] or γ-zirconium phosphates [3] (α-ZrP, γ-ZrP) and γ-titanium phosphate (γ-TiP) [4], are employed not only for their properties as ion-exchangers [5] or intercalating polar organic molecules [6, 7], but also as starting materials for the preparation of several catalysts [8, 9]. They behave as 'heterogenizing' support for various heterogeneous catalytic processes and have induced us to study the phases that can be utilized. Our first studies showed that the Pd^{2+} materials obtained from α-ZrP diamines [such as 2,2'-bipyridyl(bipy), 1,10-

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phenanthroline(phen), 2,9-dimethyl-1,10-phenanthroline(dmp)] intercalation compounds catalyze the oxidative carbonylation of aniline [10, 11]. Rh^{3+} ions or their complexes with N-materials, obtained from α- and γ-ZrP, effectively catalyze the oxidation of CO to CO_2 [12] and act as a selective catalyst for the oxidative carbonylation of aniline and the reductive carbonylation of nitrobenzene to give N,N'-diphenylurea and/or N-phenyl carbamate ester [13, 14]. In continuing the work we want to show, in this paper, the preparation, characterization and thermal behaviour of some platinum materials derived from γ-ZrP [15] and γ-TiP intercalation compounds, that can be successfully applied in heterogeneous catalysis.

Experimental

Chemicals

Platinum chloride, 2,2'-bipyridyl, 1,10-phenanthroline and 2,9-dimethyl-1, 10-phenanthroline were Fluka puriss. products. All the other chemicals were of the highest purity available commercially and used as received.

Preparation of materials

γ-zirconim phosphate and γ-titanium phosphate

$\gamma\text{-}Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ and $\gamma\text{-}Ti(PO_4)(H_2PO_4)\cdot 2H_2O$ were prepared hydrothermally according to the method of S. Yamanaka [16] and Allulli *et al.* [17], respectively.

γ-ZrP intercalation compounds

Four different intercalation materials with ligand: γ-ZrP ratios of about 1:4 and 1:2, were obtained with bipy and dmp.
Their formulas were

$\gamma\text{-}Zr(PO_4)(H_2PO_4)bipy_{0.26}\cdot 1.64H_2O$ ($\gamma\text{-}ZrPbipy_{0.26}$);

$\gamma\text{-}Zr(PO_4)(H_2PO_4)bipy_{0.44}\cdot 0.30H_2O$ ($\gamma\text{-}ZrPbipy_{0.44}$) and

$\gamma\text{-}Zr(PO_4)(H_2PO_4)dmp_{0.26}\cdot 1.73H_2O$ ($\gamma\text{-}ZrPdmp_{0.26}$);

$\gamma\text{-}Zr(PO_4)(H_2PO_4)dmp_{0.44}\cdot 2.98H_2O$ ($\gamma\text{-}ZrPdmp_{0.44}$).

A fifth material was obtained with phen, with ligand: γ-ZrP ratio of about 1:2, of formula $\gamma\text{-}Zr(PO_4)(H_2PO_4)phen_{0.44}\cdot 2.04H_2O$($\gamma\text{-}ZrPphen_{0.44}$). The materials with high ligand content, were obtained by contacting at 45°C the pre-swelled ethanolic form of γ-ZrP(γ-ZrPEtOH, d_{002}=16.4 Å) (1 g), freshly prepared before each reaction, with a 0.1 mol dm^{-3} solution of bipy, phen or dmp in ethanol-water (1:1) (100 cm^3) for a week. The materials with lower ligand content were obtained in the same way, but using a 0.01 mol dm^{-3} solution of the ligand.

γ-TiP intercalation compounds

The pre-swelled ethanolic form of γ-TiP(γ-TiPEtOH, d_{002}=15.22 Å) (1 g) was contacted with a 0.01 mol dm^{-3} solution of bipy, phen or dmp in ethanol-water (1:1) (100 cm^3) for a week, at 45°C. Three intercalation compounds of formula composition

γ-$Ti(PO_4)(H_2PO_4)bipy_{0.43}\cdot 0.53H_2O$(γ-TiPbipy$_{0.43}$);

γ-$Ti(PO_4)(H_2PO_4)phen_{0.47}\cdot 2.06H_2O$(γ-TiPphen$_{0.47}$) and

γ-$Ti(PO_4)(H_2PO_4)dmp_{0.26}\cdot 2.83H_2O$(γ-TiPdmp$_{0.26}$) were obtained.

Platinum intercalation compounds

The platinum γ-ZrP and γ-TiP intercalation compounds were prepared by ion exchange, by equilibrating the intercalation compounds (0.1 g) with a volume of the $PtCl_2$ solution 5×10^{-4} mol dm^{-3}, such that the amounts of ligands in the solid, and of Pt^{2+} in the solution, were in a 1:1 molar ratio. All the batches were thermostatted at 25 and 45°C, for several sets of times. The suspensions were then filtered, the solutions analyzed for metal content and final pH, and the solids were washed with distilled water and air dried.

Physical measurements and chemical analysis

The thermal curves were recorded on a simultaneous TG/DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 10°C min^{-1}, ignition up to 1100°C to constant mass, in an air and nitrogen flow. All the materials were submitted to X-ray diffraction analysis, especially by monitoring the d_{002} reflection (which is known to correspond to the interlayer distance for these ion-exchangers) in order to obtain information whether or not the layered structure was maintained. The XRD patterns were taken on a Philips diffractometer; Ni-filtered and CuK_α radiation was used. Platinum ion contents were determined by following the concentration changes in the supernatants by atomic absorption spectrometry using a G.B.C. 903 instrument. The water and ligand contents of the solids were determined from the TG curves. In Table 1 the compositions of bipy, phen and dmp γ-ZrP, γ-TiP intercalation compounds, from elemental chemical analysis and thermogravimetric analysis, are listed.

Results and discussion

Materials derived from γ-ZrP intercalation compounds

Platinum uptake

The platinum uptake by γ-ZrP-diamine intercalation compounds was carried out via the batch procedure with solutions of Pt^{2+} ions, at different temperatures

Table 1 Composition of bipy, phen and dmp γ-ZrP, γ-TiP intercalation compounds from thermogravimetric and elemental chemical analysis

Formula	% calculated			% observed		
γ-ZrPL	C	H	N	C	H	N
γ-$Zr(PO_4)(H_2PO_4)bipy_{0.26}\cdot 1.64H_2O$	8.80	2.08	2.06	8.65	2.08	2.03
γ-$Zr(PO_4)(H_2PO_4)bipy_{0.44}\cdot 0.30H_2O$	14.70	1.71	3.45	14.65	1.79	3.40
γ-$Zr(PO_4)(H_2PO_4)phen_{0.44}\cdot 2.04H_2O$	15.80	2.40	3.08	15.55	2.40	3.02
γ-$Zr(PO_4)(H_2PO_4)dmp_{0.26}\cdot 1.73H_2O$	11.86	2.46	1.98	11.80	2.46	1.78
γ-$Zr(PO_4)(H_2PO_4)dmp_{0.44}\cdot 2.98H_2O$	17.26	3.29	2.88	17.26	3.15	2.80
γ-TiPL						
γ-$Ti(PO_4)(H_2PO_4)bipy_{0.43}\cdot 0.53H_2O$	16.31	2.05	3.89	16.18	2.10	3.87
γ-$Ti(PO_4)(H_2PO_4)phen_{0.47}\cdot 2.06H_2O$	18.73	2.73	3.64	18.70	2.68	3.60
γ-$Ti(PO_4)(H_2PO_4)dmp_{0.25}\cdot 2.83H_2O$	12.67	3.27	2.11	12.57	3.25	2.11

(25 and 45°C) and for different times (1 and 3 weeks) in order to understand the parameters that influence the uptake [15]. The solids were then filtered off and washed with distilled water. The supernatant solutions were analyzed for their Pt^{2+} content and pH. All the materials obtained are light or dark yellow, depending on either the platinum content or the temperature (25 or 45°C). The temperature of batch contact and the time length both influence the platinum uptake, but we can conclude that the temperature of the experiment (45°C) achieves more than the time length. Platinum-exchanged materials were obtained by contacting samples of 0.5 mmol of the γ-ZrP-diamine intercalation compounds with volumes of a 5×10^{-4} mol dm^{-3} $PtCl_2$ solution in order to obtain compounds with a molar ratio, inside the solid, 1:1=Pt:L (*L*=bipy, phen, dmp). At 25°C the yellow materials obtained show a lower platinum content, regardless of whether the experiments were performed for a week or for three weeks. Table 2 shows the chemical composition of the compounds obtained at 45°C, after one and three weeks of batch contact. The pH of the supernatant solution, after the batch contact, is generally lower than that at the start of the experiment: this means that the exchange between the H^+ ions of the exchanger and the platinum ions is incoming. The most obvious point to make from inspection of the chemical composition is that the maximum Pt^{2+} ion uptake for all the γ-ZrP-diamine intercalation compounds is reached at 45°C, after three weeks. The platinum uptake for all the γ-ZrP-diamine intercalation compounds is, in the order, bipy>dmp>phen. For the materials derived from γ-ZrPbipy$_{0.44}$ and γ-ZrPdmp$_{0.44}$ we obtain compounds that have, in the solid, a molar ratio of Pt^{2+}:L=1. The material derived from γ-ZrPphen$_{0.44}$ has, in the solid, a molar ratio of Pt^{2+}:L=1:2, after a week of batch contact. Note that the TG curves confirm that diamines are not severely eluted during the exchange process, as is the case for the other t.m.i. intercalation compounds (Rh, Pd). A small elution (<5%) is found in γ-Zr(PO$_4$)(H$_{1.20}$PO$_4$)Pt$_{0.40}$bipy$_{0.42}$·2.05H$_2$O and in γ-Zr(PO$_4$)(H$_{1.20}$PO$_4$)Pt$_{0.40}$dmp$_{0.42}$·1.73H$_2$O, probably due to the complexes in the exchangers.

XRD results

The X-ray diffraction patterns of all materials containing platinum (obtained after 3 weeks) are slightly different and reflect a lower degree of crystallinity than those of their precursors. The interlayer distance d_{002} changes, except for the materials derived from γ-ZrPbipy$_{0.44}$. So we always have, after the platinum uptake, a decrease in d_{002}. Other peaks we noted were: at 9.02 Å (small), at 7.85 Å and 4.55 Å (strong and sharpened); at 8.58 Å (small), at 7.89 Å and 4.52 Å (strong and sharpened), for the compounds derived from γ-ZrPbipyPt and γ-ZrPphenPt, respectively. We assume that these peaks are due to the LPt complexes in the exchangers. In fact we tested the bipy-Pt and phen-Pt complexes (synthesized, not obtained by exchanging in γ-ZrP intercalation compounds the

Table 2 Chemical composition of the compounds obtained from γ-ZrPL

γ-ZrPL	Pt^{2+} materials obtained after 1 week	Pt^{2+} materials obtained after 3 weeks
γ-ZrPbipy	γ-$Zr(PO_4)(H_{1.68}PO_4)Pt_{0.16}bipy_{0.26}\cdot 1.60H_2O$	γ-$Zr(PO_4)(H_{1.58}PO_4)Pt_{0.21}bipy_{0.26}\cdot 1.83H_2O$
γ-$ZrPbipy_{0.44}$	γ-$Zr(PO_4)(H_{1.30}PO_4)Pt_{0.35}bipy_{0.44}\cdot 2.03H_2O$	γ-$Zr(PO_4)(H_{1.20}PO_4)Pt_{0.40}bipy_{0.42}\cdot 2.05H_2O$
γ-$ZrPphen_{0.44}$	γ-$Zr(PO_4)H_{1.56}PO_4)Pt_{0.22}phen_{0.44}\cdot 1.07H_2O$	γ-$Zr(PO_4)(H_{1.38}PO_4)Pt_{0.31}phen_{0.43}\cdot 2.30H_2O$
γ-$ZrPdmp_{0.26}$	γ-$Zr(PO_4)(H_{1.78}PO_4)Pt_{0.11}dmp_{0.26}\cdot 1.40H_2O$	γ-$Zr(PO_4)(H_{1.64}PO_4)Pt_{0.18}dmp_{0.26}\cdot 2.20H_2O$
γ-$ZrPdmp_{0.44}$	γ-$Zr(PO_4)(H_{1.38}PO_4)Pt_{0.31}dmp_{0.44}\cdot 1.70H_2O$	γ-$Zr(PO_4)(H_{1.20}PO_4)Pt_{0.40}dmp_{0.42}\cdot 1.73H_2O$

exchanger) by the diffractometer and we obtained the same kind of peaks. The platinum materials derived from γ-ZrPdmp show only one small peak related to dmp-Pt at 9.25 Å. Figure 1 shows the XRD patterns referring to sample γ-$Zr(PO_4)(H_{1.20}PO_4)Pt_{0.40}bipy_{0.42}\cdot 2.05H_2O$ at r.t, 400 and 1000°C. It is worth noting that the big peak at 7.89 Å (related to the bipy-Pt complex in the exchanger) is reduced in intensity at 400°C, when the reduction of $Pt^{2+}\rightarrow Pt^0$ is almost completed. At 1000°C we obtain only the pyrophosphates and the $Pt^0(d_{hkl}=2.26$ Å–1.95 Å) [18]. In Table 3 we list the d_{002} of the precursors and the d_{002} changes, at increasing temperature, of the γ-zirconium platinum intercalated materials. As we can see, the layered structure of the materials is already present if they are heated at 450°C, except for the materials derived from γ-ZrPphen. All the interlayer distances in the heated materials are smaller than those of the materials studied at room temperature. We prepared the XRD patterns of the platinum γ-zirconim intercalation compounds heated at 500°C in the simultaneous TG/DTA apparatus, under a nitrogen flow, with the aim to find some difference in the Pt^0 formation. We have obtained the same results as in an air flow; so we can assume that at temperatures ≤ 500°C platinum reduction occurs in both gases and the materials are still layered.

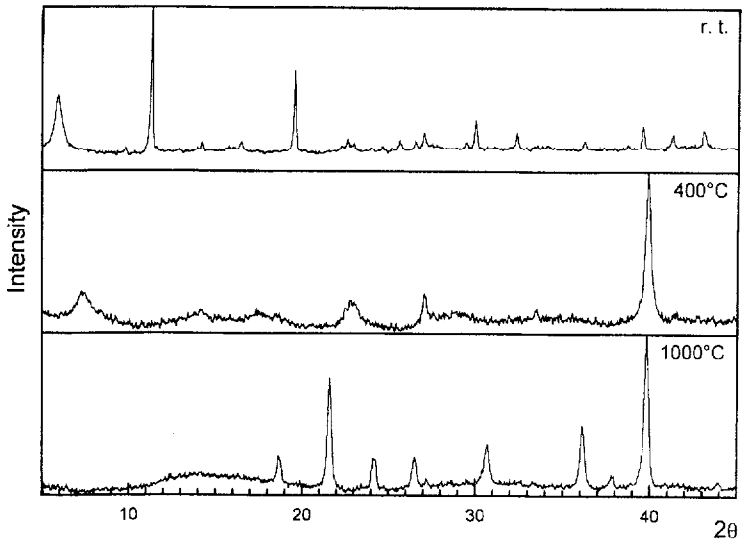

Fig. 1 XRD of γ-$Zr(PO_4)(H_{1.20}PO_4)Pt_{0.40}bipy_{0.42}\cdot 2H_2O$ at r.t, 400 and 1000°C

Thermal behaviour

Figures 2 and 3 show the TG/DTA curves of the platinum intercalation compounds (materials obtained at 45°C, after 3 weeks) compared with those of their

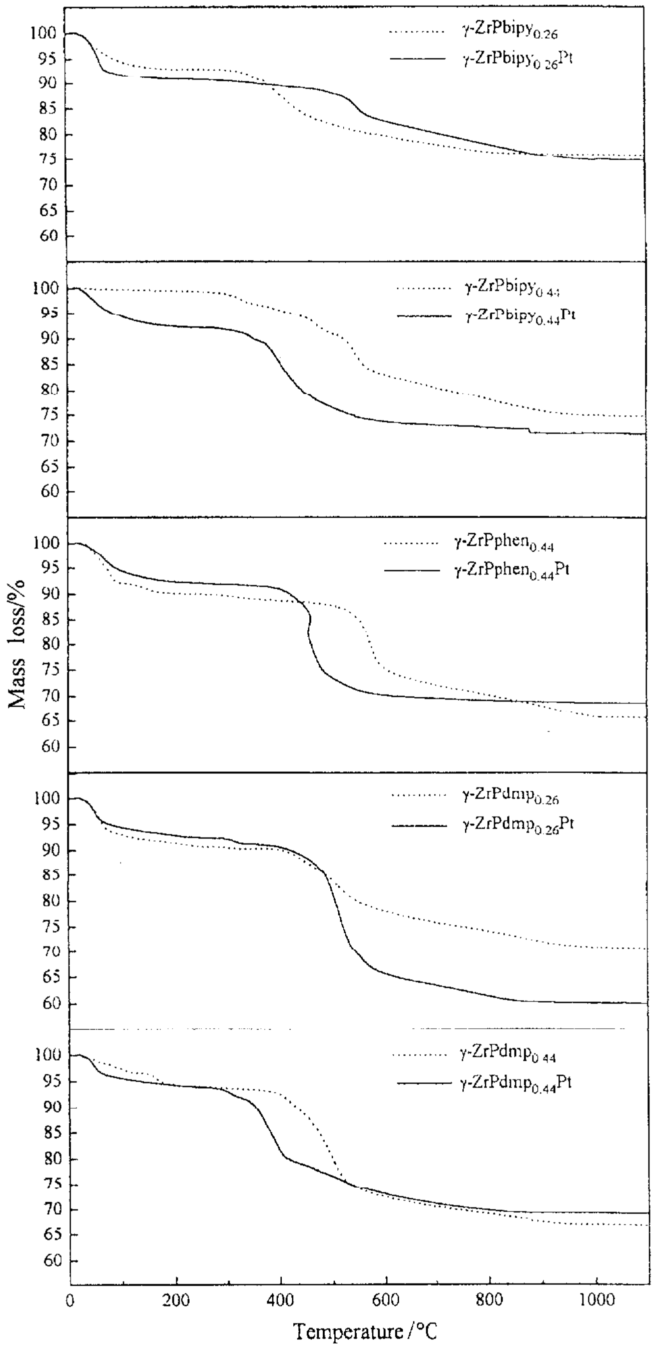

Fig. 2 TG curves of platinum γ-zirconium phosphate intercalation compounds in comparison with their precursors

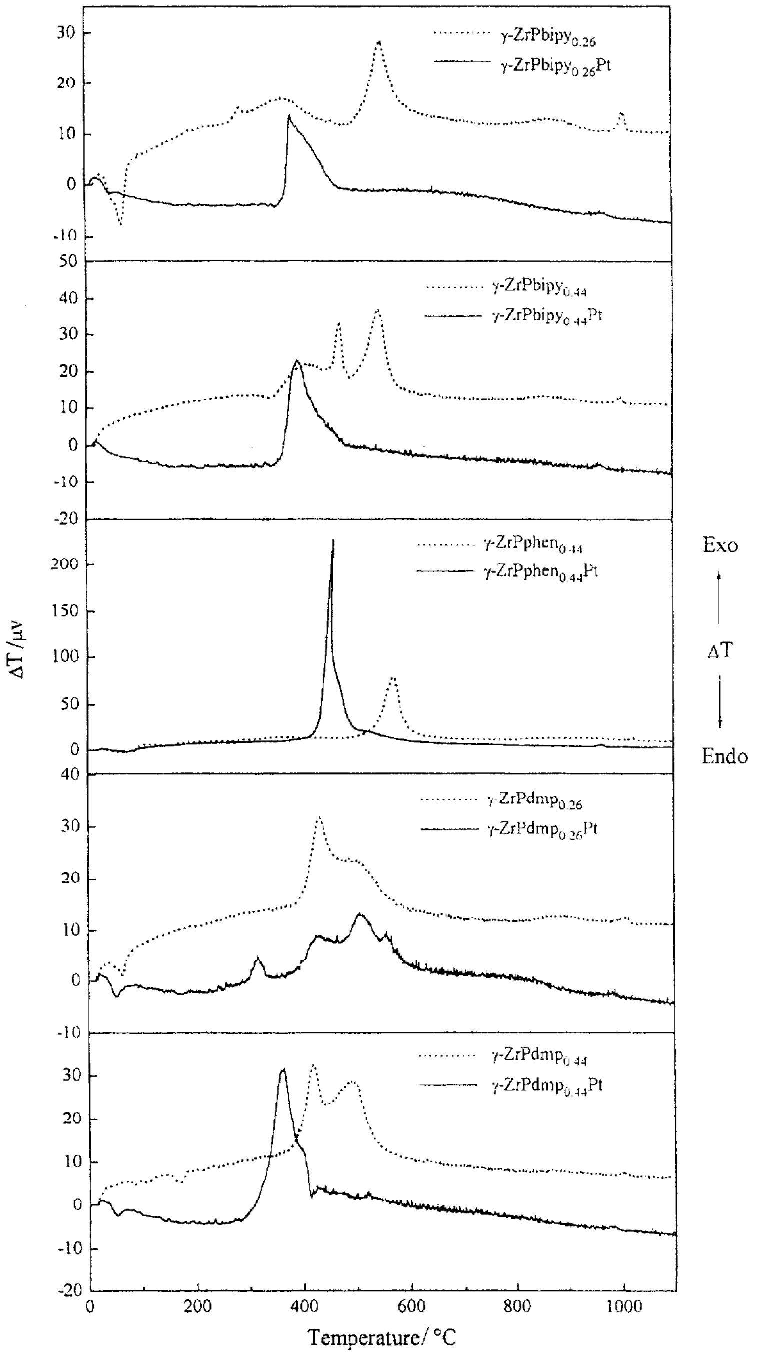

Fig. 3 DTA curves of platinum γ-zirconium phosphate intercalation compounds in comparison with their precursors

Table 3 XRD of the γ-ZrPLPt materials heated at some temperatures

γ-ZrPL	d_{002}/Å	γ-ZrPLPt^{2+}	d_{002}/Å			
	r.t.		r.t.	250°C	350°C	450°C
γ-ZrPbipy$_{0.26}$	15.00	γ-Zr(PO$_4$)(H$_{1.58}$PO$_4$)Pt$_{0.21}$bipy$_{0.26}$·1.83H$_2$O	13.59	12.19	11.48	10.85
γ-ZrPbipy$_{0.44}$	14.25	γ-Zr(PO$_4$)(H$_{1.20}$PO$_4$)Pt$_{0.40}$bipy$_{0.42}$·2.05H$_2$O	14.25	14.25	14.25	11.26
γ-ZrPphen$_{0.44}$	19.00	γ-Zr(PO$_4$)(H$_{1.38}$PO$_4$)Pt$_{0.31}$phen$_{0.43}$·2.30H$_2$O	16.06	13.81	13.81	
γ-ZrPdmp$_{0.26}$	17.70	γ-Zr(PO$_4$)(H$_{1.64}$PO$_4$)Pt$_{0.18}$dmp$_{0.26}$·2.20H$_2$O	16.06	14.25	14.25	12.11
γ-ZrPdmp$_{0.44}$	19.40	γ-Zr(PO$_4$)(H$_{1.20}$PO$_4$)Pt$_{0.40}$dmp$_{0.42}$·1.73H$_2$O	16.67	14.25	14.25	12.99

precursors. Figure 2 shows the mass loss of the γ-ZrPLPt samples in comparison with their parent compounds. For all the obtained materials two pronounced losses are observed in the TG curves: the first is due to the elimination of interlamellar water and occurs between 25 and 250°C; the second, in the range 250–850°C, is related either to the decomposition of the organic diamine or to the loss of water, owing to the condensation of the existing hydrogen phosphate group to the zirconium pyrophosphate phase. The decomposition of the organic ligand takes place at different temperatures, depending on the diamine present, the last traces of carbonaceous residues being completely lost at 1100°C. At 350°C (for the γ-ZrPbipyPt and γ-ZrPdmpPt materials) and at 420°C (for the γ-ZrPphenPt) the TG curves show a small and marked step. At these temperatures we have together with the combustion of the ligands the $Pt^{2+} \rightarrow Pt^0$ reduction. This is confirmed by the X-ray diffraction as we have seen previously. When these temperatures are reached, the Pt^{2+} present in the solid, linked to the ligands, undergoes a sudden reduction to Pt^0. Particular attention should be paid to the TG curve obtained for the γ-ZrPphenPt material which shows an unusual behaviour in the curve at the temperature previously mentioned (420°C). We shall see the same behaviour in the analogue material derived from γ-TiPphen. Figure 3 gives the DTA curves for all the γ-ZrPLPt samples, compared with those of their precursors. Note that for all the materials, except for those derived from γ-$ZrPdmp_{0.26}Pt$, the diamine begins to decompose at lower temperatures (~70–100°C) than their parents. That could be a consequence of the good catalytic effect of the platinum on the complete oxidation of the carbon formed in the solid during ligand decomposition. Furthermore, in all the precursors the diamine decomposes and combusts with two more or less pronounced exothermic peaks for the platinum compounds (except for the material derived from γ-$ZrPdmp_{0.26}$), only one exothermic peak with a shoulder is present. We deduce that in these materials the diamine is mostly co-ordinated to the metal ion; the quantity not coordinated to the platinum interacts directly with the exchanger. We also performed some experiments in a nitrogen flow, to discover eventual differences and to confirm that the exothermic peaks are related to the decomposition of diamine. The furnace atmosphere is particularly important in the examination of organic materials and the selection of the most appropriate atmosphere can greatly enhance the value of the method. Figure 5 gives the DTA curves of γ-$ZrPdmp_{0.26}Pt$ and γ $TiPbipy_{0.43}Pt$ under different gas flows air and nitrogen. The curves obtained under a nitrogen flow show betwen 250 and 500°C endothermic peaks, and not exothermic ones, as would be expected for organic decomposition, based on literature reports [19]. We note that these endothermic peaks occur at temperatures lower than those of the corresponding exothermic peaks. May be in a nitrogen flow the decomposition of the organic matter occurs earlier.

Table 4 Chemical composition of the compounds obtained from γ-TiPL

γ-TiPL	Pt^{2+} materials obtained after 1 week	Pt^{2+} materials obtained after 3 weeks
γ-TiPbipy$_{0.43}$	γ-Ti(PO$_4$)(H$_{1.48}$PO$_4$)Pt$_{0.26}$bipy$_{0.43}$·1.94H$_2$O	γ-Ti(PO$_4$)(H$_{1.44}$PO$_4$)Pt$_{0.28}$bipy$_{0.43}$·1.96H$_2$O
γ-TiPphen$_{0.47}$	γ-Ti(PO$_4$)(H$_{1.82}$PO$_4$)Pt$_{0.09}$phen$_{0.47}$·1.93H$_2$O	γ-Ti(PO$_4$)(H$_{1.76}$PO$_4$)Pt$_{0.12}$phen$_{0.47}$·1.97H$_2$O
γ-TiPdmp$_{0.26}$	γ-Ti(PO$_4$)(H$_{1.74}$PO$_4$)Pt$_{0.13}$dmp$_{0.26}$·1.40H$_2$O	γ-Ti(PO$_4$)(H$_{1.66}$PO$_4$)Pt$_{0.17}$dmp$_{0.26}$·2.20H$_2$O

Table 5 XRD of the γ-TiPLPt materials heated at some temperatures

γ-TiPL	d_{002}/Å	γ-TiPLPt^{2+}	d_{002}/Å		
	r.t.		r.t.	250°C	350°C
γ-TiPbipy$_{0.43}$	14.70	γ-Ti$(PO_4)(H_{1.44}PO_4)Pt_{0.28}$bipy$_{0.43}\cdot 1.96H_2O$	14.47	13.79	13.58
γ-TiPphen$_{0.47}$	17.70	γ-Ti$(PO_4)(H_{1.76}PO_4)Pt_{0.12}$phen$_{0.47}\cdot 1.97H_2O$	17.33	14.96	14.96
γ-TiPdmp$_{0.26}$	17.60	γ-Ti$(PO_4)(H_{1.66}PO_4)Pt_{0.17}dmp_{0.26}\cdot 2.20H_2O$	16.07	14.96	14.72

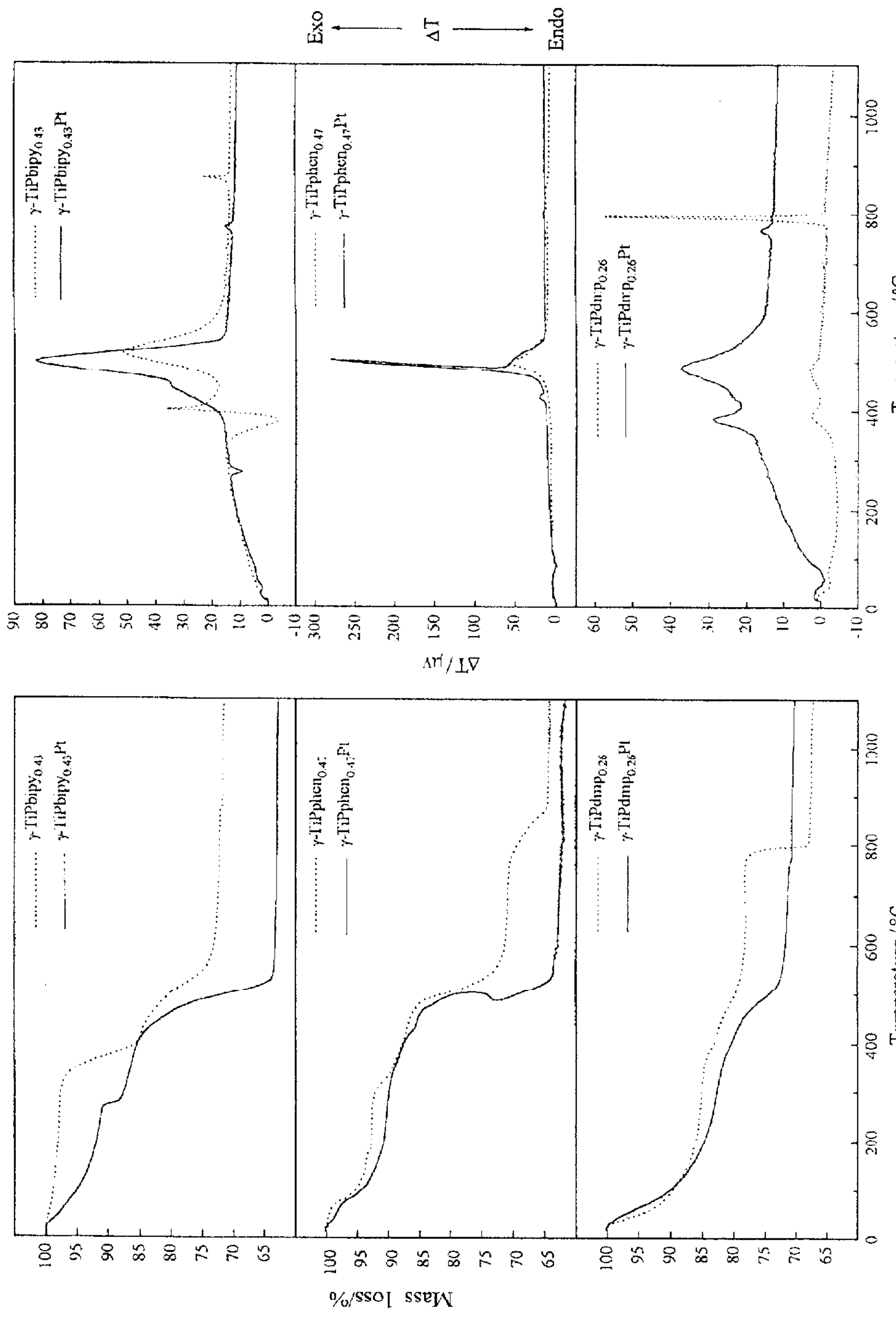

Fig. 4 TG/DTA curves of platinum γ-titanium phosphate intercalation compounds in comparison with their precursors

Materials derived from γ-TiP intercalation compounds

Platinum uptake

The platinum uptake by γ-TiP-diamine intercalation compounds was effected employing the same procedure as for γ-ZrP-diamines, at 25 and 45°C, for 1 and 3 weeks of batch contact, with a $PtCl_2$ solution. The experiments performed at 25°C showed that the Pt^{2+} uptake by the γ-TiP intercalation compounds was the same, for both 1 and 3 weeks; so we can deduce that the uptake does not depend on the time of contact between the exchanger and the platinum ions, but depends on the temperature. The batch contact time length is not as important as in the case of γ-ZrPL. Table 4 shows the chemical composition for the platinum materials obtained at 45°C, after 1 and 3 weeks of batch contact, between platinum chloride solution and the intercalated γ-titanium phosphate samples. The materials are yellow (dark or light depending on the platinum content and the temperature at which the experiments were performed. We note that in the case of γ-titanium intercalation compounds both the temperatures and the ligand present inside the exchanger are parameters that influence the platinum uptake. As was the case for the γ-ZrP-diamines, the ion uptake is in the order bipy>dmp>phen. The material $\gamma\text{-Ti(PO}_4\text{)(H}_{1.74}\text{PO}_4\text{)Pt}_{0.13}\text{dmp}_{0.26}\cdot 1.40\text{H}_2\text{O}$ has a ratio Pt^{2+}:L=1:2; we do not obtain materials with a ratio Pt^{2+}:L=1:1.

XRD results

The XRD patterns of the platinum materials are very similar to those of their precursors; we note only a light amorphization and a small reduction in d_{002} (~0.5 Å), almost negligible with respect to their parents. The maximum amorphization that we note is in the materials derived from γ-TiPdmp; in all cases the amorphization increases with the increase of uptake of Pt^{2+}ions. We note also the peaks related to the LPt complexes, the same as in the case of platinum γ-zirconium intercalation compounds. The material derived from γ-TiPdmp shows a sharpened peak (when the uptake is appreciable) at 8.42 Å. In this case the intensity of this peak is greater than that of the interlayer distance d_{002}=17.87 Å and it is proportional to the platinum content. When the platinum materials are heated at 350–450°C, the peak at 8.42 Å (related to LPt) starts to decrease and the Pt^0 peaks appear, as happens in the similar platinum materials derived from γ-ZrPL. Table 5 gives the d_{002} values of the γ-TiPLPt compounds heated at some temperatures. The materials remain layered up to 350°C (with a decrease of 0.89–2.37 and 1.35 Å compared with the value obtained at room temperature) but they are rather amorphous. At ≤ 500°C the LPt peaks disappear completely and in the amorphous materials (due to the ligand combustion) only Pt^0 is present. If the heating is performed in a nitrogen flow we obtain the same results as in an air flow.

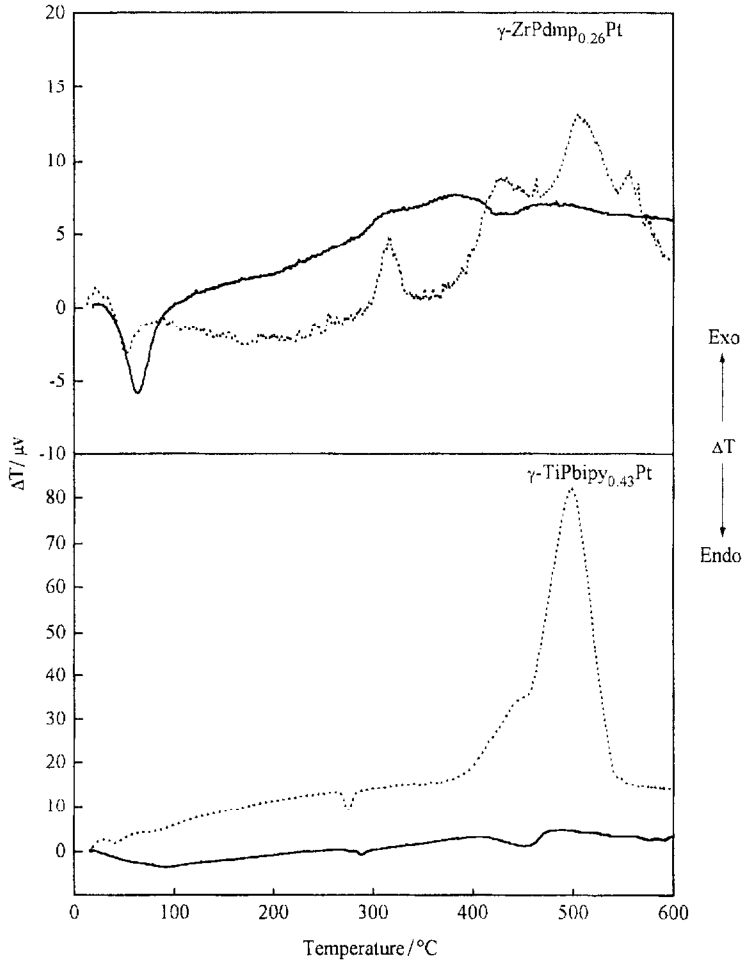

Fig. 5 DTA curves of γ-ZrPdmp$_{0.26}$Pt and γ-TiPbipy$_{0.43}$Pt under different gas flows (air ··· and nitrogen —)

Thermal behaviour

Figure 4 gives the TG/DTA curves of the γ-titanium platinum intercalation compounds as compared with those of their precursors. The thermal behaviour is similar for all materials, the common result being the small step in the TG curves, at different temperatures (depending on the ligand present) related to the reduction of $Pt^{2+} \rightarrow Pt^0$. As we can see in the figure, the steps occur at 280, 350 and 420°C for the materials derived from γ-TiPbipy, γ-TiPdmp and γ-TiPphen, respectively. We noted the same behaviour for the platinum materials derived from γ-zirconium intercalation compounds. We see only in the case of the materials derived from γ-TiPbipyPt that the temperature of the step was lower than that observed for the derivatives of γ-zirconium (280°C *vs.* 350°C). The decomposition temperatures of the ligands are the same as those of their precursors, exept for γ-TiPbipyPt which is lower (~50°C). The DTA curves have stronger and more sharpened exothermic peaks compared to their precursors, related to the decomposition of the ligands and we suppose also the reduction of platinum. This is evident especially as concerns γ-TiPphenPt whose TG curve shows no step, but a very complicated inflection as we saw for the analogous derivative of γ-ZrP. For the platinum material derived from γ-TiPdmp the evidence, in the DTA curve, is that the strong exothermic peak at 800°C due to pyrophosphate formation, is significantly reduced in the presence of platinum ions. The hydration water of the materials is lost at 25–250°C and the value does not exceed 2.5 mol/mol exchanger (as we can see in the chemical composition of Table 4). The last loss in the TG curves is due to the water loss in the condensation to pyrophosphate, of the phosphate group: it is interesting to note that in the DTA curves the temperature of α-cubic pyrophosphate formation of the platinum compounds is lower (~100°C) than that of the analogous precursors. We performed some experiments in a nitrogen flow (Fig. 5) and we have drawn the same conclusion as in the case of the γ-zirconium platinum materials.

Conclusions

Platinum ions can be inserted between the layers of γ-zirconium and γ-titanium phosphates by ion exchange, at 25 or 45°C, using as starting materials their intercalation compounds with bipy, phen or dmp aromatic diamines. The interlayer distances of these compounds are large enough to allow the diffusion of Pt^{2+} ions and hence Pt^{2+}/H^+ ion exchange. γ-ZrP intercalation compounds exchange more platinum ions than γ-TiP intercalation compounds; in the obtained yellow materials there is no release of diamines. The obtained materials are not as crystalline as their precursors. The interlayer distance remains that of the respective starting compounds, for materials derived from γ-TiPL, but there is a decrease for materials derived from γ-ZrPL, except for those derived from γ-$ZrPbipy_{0.44}$. All materials show, in the XRD pattern, peaks related to the LPt complexes; these peaks decrease when the materials are heated and they disappear completely at ~450°C, when Pt^0 is formed. The thermal behaviour of all platinum materials is very similar for the compounds derived from γ-ZrPL or γ-TiPL; in the latter case we do not have the catalytic effect of the platinum on the temperature of ligand decomposition. In the TG curves we note, at different temperatures depending on the ligand present, a small step and simultaneously the $Pt^{2+}\rightarrow Pt^0$ reduction. When the experiments are performed in a nitrogen flow the reduction of platinum is obtained under the same conditions as in an air flow.

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