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THERMAL BEHAVIOUR OF MIXED Sn AND Ge PHOSPHATES

Correlations with their catalytic properties

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Pure and mixed Ge and Sn hydrogenphosphates, prepared either by refluxing in 8 *M* H_3PO_4 or by hydrothermal treatment at 180° or 300°C, have been characterized in terms of chemical composition and thermal behaviour, and also tested as catalysts in the 1-butene isomerization, in order to correlate acidic properties with preparation method. Solid solutions for every composition in this system are formed only when using the refluxing method, as proved by X-ray and TG-DTA data. The hydrothermal treatments are strongly influenced by the hydrolysability of the Ge phosphate: in almost all the samples, where Ge was present, $GeOHPO_4$ was identified on TG-DTA curves by the endothermic H_2O weight loss at 700°–800°C. The acidic properties of the various materials decrease as $GeOHPO_4$ content increases.

Keywords: mixed Sn and Ge phosphates, TG-DTA, X-ray

Introduction

Over the past few years the hydrogen phosphates of tetravalent elements, which are well known as inorganic ion-exchangers with a non-rigid structure, have been increasingly studied for potential use in acid catalysis, since they can give rise to products with modulated acidic strength. All the pure Zr, Ti, Sn and Ge compounds are isostructureal, and presumably solid solutions can easily be formed between them. In this case, a gradual variation of the acidic strength, which depends on the *M*(IV) electronegativity [1], can be achieved. This is the case for the Sn-Zr system [2] but, for other system such as Zr-Ti [3] and Zr-Ge [4], only limited solid solutions form when the most common reflux method in H_3PO_4 is employed for preparing crystalline compounds. We have verified [5] that hydrothermal treatments can be very effective for obtaining stable crystalline phases rapidly.

In previous experiments [1] we have observed that, among this class of materials, Ge and Sn hydrogen phosphates can give products with the highest

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acidic strength using appropriate thermal treatments. For this reason we have studied the Sn-Ge mixed compounds, utilizing both the reflux method or hydrothermal synthesis, in order to optimize the preparation conditions for solid solutions of this mixed system and to investigate how the preparation method can influence the catalytic properties of the products. An important role in the detection of formation of solid solutions or other hydrolysed compounds has been played by simultaneous TG-DTA, which permits detection, in a very short time, of the eventual chemical and structural modifications of these mixed phosphates, that can involve a drastic decrease in their acidic properties.

Experimental

Preparation

Preparation of the crystalline compounds by the reflux method was performed by boiling the amorphous precipitates in 8 *M* H_3PO_4 for 100 h. The mixed systems prepared were limited to only the Ge-Sn coprecipitates derived from a starting ratio of the corresponding chlorides of 3/1, 1/1 and 1/3, and are referred as GS31, GS11 and GS13 respectively. The hydrothermal syntheses were carried out by treating 5 g of amorphous or refluxed compounds with 5 *M* or 10 *M* H_3PO_4 up to 2/3 of the volume in a sealed glass tube. The sealed tube was heated at 180° or 300°C for 6 to 24 h.

Chemical analysis

Tin was determined by atomic absorption spectrophotometry. Germanium and phosphorus were determined by a spectrophotometric method [6, 7]: because of strong interference due to the presence of the phosphate ion in the germanium sample, elimination of phosphate using anionic resins was necessary prior to determination.

Thermal and X-ray analysis

TG and DTA analyses were performed on a Stanton Redcroft TG-DTA model 801 instrument (Pt crucibles, Pt-Pt/Rh thermocouples, heating rate 5 deg·min^{-1}). X-ray powder patterns of the various materials were obtained on a Philips diffractometer.

Catalytic tests

Samples, preheated at 450°C for 12 h, were submitted to the catalytic test of 1-butene isomerization at 430°C in a flux microreactor ($\tau = 2.4$ g cat./g 1-butene/h). The products obtained at different times were analysed using a Carlo Erba model 4300 gas chromatograph, with a spherosil XOB-075/10% squalane column. The isobutene yields allow evaluation of the presence of acidic sites of medium-high strength, the only ones able to give rise to skeletal isomerisation.

Table 1 Compositions and interlayer spacings of products prepared by the reflux method in 8 *M* H_3PO_4 for 100 hrs

Abbreviation	Composition	d_{002}/A°
GeP	$Ge(HPO_4)_2 \cdot H_2O$	7.78
GS31	$Ge_{0.8}Sn_{0.20}(HPO_4)_2 \cdot H_2O$	7.79
GS11	$Ge_{0.59}Sn_{0.41}(HPO_4)_2 \cdot H_2O$	7.82
GS13	$Ge_{0.48}Sn_{0.52}(HPO_4)_2 \cdot 1.1H_2O$	7.85
SnP	$Sn(HPO_4)_2 \cdot H_2O$	7.89

Table 2 Chemical composition and interlayer spacing of products obtained by hydrothermal treatments under different conditions

	Temperature of hydrothermal treatment/°C	Concentration of H_3PO_4/ *M*	Composition	d_{002}
	180	5	$GeOHPO_4$	
GeP	180	10	$0.86GeOHPO_4+0.14Ge(HPO_4)_2 \cdot H_2O$	7.78
	300	10	$GeOHPO_4$	
	180	5	$0.17GeOHPO_4+0.83Ge_{0.59}Sn_{0.41}(HPO_4)_2$	7.8
GS31	180	10	$0.11GeOHPO_4+0.89Ge_{0.69}Sn_{0.31}(HPO_4)_2$	7.78–7.46
	300	10	$0.51GeOHPO_4+0.49Ge_{0.55}Sn_{0.45}(HPO_4)_2$	7.49
	180	5	$0.20GeOHPO_4+0.80Ge_{0.18}Sn_{0.82}(HPO_4)_2 \cdot 0.82H_2O$	7.82
GS11	180	10	$Ge_{0.54}Sn_{0.46}(HPO_4)_2$	7.82–7.46
	300	10	$0.31GeOHPO_4+0.69Ge_{0.43}Sn_{0.57}(HPO_4)_2$	7.46
	180	5	$0.35GeOHPO_4+0.65Ge_{0.33}Sn_{0.67}(HPO_4)_2 \cdot 1.06H_2O$	7.75
GS13	180	10	$0.35GeOHPO_4+0.65Ge_{0.30}Sn_{0.70}(HPO_4)_2 \cdot 1.06H_2O$	7.82
	300	10	$0.40GeOHPO_4+0.60Ge_{0.14}Sn_{0.86}(HPO_4)_2$	7.55–7.43
	180	5	$Sn(HPO_4)_2 \cdot 0.02H_3PO_4 \cdot 1.4H_2O$	7.78
SnP	180	100	$Sn(HPO_4)_2 \cdot 0.16H_3PO_4 \cdot 1.08H_2O$	7.89
	300	10	$Sn(HPO_4)_2 \cdot 0.04H_3PO_4 \cdot 0.03H_2O$	7.58

Results

Chemical compositions and interlayer spacings of the samples obtained by the refluxing method are given in Table 1. The pure tin and germanium hydrogen phosphates are shown as SnP and GeP respectively. Table 2 shows the composition of the same samples hydrothermally treated (HT) at 180°C or 300°C in 5 or 10 *M* H_3PO_4. Figure 1 shows TG and DTA curves of samples prepared by the reflux method. Figures 2–5 show curves of the samples obtained by hydrothermal treatment at 180°C with 5 or 10 *M* H_3PO_4 and at 300°C in 5 or 10 *M* H_3PO_4 respectively.

Results of catalytic tests on 1-butene isomerisation at 430°C after 1 h for the different samples, all preheated at 650°C for 12 h, are reported in Table 3.

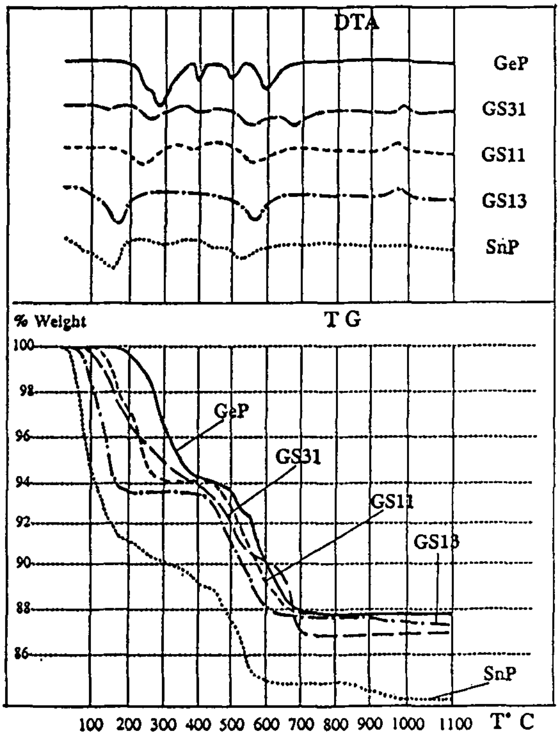

Fig. 1 TG and DTA curves of mixed Sn-Ge hydrogen phosphates of different composition prepared by reflux for 100 hrs in 8 *M* H_3PO_4 (refl./8 *M*/100 h)

Discussion

We have verified that solid solutions between Ge and Sn hydrogen phosphates occur only by using the reflux method: both X-ray powder diffraction patterns and TG and DTA curves of the different mixed systems GS31, GS11 and GS13 support this interpretation. From chemical analyses, it is evident that the crystalline phases contain a Ge/Sn atomic ratio greater than expected from the amount of the single reactants utilized. This can be explained by considering that the solubility of the Sn phosphate in 8 *M* H_3PO_4 is greater than that of Ge phosphate.

The mixed products prepared by hydrothermal synthesis generally suffer from the easy hydrolysability of Ge phosphate: to a greater or lesser extent the $GeOHPO_4$ phase is present in almost all the mixed samples. As it can be seen from Table 2, hydrolysis is highest with lowest H_3PO_4 concentration and highest temperature of hydrothermal treatment. Compositions of the $Ge_xSn_{1-x}(PO_4)_2$ phases present with $GeOHPO_4$ approach more closely that of the starting mixtures than the solid solutions obtained by the reflux method.

TG and DTA curves of the different products permit evaluation of formation of the mixed layered hydrogen phosphate phases and/or that of hydrolysed $GeOHPO_4$. The first ones, more or less hydrated depending on the temperature of the hydrothermal treatment, undergo dehydration in the range 100°–200°C (SnP) and 200°–300°C (GeP); at about 360°–400°C an endothermic phase transition of the anhydrous phase is clearly evident (GeP refl. and SnP HT/300°C 5 or 10 *M*);

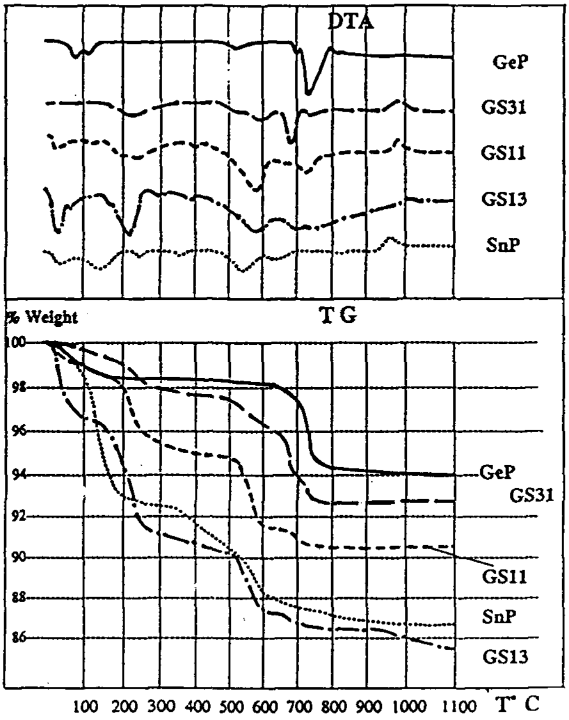

Fig. 2 TG and DTA curves of mixed Sn-Ge hydrogen phosphates of different composition after hydrothermal treatment at 180°C in 5 *M* H_3PO_4 (HT/180°C/5 *M*)

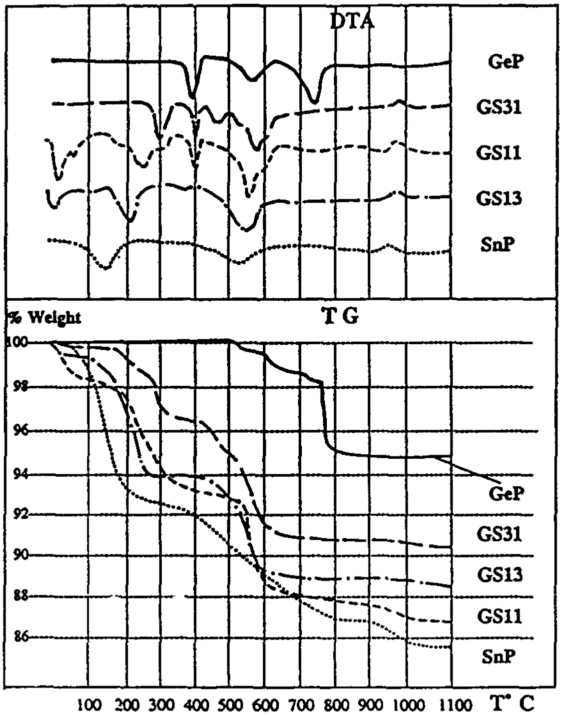

Fig. 3 TG and DTA curves of mixed Sn-Ge hydrogen phosphates of different composition after hydrothermal treatment at 180°C in 10 *M* H_3PO_4 (HT/180°C/10 *M*)

the condensation process to layered pyrophosphates occurs between 350°–600°C (SnP) or 450°–650°C (GeP). The exothermic peak at 950°–1000°C indicates crystallization of the cubic α-pyrophosphates. Apart from dehydration at low temperatures (100°C), $GeOHPO_4$ shows a clear endothermic effect in the range 700°–800°C due to the reaction:

$$2GeOHPO_4 \longrightarrow Ge_2P_2O_9 + H_2O$$

TG and DTA curves allow evaluation of the co-presence of layered and hydrolysed phases for mixtures HT 180°C/5 *M* or 10 *M* (except GS11 in the last case) as well as for samples HT 300°C. The step at 700°–800°C for hydrolysed GeP is sometimes less evident when well-crystalline mixed phases undergo condensation to pyrophosphate: the process shifts to higher temperatures since water elimination is hindered by the decrease in the interlayer distance of a well-ordered phase.

Further information is given by TG curves concerning the weight loss sometimes present above 900°C, especially in the case of SnP samples: it is indicative of strongly adsorbed H_3PO_4 on the surface of this type of compounds [8]. We have verified that the presence of P_2O_5 on the surface of these materials can strongly enhance acidic properties when these products are used as catalysts. By taking into account this eventual weight loss we provide a good explanation for the high acidic properties sometimes observed for these materials.

It is clearly evident that formation of $GeOHPO_4$ drastically decreases the acidic properties of these mixed hydrogen phosphates, or of the layered pyrophosphates, which must be present [9], since the catalytic tests were performed on samples preheated to 650°C. We have found that the acidic properties of the layered pyrophosphates [1, 10] are due to residual surface P-OH groups still present in the pyrophosphate not yet crystallized into the α-cubic $M(IV)P_2O_7$ form, and their resulting acid strength is greater than that of the surface P-OH groups present on the original hydrogen phosphates. Evidently, the hydrolysis process leads to formation of another solid phase, where the hydrogen phosphate groups are missing.

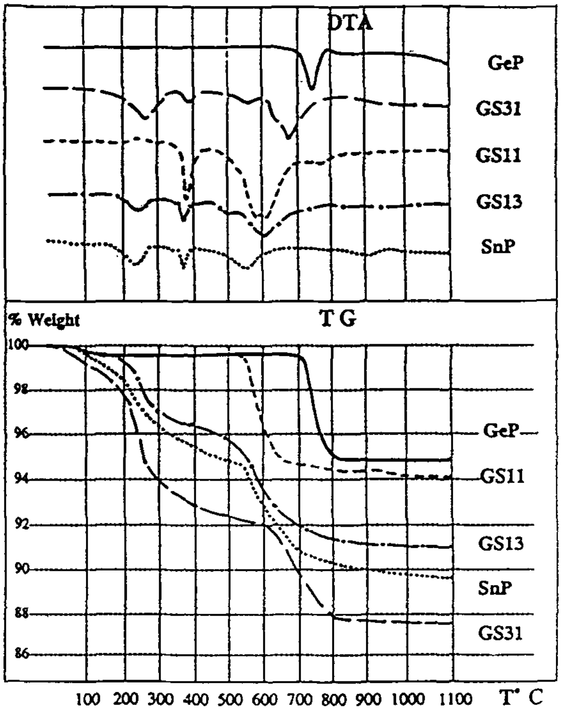

Fig. 4 TG and DTA curves of mixed Sn-Ge hydrogen phosphates of different composition after hydrothermal treatment at 300°C in 5 *M* H_3PO_4 (HT/300°C/5 *M*)

The catalytic acidic behaviour determined from isobutene yield for differently prepared samples of GeP clearly indicates that the medium-high acidic sites disappear when $GeOHPO_4$ is formed. This occurs for all the products prepared by the HT method. The sample GeP HT/180°C/5 *M* also shows the smallest conversion of 1-butene. At present we have no clear explanation for this very low value, since GeP HT/300°C 5 *M* or 10 *M* also are completely hydrolysed. By examining the catalytic results obtained with the mixed systems we can see that for GS31, GS11 and GS13 the isobutene yields are also lower as the amounts of $GeOHPO_4$ present in the various samples increase. For the SnP samples the common presence of adsorbed H_3PO_4 revealed by the weight losses above 900°C may explain the highest values for isobutene yields recorded for the samples SnP refl/8/100 and HT 180°C/5 or 10 *M*. The low yields of isobutene given by SnP HT/300°C may be due to the marked decrease in the surface area due to this drastic hydrothermal treatment, concomitant with a greater ordering of the layered structure (suggested by the endothermic phase transition not observed in other SnP samples [5]).

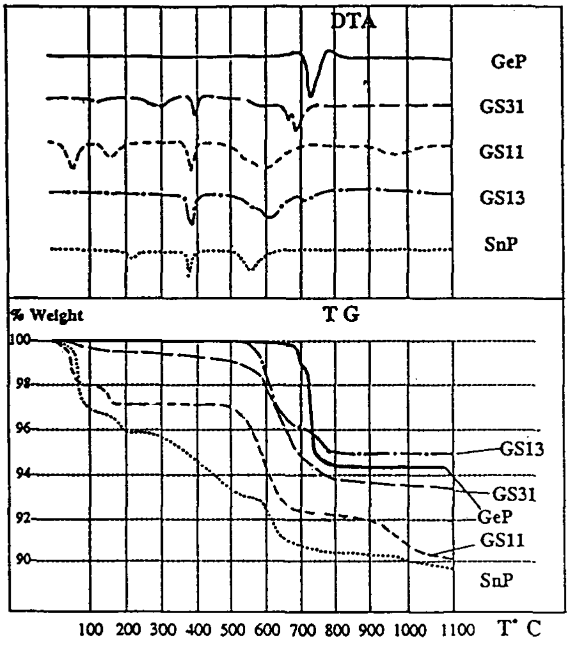

Fig. 5 TG and DTA curves of mixed Sn-Ge hydrogen phosphates of different composition after hydrothermal treatment at 300°C in 10 *M* H_3PO_4 (HT/300°C/10 *M*)

Conclusions

The thermal behaviour of mixed Ge and Sn phosphates prepared either by the refluxing method or by hydrothermal synthesis may give valuable comparative information, rapidly, about the products. The refluxing method for this mixed system is the only one able to produce solid solutions. Since the hydrothermal treatments generally enhance the hydrolisability of the Ge phosphate, this results in the formation of $GeOHPO_4$ to a greater or lesser extent, depending on both H_3PO_4 concentration and temperature of the hydrothermal treatment.

Table 3 1-Butene conversion and isobutene yields obtained at 430°C on Ge-Sn phosphates of different composition and prepared by different methods. Working time 1 h; contact time $\tau = 2.4$ g cat/g 1-but/h

	Preparation method	Concentration of H_3PO_4/ *M*	1–butene conversion/ %	Isobutene yield/ %
GeP	Refl./100 h	8	74.76	12.03
	HT*/180°	5	27.75	0.09
	HT/180°	10	68.95	0.30
	HT/300°	5	75.09	1.09
	HT/300°	10	70.60	0.80
GS31	Refl./100 h	8	79.22	15.04
	HT/180°	5	76.48	6.37
	HT/180°	10	77.49	9.37
	HT/300°	5	77.09	7.27
	HT/300°	10	51.60	0.11
GS11	Refl./100 h	8	81.72	23.72
	HT/180°	5	78.60	13.94
	HT/180°	10	80.49	20.35
	HT/300°	5	75.44	2.33
	HT/300°	10	76.39	7.06
GS13	Refl./100 h	8	76.73	6.68
	HT/180°	5	76.00	4.49
	HT/180°	10	75.55	3.91
	HT/300°	5	70.60	0.20
	HT/300°	10	75.52	1.91
SnP	Refl./100 h	8	84.23	25.96
	HT/180°	5	82.77	28.62
	HT/180°	10	82.65	27.55
	HT/300°	5	75.72	1.50
	HT/300°	10	77.21	7.37

*Hydrothermal treatment

The catalytic behaviour of the different mixed products confirms that the best acidic properties are shown only by the hydrogen phosphate phases or the layered pyrophosphates derived from them; the presence of $GeOHPO_4$, revealed by the endothermic effect and weight loss at 700°–800°C, drastically reduces the acidic strength of the surface sites present on these materials.

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Zusammenfassung — Reine und gemischte Ge- und Sn-Hydrogenphosphate, hergestellt entweder durch Reflux in 8*M* H_3PO_4 oder durch hydrothermische Behandlung bei 180° oder 300°C wurden hinsichtlich der chemischen Zusammensetzung und des thermischen Verhaltens charakterisiert und auch als Katalysator für die Isomerisation von 1-Buten erprobt, um saure Eigenschaften mit der Präparationsmethode zu korrelieren. Wie durch Röntgendiffraktion und TG/DTA bestätigt wurde, werden für jede Zusammensetzung in diesem System Mischkristalle nur dann gebildet, wenn die Reflux-Methode angewendet wird. Die hydrothermischen Behandlungsarten werden stark von der Hydrolisierbarkeit des Ge-Phosphates beeinflußt: in fast allen Proben mit Ge wurde anhand der TG-DTA-Kurven durch den endothermen H_2O-Gewichtsverlust $GeOHPO_4$ identifiziert. Die sauren Eigenschaften der verschiedenen Materialien sinken mit zunehmendem $GeOHPO_4$-Gehalt.