

## **DETERMINATION OF THE SURFACE ACIDITY OF LAYERED METAL PHOSPHATES BY NH<sub>3</sub> TEMPERATURE-PROGRAMMED DESORPTION \***

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### **ABSTRACT**

The acid properties of layered Me phosphates (Me ≡ Ti, Ge, Zr, Sn) were determined by NH<sub>3</sub> temperature-programmed desorption. Careful establishment of the preheating conditions suppressed interference from NH<sub>3</sub> intercalation and allowed the surface acidity to be measured. A scale of acidity strength in line with the catalytic behaviour of these phosphates in acid-catalysed reactions was obtained.

### **INTRODUCTION**

Layered acid phosphates of tetravalent metals have been studied as potential catalysts for acid-catalysed reactions [1–3]. Measurement of their acid properties, such as acid-site concentration and strength, should thus make a significant contribution to the understanding of their catalytic behaviour. Moreover, it is meaningful to distinguish between their internal and external acidity as at high temperatures reacting molecules can only interact with sites on the external surface owing to the small distance between the layers. Acidity measurements with methods usually employed for acid solids, such as base-molecule adsorption or titration with indicators, are therefore strongly affected by intercalation phenomena which are responsible for incorrect determinations, because layered metal phosphates intercalate many molecules that penetrate and widen the interlayer space [4]. On the other hand, only indirect evaluations of acid properties can be obtained by catalytic reaction tests [5].

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In a previous paper [6], we have shown that suitable experimental conditions can be set up to evaluate the external acidity of zirconium phosphate through ammonia temperature-programmed desorption ( $\text{NH}_3$ -tpd). In this work,  $\text{NH}_3$ -tpd has been used to determine the acid properties of different phases of Ti, Ge, Zr and Sn phosphates.

## EXPERIMENTAL

Titanium (TiP), germanium (GeP), zirconium (ZrP) and tin (SnP) phosphate samples were prepared by precipitation from metal chloride or oxychloride solutions after  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$  addition [3,5,7].

Surface areas were measured by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  (BET method) with a Carlo Erba Sorptomatic 1800 apparatus.

The acidity measurements were carried out by  $\text{NH}_3$ -tpd using a flow apparatus with a thermal conductivity detector. The sample (0.1–2 g) was loaded in a quartz tube (i.d. 10 mm) heated by an electrical oven driven by a Linseis temperature programmer-controller, preheated at a given temperature for 12 h in He flow, and cooled to the temperature of  $\text{NH}_3$  adsorption. A gas mixture containing 5%  $\text{NH}_3$  in He was then fed to the sample until the adsorption equilibrium was reached. After He washing, desorption was started at  $10^\circ\text{C min}^{-1}$  heating rate and  $100\text{ cm}^3\text{ min}^{-1}$  He flow. The water evolved from the samples during the desorption (which would have affected the signal of the detector) was removed by a KOH trap located before the detector for  $\text{NH}_3$  analysis.

## RESULTS AND DISCUSSION

The  $\text{Me}^{\text{IV}}$  phosphates investigated have the general formula  $\text{Me}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$  and crystallise in different forms, the  $\alpha$ - and  $\gamma$ -phases being the best known [8]. Their physical and chemical properties are strongly affected by thermal treatment [8].

Temperature-programmed desorption spectra of  $\text{NH}_3$  adsorbed at  $20^\circ\text{C}$  on SnP preheated at  $170^\circ\text{C}$  and on TiP preheated at  $240^\circ\text{C}$  are reported in Figs. 1 and 2 respectively. These pretreatment temperatures correspond to the complete removal of hydration water. In Fig. 1, a rather sharp peak centred at  $140^\circ\text{C}$  with a broad shoulder at about  $340^\circ\text{C}$  can be observed. The total amount of desorbed  $\text{NH}_3$  evaluated from the peak area was 1.9 mol of  $\text{NH}_3$  per mol of phosphate. Two well-resolved peaks centred at  $131^\circ\text{C}$  and  $412^\circ\text{C}$  respectively were displayed by TiP (Fig. 2). The amount of desorbed ammonia was the same as in the case of SnP. The same behaviour as TiP has been previously found for ZrP preheated at  $T < 300^\circ\text{C}$  (peak temperatures of  $165^\circ\text{C}$  and  $350^\circ\text{C}$ , respectively [6]). Because the

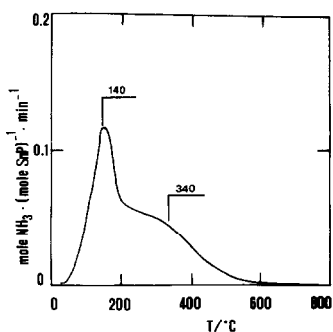


Fig. 1. NH<sub>3</sub>-tpd curve of SnP after heating at 170 °C.

uptake of NH<sub>3</sub> always corresponded to almost complete neutralisation of -POH acid groups, the two desorption peaks are attributed to the loss of NH<sub>3</sub> in two steps. In the case of ZrP, the formation of the diammonium phase, Zr(NH<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>, after NH<sub>3</sub> adsorption and of the monoammonium phase, ZrNH<sub>4</sub>PO<sub>4</sub>HPO<sub>4</sub>, after the loss of the first mole of NH<sub>3</sub>, has been demonstrated [6]. Moreover it must be remembered that the expected number of external -POH sites is two orders of magnitude lower than the internal sites. Therefore the titration of internal and external acid sites cannot be distinguished in these conditions.

The NH<sub>3</sub>-tpd curves for GeP preheated at temperatures up to 300 °C displayed two symmetric peaks centred at 150 and 540 °C, but the total amount of desorbed NH<sub>3</sub> was only 0.5 mol per mol, markedly lower than the value for the other phosphates. This result could be attributed to partial hydrolysis since GeP is more susceptible to this than the other three phosphates, leading to the formation of different phases. Structural characterisation of the GeP obtained after hydrothermal treatments is currently being carried out to test the validity of this hypothesis.

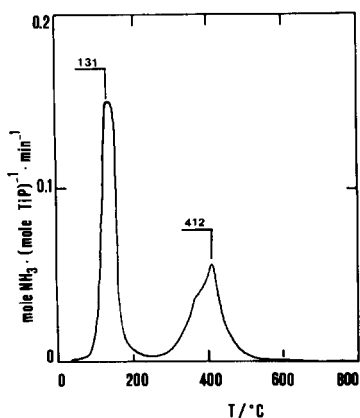


Fig. 2. NH<sub>3</sub>-tpd curve of TiP after heating at 240 °C.

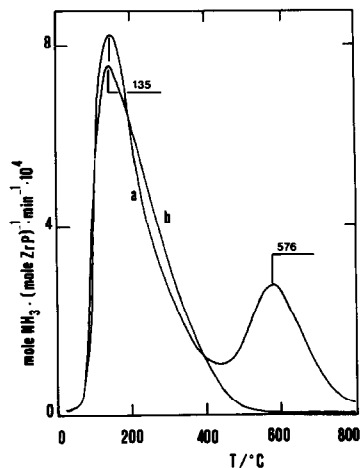


Fig. 3.  $\text{NH}_3$ -tpd curve of ZrP after heating at: a, 450  $^\circ\text{C}$ ; b, 600  $^\circ\text{C}$ .

The effect of higher temperature preheating on the tpd curves is illustrated in Figs. 3–6. After heating at 450  $^\circ\text{C}$  (curves a), all the samples displayed two desorbed  $\text{NH}_3$  signals: a low-temperature, tailed peak (maxima from 135 (ZrP) to 150  $^\circ\text{C}$  (SnP)) and a high temperature, more symmetric peak (maxima higher than 500  $^\circ\text{C}$ ). Moreover, the intensity of the signals was reduced by about three orders of magnitude with respect to Figs. 1 and 2. It must be remembered that after this treatment layered mixed phases,  $\text{Me}(\text{HPO}_4)_2\text{-MeP}_2\text{O}_7$ , were formed owing to partial condensation of  $\text{HPO}_4$  groups and formation of P–O–P bridges between the layers [8]. The inter-layer distance thus decreased, resulting in higher resistance to the access and

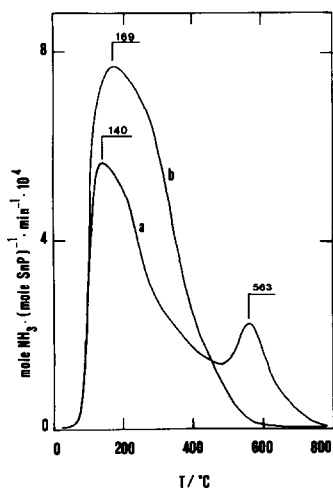


Fig. 4.  $\text{NH}_3$ -tpd curve of SnP after heating at: a, 450  $^\circ\text{C}$ ; b, 600  $^\circ\text{C}$ .

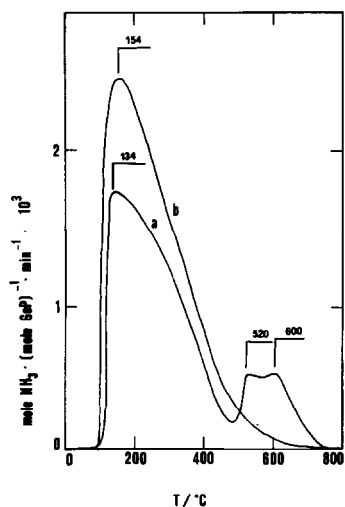


Fig. 5.  $\text{NH}_3$ -tpd curve of GeP after heating at: a, 450  $^\circ\text{C}$ ; b, 600  $^\circ\text{C}$ .

diffusion of  $\text{NH}_3$  into the interlayer region. This decrease in intercalated  $\text{NH}_3$  is not itself sufficient to balance the reduction of the  $-\text{POH}$  concentration, since less than 15% of the  $\text{HPO}_4$  groups were condensed to pyrophosphate after treatment at 450  $^\circ\text{C}$  [8].

The possibility that the reduction observed was mainly due to diffusive limitations caused by the formation of some P–O–P bridges between the layers was investigated through tpd experiments after heating the samples at 600  $^\circ\text{C}$  for 12 hours. Here, in fact, the condensation of  $\text{HPO}_4$  groups was complete and the layered pyrophosphate phase was formed for all the

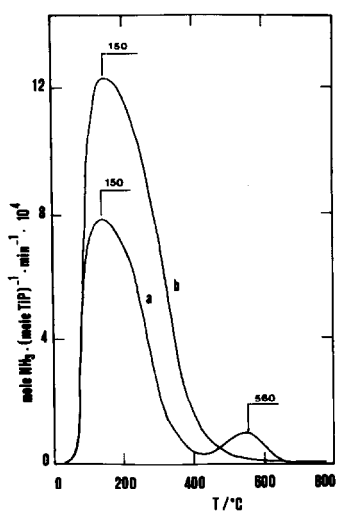


Fig. 6.  $\text{NH}_3$ -tpd curve of TiP after heating at: a, 450  $^\circ\text{C}$ ; b, 600  $^\circ\text{C}$ .

TABLE 1

Effect of preheating temperature on the surface area, maximum of low-temperature peaks and acid-site concentration of ZrP, SnP, TiP and GeP

Sample	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Max. temperature ( $^{\circ}\text{C}$ )	Acid-site concentration ( $10^{14} \text{cm}^{-2}$ )
ZrP <sup>a</sup>	10.0	135	3.0
ZrP <sup>b</sup>	10.0	135	3.0
SnP <sup>a</sup>	9.8	140	2.2
SnP <sup>b</sup>	19.7	169	2.2
GeP <sup>a</sup>	5.7	134	6.4
GeP <sup>b</sup>	15.3	154	7.3
TiP <sup>a</sup>	13.3	150	3.3
TiP <sup>b</sup>	14.5	150	3.9

<sup>a</sup> After preheating at  $450^{\circ}\text{C}$ .

<sup>b</sup> After preheating at  $600^{\circ}\text{C}$ .

phosphates [7,8]. The results (curves b of Figs. 3–6) showed that the high-temperature peak was no longer present while the maxima of the tailed peaks ranged from  $135^{\circ}\text{C}$  (ZrP) to  $169^{\circ}\text{C}$  (SnP). Moreover tpd tests carried out after adsorbing  $\text{NH}_3$  at high temperatures ( $200\text{--}450^{\circ}\text{C}$ ) showed that  $\text{NH}_3$  uptake increased as a result of the lower resistance to  $\text{NH}_3$  diffusion and interaction between the layers, according to previous findings [6]. All these results indicated that the low-temperature peaks relate to  $\text{NH}_3$  bonded to acid sites present on the external surface, whereas the high-temperature peaks relate to intercalated  $\text{NH}_3$ , as previously suggested [6]. Therefore heating at the temperature corresponding to total condensation of the  $\text{HPO}_4$  groups and adsorbing  $\text{NH}_3$  at  $20^{\circ}\text{C}$  allow the surface acidity of metal phosphates to be measured by  $\text{NH}_3$ -tpd.

The BET surface-area values determined after heating at  $450$  and  $600^{\circ}\text{C}$  were used to evaluate the acid-site concentrations as the number of sites per unit surface (Table 1). In the case of ZrP and SnP, the concentration was not affected by the preheating temperature, suggesting that in this temperature range there is no condensation of adjacent  $-\text{POH}$  groups on the external surface because they are too distant for the formation of  $\text{P}-\text{O}-\text{P}$  bridges [3]. By contrast, the concentration for TiP and GeP was increased by preheating at  $600^{\circ}\text{C}$ . Hydrolysis of some  $\text{Me}-\text{OP}$  bonds by water formed during condensation could be responsible for this effect. It is worth noting that the concentrations evaluated are of the same order of magnitude as the values expected for the concentration of  $-\text{POH}$  groups located on the external surface of the crystals [4].

Figures 3–6 and Table 1 also show that acid-site strength is affected by the preheating temperature. At  $600^{\circ}\text{C}$ , the maximum of the low-temperature peak corresponding to the titration of external acid sites, was shifted to higher temperatures, indicating that acidity strength was increased. More-

over, preheating at 600 °C always resulted in a more pronounced tailing of the low-temperature peak to higher values. Enhancement of the acidity strength of -POH groups on the external surface can be related to the increase of ionicity of the P-O-P bonds between the layers [3]. Moreover, the maximum temperature of the tpd peak after preheating at 600 °C gives the following scale of acidity: SnP > GeP > TiP > ZrP, which is in good agreement with the results of catalytic tests for 1-butene isomerisation and isopropanol dehydration carried out on these phosphates [5]. The tests have also shown that pyrophosphate phases are more active than partially condensed phases owing to their stronger acidity [3].

## CONCLUSIONS

It has been shown that NH<sub>3</sub>-tpd can be used to determine the acid properties of layered metal phosphates. NH<sub>3</sub> intercalation affecting acidity measurements is suppressed by preheating at temperatures leading to the formation of pyrophosphate phases resulting from the condensation of interlayer -POH groups. After preheating and NH<sub>3</sub> adsorption at room temperature, the surface acidity of layered metal phosphates can be determined. Weak and medium strength acid-sites have been detected. These could be responsible for the catalytic activity displayed by metal phosphates in acid-catalysed reactions. A scale of acidity strength in line with that indicated by catalytic tests for 1-butene isomerisation and isopropanol dehydration [5] was obtained in this study.

## REFERENCES

- 1 A. Clearfield, in A. Clearfield (Ed.), *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, FL, 1982, p. 1.
- 2 K. Segawa, Y. Kurusu, Y. Nakajima and M. Kinoshita, *J. Catal.*, 94 (1985) 491.
- 3 A. La Ginestra, P. Patrono, M.L. Berardelli, P. Galli, C. Ferragina and M.A. Massucci, *J. Catal.*, 103 (1987) 346.
- 4 G. Alberti and U. Costantino, in M.S. Whittingham and A.J. Jacobson (Eds.), *Intercalation Chemistry*, Academic Press, London, 1982, p. 147.
- 5 A. La Ginestra and P. Patrono, *Mater. Chem. Phys.*, 17 (1987) 161.
- 6 M. Turco, G. Bagnasco, P. Ciambelli, A. La Ginestra, P. Galli and C. Ferragina, *J. Catal.*, 117 (1989) 355.
- 7 A. La Ginestra, P. Galli, M.L. Berardelli and M.A. Massucci, *J. Chem. Soc., Dalton Trans.*, (1984) 524.
- 8 A. La Ginestra, C. Ferragina, M.A. Massucci, P. Patrono, R. Di Rocco and A. Tomlinson, *Gazz. Chim. Ital.*, 113 (1983) 357.