# TPD Study of NH$_3$ Adsorbed by Different Phases of Zirconium Phosphate

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Thermodesorption of NH$_3$ has been used to measure the acidity of $\alpha$-zirconium hydrogen phosphate and different phases obtained from this material by thermal treatments. It was found that samples treated at temperatures lower than 300°C, consisting of hydrated or anhydrous $\alpha$-phases, adsorbed an amount of ammonia corresponding almost to neutralization of all acidic –POH groups and formation of a well-characterized diammonium phase. Samples treated at $t \geq 400$°C, in which partial or total condensation of interlayer –POH groups occurred, showed a strongly reduced capacity for adsorption of NH$_3$, because of the formation of P–O–P bridges between layers which hindered diffusion of NH$_3$. After pretreatment of Zr hydrogen phosphate at 600°C, the TPD spectrum of ammonia adsorbed at room temperature showed only the signal of NH$_3$ adsorbed by surface –POH sites, indicating that its interaction with internal sites was now precluded. From the shape of the TPD curves from these samples information on the strength of surface acidic sites was deduced. © 1989 Academic Press, Inc.

## INTRODUCTION

In recent years layered inorganic ion exchangers (such as zirconium hydrogen phosphate and related compounds) with the formula $Me(\text{IV}) (\text{H}X\text{O}_4)_2 \cdot \text{H}_2\text{O}$ ($Me$: Ti, Zr, Sn, Ge; $X$: P, As) have been studied as catalysts for several reactions in which activity is markedly influenced by their acidic properties (*1–4*). For this reason it seemed interesting to define methods to measure their acid properties, i.e., acid site concentration and strength, in the phases that can be obtained by different thermal treatments.

The most common method employed up to now for this purpose has been butylamine titration in the presence of Hammett indicators (*2, 5, 6*). Nevertheless, it has been pointed out that these phosphates show a great tendency to intercalate organic bases between their layers, thus producing compounds with a maximum base/ $Me(\text{IV})$ molar ratio of 2 which corresponds to neutralization of each –POH group by one base molecule (*7–9*). This ratio is reached with the original hydrogen phosphate phase, while base intercalation is greatly hindered (*5*) when even a partial condensation to layered pyrophosphate takes place.

On the other hand the measurement of the acid concentration and strength due to sites on the external surfaces of these materials is necessary because it has been shown that their catalytic activity is mainly related to their surface acidic centers (*2, 10, 11*). The characterization of these sites has been performed by means of certain acid-catalyzed reactions (alcohol dehydration or 1-butene isomerization (*11*)) and by FTIR spectroscopy using probe molecules (*12*): with such methods it has been shown that the active acid sites are mainly surface Brønsted sites, although Lewis centers, to a lesser extent, can also be evidenced.

Furthermore, it has been shown that the layered pyrophosphates (L-Py), obtained

through the condensation of hydrogen phosphates by thermal treatment at temperatures higher than 400°C, also have residual surface –POH groups, the strength of which seems to be higher than that of groups present on the surfaces of the precursor hydrogen phosphates (4, 13).

Temperature-programmed desorption (TPD) of ammonia, which has been widely used to measure acidity of zeolites (14–17), has not to our knowledge been applied to layered Me(IV) phosphates in order to define the experimental conditions which enable one to differentiate between surface and bulk acidity of such materials. In the present work we have therefore studied the possibility and limits of the use of this method to measure the strength and concentration of acidic sites of zirconium hydrogen phosphate and pyrophosphate phases, with the aim of distinguishing between surface and bulk sites.

## EXPERIMENTAL

### Materials

Amorphous materials were first prepared by adding 1 liter of a solution of $H_3PO_4$ and HCl (both 1.7 $M$) to 0.15 mol of $ZrOCl_2 \cdot 8H_2O$ dissolved in 1 liter of 3 $M$ HCl, by stirring at 80°C; after 2 h of digestion at 60–70°C, the precipitate was filtered, washed to pH 4.5, and then air-dried (11). Crystalline $\alpha$-zirconium hydrogen phosphates, $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$, were prepared by refluxing the amorphous materials in 10 $M$ $H_3PO_4$ for 100 h (ZrP-1) or 70 h (ZrP-2).

A sample of ZrP-2 was ion exchanged using a CsCl solution after a thermal treatment at 600°C for 6 h (ZrP-2-Cs).

### Physicochemical Measurements

X-ray diffraction patterns of the samples were obtained with a Philips diffractometer (Ni-filtered $CuK\alpha$ radiation).

The thermal behavior of the samples was studied by comparing DTA, TG and DTG curves obtained by a Stanton Model 781 simultaneous DTA-TG thermoanalyzer (Pt crucibles, Pt-Pt/Rh thermocouples, heating

rates 2–5°C/min) before and after $NH_3$ adsorption.

Surface areas were determined by $N_2$ adsorption at –196°C (BET method) using a Carlo Erba Sorptomatic 1800.

The $NH_3$ thermodesorption spectra were obtained using a flow apparatus. The sample, contained in a fused silica tube (i.d. = 1 cm), was heated at 1°C/min to the desired temperature in a helium flow and kept at that temperature for 12 h; then it was cooled to the adsorption temperature and a 5% $NH_3/He$ mixture was admitted. After equilibrium was attained the sample cell was purged with helium at the same temperature and then $NH_3$ thermodesorption was carried out by heating at 10°C/min in flowing He, starting from the adsorption temperature and proceeding up to 800°C. The $NH_3$ desorbed from the sample was monitored by a thermal conductivity detector (TCD). $H_2O$ from the samples was removed by a trap containing anhydrous KOH. The complete removal of water was ascertained by blank experiments (Fig. 1).

## RESULTS AND DISCUSSION

TPD curves of samples after pretreatment at different temperatures followed by adsorption of $NH_3$ at 20°C are shown in Figs. 1–3: the corresponding amounts of
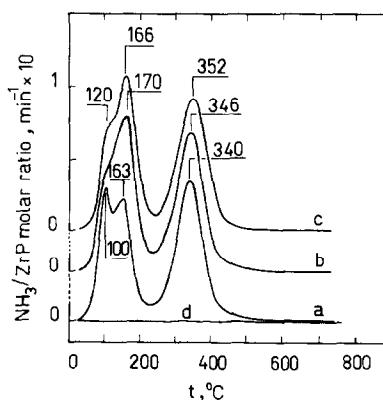


FIG. 1. TPD curves of $NH_3$ (adsorbed at 20°C) from sample ZrP-1 pretreated at (a) 20°C; (b) 170°C; (c) 300°C; curve (d) blank experiment on sample treated as (a).
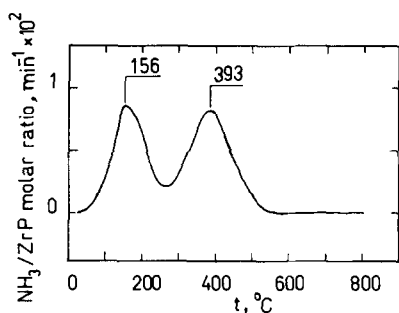
FIG. 2. TPD curve of $NH_3$ (adsorbed at 20°C) from sample ZrP-1 pretreated at 400°C.

**TABLE 1**

TPD of $NH_3$ Adsorbed at 20°C on ZrP-1 after Different Pretreatments

| Pretreatment temp. (°C) | Phases[a] | Peak temp. (°C) | NH₃/ZrP[b] |
|---|---|---|---|
| 20 | ZrPH₂ · H₂O | 100(sh),[c] 163 | 79 |
| | | 340 | 88 |
| 170 | ZrPH₂ | 115(sh), 170 | 98 |
| | | 346 | 93 |
| 300 | ZrPH₂ | 120(sh), 166 | 93 |
| | | 352 | 90 |
| 400 | ZrPH₂ + L-ZrPy | 156 | 4 |
| | | 393 | 6 |
| 450 | ZrPH₂ + L-ZrPy | 135 | 1.3 |
| | | 576 | 3.4 |
| 600 | L-ZrPy | 135 | 1.3 |

[a] ZrPH₂ · H₂O = Zr(HPO₄)₂ · H₂O; ZrPH₂ = Zr(HPO₄)₂; L-ZrPy, layered ZrP₂O₇.
[b] Molar ratio ×50.
[c] sh, shoulder.

desorbed $NH_3$ and the peak temperatures measured in these curves are reported in Table 1. TPD curves in Fig. 1 for the hydrogen phosphate (i.e., samples pretreated at $t \leq 300$°C) show two ammonia peaks with maxima at ca. 165 and 350°C; however, in the curve of the original sample a peak at ca. 100°C is evident, becoming a shoulder for the samples pretreated at 170 or 300°C. The total amount of $NH_3$ desorbed corresponded to an NH₃/ZrP molar ratio close to ca. 2 in all these experiments.

X-ray powder patterns revealed that the phase formed under these conditions was always the hydrated diammonium phase $Zr(NH_4)_2(PO_4)_2 \cdot xH_2O$ ($x \leq 1$) with an interlayer distance of 9.4 Å, the hydration ex-

tent of this phase being related to the exposure to the air necessary for X-ray or thermal measurements. Thus the intercalation of ca. 2 moles of $NH_3$ per mole of Zr bis-hydrogen phosphate leads to an increase of the initial interlayer distance from 7.43 to 9.4 Å. DTA and TG curves of the same phase are reported in Fig. 4 together with the curve of the sample pretreated at 300°C without ammonia adsorption and left to air just like the sample treated with ammonia. The more limited rehydration of the NH₃-free sample, as shown from DTA and TG curves, is to be ascribed to the lower
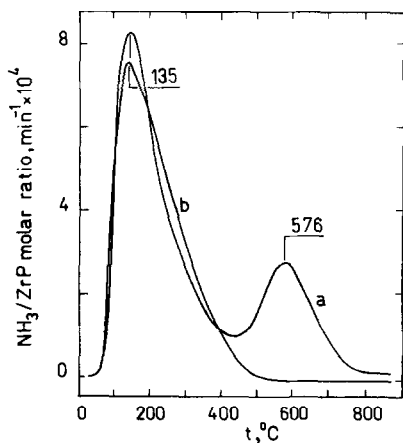


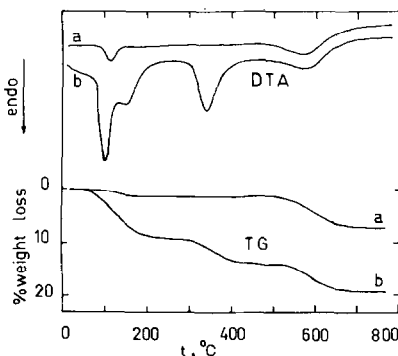FIG. 3. TPD curves of $NH_3$ (adsorbed at 20°C) from sample ZrP-1 pretreated at (a) 450°C; (b) 600°C.



FIG. 4. TG and DTA curves of sample ZrP-1 (a) pretreated at 300°C; (b) same as (a) after $NH_3$ adsorption at 20°C.

$d_{002}$ value (7.43 Å) of this phase which hinders the $H_2O$ re-uptake. These data confirm the formation of the hydrated diammonium phase of zirconium phosphate, which loses the hydration water and 1 mole of $NH_3$ below 200°C, giving the anhydrous monoammonium phase, $ZrNH_4PO_4HPO_4$, which in turn loses a second mole of $NH_3$ between 300 and 400°C and finally the hydroxyls as evolved water above 400°C, giving rise to $ZrP_2O_7$. The monoammonium phase was also detected by X-ray analysis (interlayer distance = 7.52 Å at room temperature after treatment at 250°C). Thus we can say that the two peaks in the TPD results for samples pretreated at $t \leq 300°C$ correspond exactly to the loss of the 2 moles of $NH_3$ of the diammonium form of zirconium phosphate formed by $NH_3$ intercalation.

The shoulders on the first TPD peak indicate the presence of a less strongly bonded ammonia, perhaps because of hydrogen bonding between $HPO_4$ groups and residual cavity water, which can hinder to some extent the direct interaction of $NH_3$ with the –POH groups. The presence of a signal at low temperature and the slightly lower amount of adsorbed ammonia on the original (untreated) sample seem to confirm this hypothesis.

The ammonia desorption peak intensity strongly decreases after a pretreatment at 400°C (Fig. 2), while the maximum of the high-temperature peak is now shifted toward higher temperatures. The amount of $NH_3$ is even less after pretreatment at 450°C, the high-temperature peak being then at 580°C; finally, after a 600°C treatment, a single tailed peak corresponding to an $NH_3/ZrP$ molar ratio of 0.014 with maximum at 135°C is observed (Fig. 3).

X-ray analysis revealed no change of crystalline structure following adsorption of $NH_3$ for samples pretreated at $t \geq 400°C$: the interlayer distance was that of the mixed hydrogen phosphate–layered pyrophosphate, i.e., between 6.3 and 6.8 Å. Thermogravimetric analysis of samples preheated at 600°C (at which temperature

the condensation to pyrophosphate was completed) showed only a very small weight loss, confirming the $NH_3$ data above.

Thus the $NH_3$ intercalation capacity is progressively reduced by increasing the temperature of thermal pretreatment starting from 400°C: this effect cannot be accounted for by reduction of the OH concentration alone, since less than 15% of zirconium hydrogen phosphate is condensed to pyrophosphate after treatment at 400°C for 12 h (11). We therefore think that this reduction is mainly due to diffusive limitations caused by the formation of some P–O–P bridges between the layers.

In order to establish whether samples pretreated at 450 or 600°C retain some intercalation ability, we carried out $NH_3$ adsorption at temperatures higher than 20°C, up to 450°C.

The desorption curves starting from the adsorption temperatures adopted in these experiments are reported in Figs. 5 and 6 and Table 2. By comparison with data in Table 1, an increase in the amount of desorbed $NH_3$ occurs after adsorption at tem-
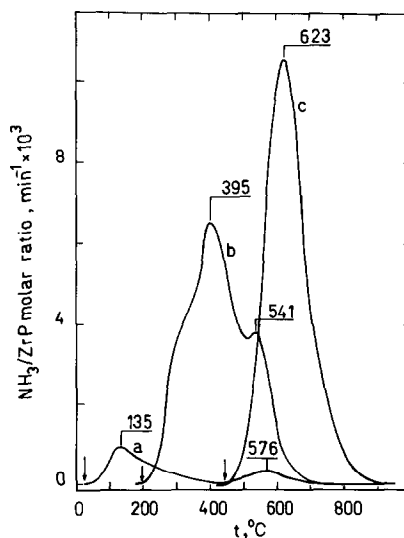


FIG. 5. TPD curves of $NH_3$ from sample ZrP-1 pretreated at 450°C and after adsorption of $NH_3$ at (a) 20°C; (b) 200°C; (c) 450°C. (Arrows indicate starting temperature for each TPD run.)

TABLE 2

TPD of $NH_3$ Adsorbed at Different Temperatures on ZrP-1 and ZrP-2

| Sample | Phases[a] | Temperature (°C) | | Peak temp. (°C) | $NH_3/ZrP$[b] |
|--------|-----------|-------------------|---|-----------------|---------------|
| | | Pretreatment | NH₃ adsorp. | | |
| ZrP-1 | $ZrPH_2$ + L-ZrPy | 450 | 200 | 395 | 6.7 |
| | | | | 541 | 0.9 |
| ZrP-1 | $ZrPH_2$ + L-ZrPy | 450 | 450 | 623 | 16.0 |
| ZrP-1 | L-ZrPy | 600 | 200 | 328 | 1.1 |
| ZrP-1 | L-ZrPy | 600 | 450 | 616 | 5.0 |
| ZrP-2 | L-ZrPy | 600 | 20 | 140 | 2.2 |
| ZrP-2-Cs | L-ZrPy-Cs+ | 600 | 20 | 137 | 0.7 |

[a] $ZrPH_2$ = $Zr(HPO_4)_2$; L-ZrPy, layered $ZrP_2O_7$.

[b] Molar ratio ×100.

peratures higher than 20°C on samples pre-treated at 450°C (Fig. 5), which indicates that an increase in the adsorption tempera-ture probably enables $NH_3$ to diffuse more easily between the layers (made narrower by the partial condensation of the interlayer –POH groups) and interact between them; at room temperature this process, involving widening of the interlayer space, would be rather unlikely due to energetic reasons.

The pretreatment at 600°C is even more effective in hindering the uptake of $NH_3$ and only after adsorption of $NH_3$ at 450°C or above can one observe a significant in-crease of desorbed ammonia (Fig. 6). In fact heating at 600°C leads to a quite com-plete condensation of –POH groups be-tween facing layers. The amount of $NH_3$ which is adsorbed at 450°C in this material, 0.05 mole of $NH_3$ per mole of Zr pyrophos-phate (Table 2), could be attributed in prin-ciple to the interaction with residual Brønsted sites, although reactions leading to the partial breaking of P–O–P bridges at this temperature cannot be excluded. In fact, since its desorption temperature is so high, we cannot attribute this $NH_3$ to sur-face bonded species.

Evaluation of the amounts of $NH_3$ corre-sponding to the low-temperature peaks in the TPD curves of Fig. 3 (ca. $3 \times 10^{14}$ molec $cm^{-2}$) suggests that it is reasonable to as-cribe these peaks to surface acid sites, which do not change when the pretreatment temperature is increased from 450 to 600°C, while the high-temperature peak, which disappears after the 600°C pretreatment, is representative of intercalated ammonia. As the surface area of the sample, measured after pretreatment at 450 and 600°C, is prac-tically the same (ca. 10 m²/g), this would imply that surface –OH concentrations are also the same, so that condensation of sur-face –OH groups does not occur in this
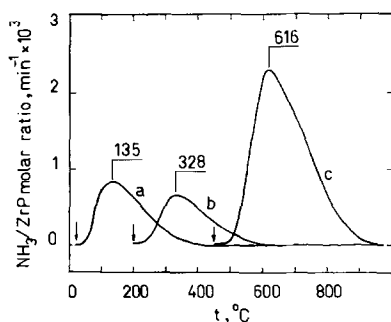


FIG. 6. TPD curves of $NH_3$ from sample ZrP-1 pre-treated at 600°C and after adsorption of $NH_3$ at (a) 20°C; (b) 200°C; (c) 450°C. (Arrows indicate starting temperature for each TPD run.)
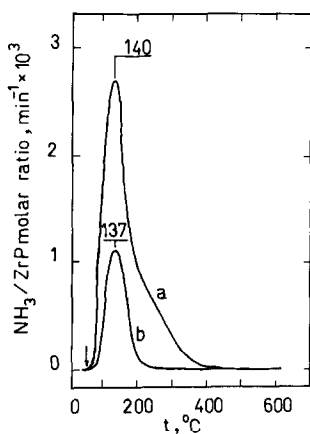
FIG. 7. TPD curves of NH$_3$ adsorbed at 20°C on samples (a) ZrP-2 and (b) ZrP-2-Cs pretreated at 600°C.

temperature range: in fact, condensation of surface –OH groups within a layer must be quite unlikely due to the large distance between two adjacent –POH groups (about 5.3 Å) (*18*). By using a material with higher surface area (namely, ZrP-2 with 17 m$^2$/g) we have observed, after heating either at 450 or at 600°C, a proportional increase of the low-temperature peak area compared to the values obtained with ZrP-1, but not an increase of its maximum temperature (see Table 2). This fact further confirms that after the transformation into pyrophosphate, NH$_3$ is adsorbed only on external sites, giving the peak having a maximum at ca. 140°C. The amount adsorbed corresponds also in this case to 2.9 × 10$^{14}$ molec cm$^{-2}$.

In order to confirm that this desorption peak from the pyrophosphate comes only from surface sites, a sample of ZrP-2 which had been calcined at 600°C was ion exchanged with Cs$^+$ ions to substitute the external Brønsted sites (*11*). As one can see in Fig. 7, the peak is now strongly reduced (up to 0.8 × 10$^{-14}$ molec cm$^{-2}$) although it remains unshifted: this can be accounted for by the partial substitution (ca. 72%) of surface H$^+$ for Cs$^+$ ions under our exchange conditions. Thus we can conclude that the peaks with maxima at ca. 140°C in Fig. 3

represent ammonia bonded to external acid sites: the marked asymmetry of these peaks, on the other hand, indicates the presence of a wide range of acid strengths (*19*), from weak (desorbing NH$_3$ at 140°C) to medium–strong (desorbing NH$_3$ at 300–350°C). In particular, since the samples heated at 600°C show more tailed peaks than samples heated at 450°C, this suggests a more heterogeneous distribution of the acid sites in the samples heated at higher temperatures with a higher concentration of strongest sites. This increase of the heterogeneity of the surface –POH strength finds an explanation in the more extended formation of interlayer P–O–P bridges, which must induce a higher ionicity on the surface Brønsted sites (*11*).

CONCLUSIONS

We conclude that the NH$_3$ TPD method used to determine the acidity of ZrP-type layered hydrogen phosphates gives results that depend on the phase investigated. Hydrated or anhydrous Zr(HPO$_4$)$_2$ · H$_2$O (pretreatment temperature ≤300°C) can intercalate about 2 moles of NH$_3$ per mole of Zr bis-hydrogen phosphate, according to a stoichiometric reaction. The measurement of surface acidity by NH$_3$ thermodesorption is possible only for those phases where the NH$_3$ intercalation process does not occur: this is the case for either layered pyrophosphates or partially condensed phases obtained by treating the materials at $t \geq$ 450°C. In fact, P–O–P bridge formation between consecutive layers, beginning at ca. 400°C, strongly hinders the diffusion of NH$_3$ into the interlayer space. Ammonia adsorption must then be carried out at room temperature since at higher temperatures different interactions involving internal sites (Brønsted sites or reactions leading to P–O–P bond breaking) may occur.

Under the above experimental conditions the shapes of the NH$_3$ thermodesorption curves obtained show long tails, giving clear evidence of the presence of surface sites of different strengths, going from me-

dium to high, in good agreement with previous catalytic results obtained with different acid-catalyzed reactions (*11, 13*).

It is likely that the method used here for the determination of surface acidity can be extended to other similar materials obtained from layered hydrogen phosphates of different tetravalent metals.

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