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STUDY OF THE TRIVALENT ELEMENTS POLYPHOSPHATES BY THERMAL ANALYSIS

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Mechanisms of formation of polyphosphates $Me^{III}(PO_3)_3$, where M^{III}=La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Fe, Ga, Al and Cr has been simulated by thermal analysis technique. Me^{III} oxides and ammonium dibasic phosphate $(NH_4)_2HPO_4$ were used as starting materials. For M^{III}=La-Lu, Y and Fe three main stages were observed: 1. elimination of water and ammonia leading to the formation of ammonium tripolyphosphate $(NH_4)_5P_3O_{10}$; 2. reaction of the latter with $Me_2^{III}O_3$ and formation of acidic polyphosphates $Me^{III}H_2P_3O_{10}$ or their isomers $Me^{III}(PO_3)_3 \cdot H_2O$; 3. final loss of water and formation of $Me^{III}(PO_3)_3$. For Me^{III}=Sc and Ga the second stage is prolonged and the polyphosphates form at higher temperatures. Aluminum and chromium polyphosphates are unstable. It is suggested that thermal behavior of the compounds is determined by Me^{III} ionic radii.

Keywords: *inorganic materials, polyphosphates, thermal analysis, trivalent elements*

Introduction

Polyphosphates of trivalent elements were proposed [1, 2] for binding metal/metal surfaces (e.g. a couple stainless steel/titanium) working at high temperatures. To ensure steadfast adhesion, the polyphosphates should form a cohesive mass with the polyphosphates of the metals to be bound together. These compounds are created on metal surface by applying a previous treatment with 85% phosphoric acid. When a finer correction to the adhesion is needed, a combination of polyphosphates can be employed in a specially designed batch composition. In these circumstances, mechanism of formation of each compound and its decomposition temperatures are of utmost importance, as they assure steady and firm attachment. As a rule, the polyphosphates are obtained *in situ*, using a starting mixture that contains the corresponding sesquioxides and phosphoric acid or ammonium mono (di) hydrogen phosphate, similarly to the preparation of recently described antimony polyphosphate [3]. When the simulation is carried out by thermal analysis technique, the method with the usage of ammonium salt is preferable because corrosive vapors of concentrated H_3PO_4 would easily damage the equipment. The aim of the present work is to study the mechanisms of formation of a series of polyphosphates in order to provide trustworthy basic data for the fabrication of refractory inorganic binders under dynamic conditions. The investigation does not deal with the individual physico-chemical properties of polyphosphates, which are relatively well known [4]. Thermal analysis was used in association with other instrumental techniques as proved serviceable in the neighboring areas [5].

Experimental

The starting oxides, their purity and origin are summarized in Table 1. Ammonium dibasic hydrogen phosphate $(NH_4)_2HPO_4$, 99.99% purity was purchased from Merck. Simple testing of oxides, especially rare earth oxides, with HCl is essential, as these compounds happen to contain uncontrollable quantities of carbonates. We have had an unpleasant experience, when half of lanthanum oxide in a sealed container was in fact a mixture of oxide and basic carbonate. Generally, it is advisable to preheat commercial reagents at 600°C for 3 h before usage.

Mechanisms of formation were studied by thermal gravimetric analysis (TG) using a 50H Shimadzu Instrument. Synthetic preparations were simulated by grinding up dibasic ammonium phosphate with the corresponding oxide and heating the test specimens (4–6 mg) up to 800°C in the flux of nitrogen at the rate 10°C min^{-1}. Previously, TG curve of pure $(NH_4)_2HPO_4$ was registered and analyzed. Mass losses observed during heating were compared to the previously calculated values. X-ray powder patterns were registered with a Siemens Kristalloflex diffractometer with a graphite diffracted beam mono-

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Table 1 Reagents characteristics and mass losses at different stages of polyphosphates synthesis calculated in relation to the initial sum of $6(NH_4)_2HPO_4$ and $Me_2^{III}O_3$

Elements	Reagents		Mass loss/%					
			$(NH_4)_5P_3O_{10}$ formation		$Me^{III}H_2P_3O_{10}$ formation		$Me^{III}(PO_3)_3$ formation	
	Purity	Origin	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Lanthanum	99.99%	UE	9.48	9.6	29.52	30.4	32.74	33.8
Praseodynmium	99.9%	Sigma	9.45	9.7	29.42	30.1	32.63	33.3
Neodymium	99.9%	Sigma	9.39	9.8	29.24	30.3	32.43	32.8
Samarium	99.9%	Sigma	9.29	9.9	28.93	30.1	32.08	32.8
Europium	99.9%	UE	9.27	10.3	28.85	28.9	32.00	32.8
Gadolinium	99.9%	Sigma	9.18	9.2	28.58	28.4	31.70	31.7
Terbium	99.999%	Acros	9.15	9.2	28.50	28.4	31.61	31.7
Dysprosium	99.9%	Fluka	9.10	8.6	28.33	27.2	31.42	29.6
Holmium	99.999%	Aldrich	9.06	9.0	28.21	30.8	31.29	31.9
Erbium	99%	UE	9.02	10.2	28.10	28.0	31.16	30.6
Thulium	99.9%	Aldrich	9.00	9.0	28.02	26.2	31.07	29.9
Ytterbium	99.9%	Aldrich	8.94	9.3	27.82	28.8	30.86	30.2
Lutetium	99.9%	Reacton	8.91	9.0	27.73	28.7	30.76	30.0
Yttrium	99.999%	Aldrich	10.41	9.8	32.42	28.8	35.96	31.9
Iron	99.9%	Aldrich	11.14	10.4	34.67	34.3	38.46	37.4
Scandium	99.999%	Goseagent	11.40	10.8	35.49	36.3	39.36	–
Gallium	99.9%	Aldrich	10.82	9.7	33.69	33.2	37.37	37.0
Aluminum	99.9%	Aldrich	11.86	12.3	36.91	–	40.94	–
Chromium	99.9%	Aldrich	11.23	12.1	34.96	–	38.77	–

chromator and Ni filter. All compounds separately prepared in static conditions were identified by comparison of experimental X-ray patterns with available ICSD database files.

Results and discussion

Thermal decomposition of phosphorus-donor reagent $(NH_4)_2HPO_4$ is represented in Fig. 1.

Mass loss 13.1% corresponds exactly to the formation of pentaammonium tripolyphosphate (calculated value 13.4%) according to the reaction

$$6(NH_4)_2HPO_4 = 2(NH_4)_5P_3O_{10} + 2NH_3 + 4H_2O$$

and not to a competing scheme involving ammonium polyphosphate $[NH_4(PO_3)]_n$. The latter would have formed only at a subsequent step, after additional elimination of $2NH_3$ and H_2O [6]. So at this early step no reaction with $Me_2^{III}O_3$ is taking place. The representative TG curve for gadolinium is given in Fig. 2. At the same time, Table 1 shows expected and experimentally found mass losses at different stages of the synthesis. It can be seen that the experimental mass losses in the interval 178–188°C really fit the values calculated for $(NH_4)_5P_3O_{10}$ formation, invariably taking into account the presence of $Me_2^{III}O_3$ in the starting mixture. So, the mechanism of $Me^{III}(PO_3)_3$ formation is different from the mechanism involved in the case of $Sb(PO_3)_3$, where intermediate compound was found to be ammonium polyphosphate $[NH_4PO_3]_n$.

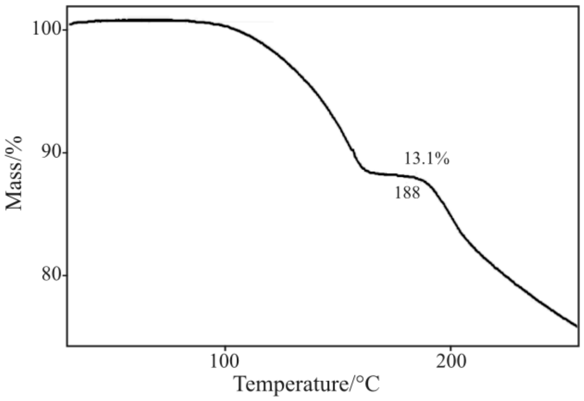

Fig. 1 TG curve of $(NH_4)_2HPO_4$

At the second step, $10NH_3$+$3H_2O$ are eliminated, so that the interaction process between $(NH_4)_5P_3O_{10}$ and $Me_2^{III}O_3$ may be described as:

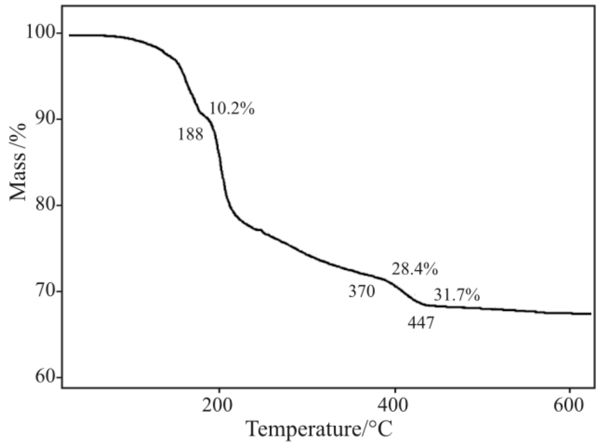

Fig. 2 TG curve simulating preparation of $Gd(PO_3)_3$

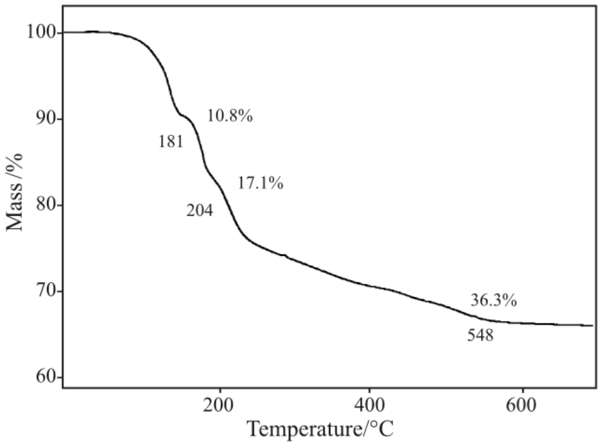

Fig. 3 TG curve simulating preparation of $Sc(PO_3)_3$

$$2(NH_4)_5P_3O_{10} + Me^{III}_2O_3 = 2Me^{III}H_2P_3O_{10} +$$

$$+ 10NH_3 + 3H_2O$$

We would like to bring into focus the fact that acidic tripolyphosphates $Me^{III}H_2P_3O_{10}$ obtained at this step and polyphosphate monohydrates $Me^{III}(PO_3)_3{\cdot}H_2O$ have identical composition and therefore can be regarded as a rare case of inorganic isomers. They are not crystalline [7] and difficult to distinguish since X-ray phase analysis is of no help. Note the differences between calculated and experimental values (Table 1), which are larger than at the first step. It is possible that the poros created at random after ejection of vapor particulates are responsible for lower diffusion rate and poor reproducibility in general.

In any case, further heating leads to the loss of water, regardless the mode of its initial coordination, and yields polyphosphates at this final step. So the whole reaction can be written as:

$$6(NH_4)_2HPO_4 + Me^{III}_2O_3 = 2Me^{III}(PO_3)_3 +$$

$$+ 12NH_3 + 6H_2O$$

For all elements of rare earth series, including yttrium, this process comes to an end in the interval 340–390°C, invariably depending on diffusion conditions, which are not proper, as samples are becoming more and more ‘fluffy’. At high temperatures, the polyphosphates obtained tend to lose small quantities of P_2O_5, but below 1000°C vapor pressure of P_2O_5 is low and consequently the decomposition negligible. There is a certain kinetic analogy with the role of CO_2 equilibrium pressure during breaking up of $CaCO_3$ [8].

In comparison with the above polyphosphates, scandium compound is formed at higher temperatures. The last substantial mass loss at 548°C (Fig. 3) marks the obtainment of the acidic tripolyphosphate $ScH_2P_3O_{10}$ (calc. 35.5%; exp. 36.3%), which, at least below 800°C, shows only a slight tendency to be transformed into polyphosphate. It is in accordance with the available experimental data reporting its complete transformation into tetramethaphosphate $Sc_4(P_4O_{12})_3$ only above 950°C [9].

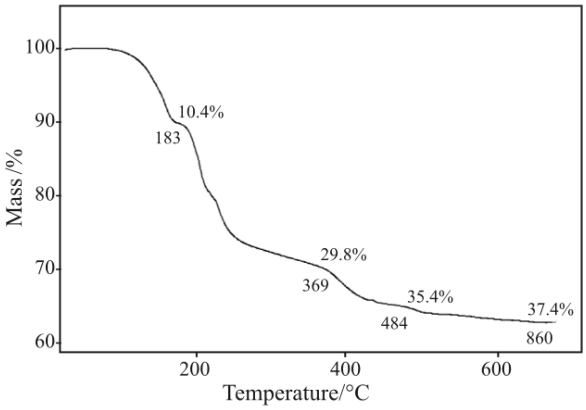

Fig. 4 TG curve simulating preparation of $Fe(PO_3)_3$

According to TG curve in Fig. 4, iron polyphosphate is formed at 640–660°C. This may vary likely dependent on the presence of a prevailing polymorphs (A, B, D and, possibly, others) formed under dynamic conditions of thermal treatment. Actually, iron is known to display a major variety of stable modifications [4]. Based on the change of slope at 369°C and corresponding mass loss (calc. 27.5; exp. 29.8), the formation of an intermediate iron ammonium tripolyphosphate $Fe(NH_4)_2P_3O_{10}$ can be suggested.

The gallium polyphosphate is formed at 520°C and is quite stable at least up to 1000°C (Fig. 5).

In this instance, similarly to the mechanism involving iron compounds, a weak mass change at 356°C may indicate the formation of another intermediate polyphosphate, e. g. gallium ammonium tripolyphosphate $Ga(NH_4)_2P_3O_{10}$ (calc. 36.3%; exp. 36.0%).

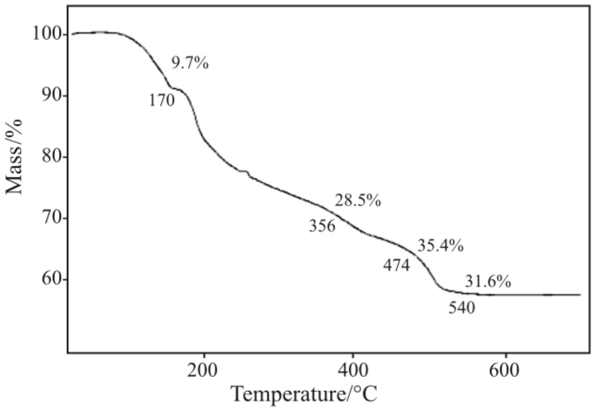

Fig. 5 TG curve simulating preparation of $Ga(PO_3)_3$

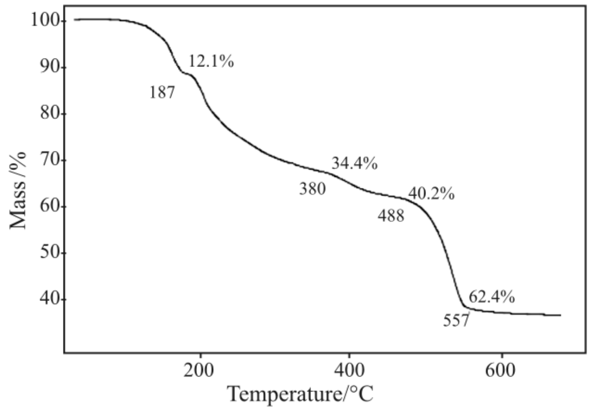

Fig. 6 TG curve simulating preparation of $Al(PO_3)_3$

The thermal behavior of aluminum polyphosphate is quite different (Fig. 6).

Mass loss corresponding to polyphosphate formation is observed at 488°C (calc. 40.9%; exp. 40.1%). Then a rapid decomposition occurs ending with a total loss 62.4%. That suggests that in contrast to similar compounds, P_2O_5 is rapidly eliminated, leaving pure orthophosphate $AlPO_4$ (calc. mass loss 61.3%).

Also unlike with other trivalent elements, chromium polyphosphate is so unstable that no definite mass loss can be assigned to its formation (Fig. 7).

After initial mass losses corresponding to the formation of $(NH_4)_5P_3O_{10}$ (calc. 11.2%; exp.12.1%) and possibly $(NH_4)_3H_2PO_4$ (calc. 17.5%; exp. 20.2%), the curve descends smoothly, with little changes or definite plateaux.

X-ray powder diffraction of the samples obtained during static heating in platinum crucibles confirms the above results. Actually, after treatment at 450°C for 3 h all polyphosphates of La-Lu and Y are perfectly crystalline. As a representative example, in Fig. 8 is given X-ray pattern of terbium polyphosphate adequately identified by comparison with the ICSD database. Vertical bars stand for reflexions available for $Tb(PO_3)_3$ in the ICSD file 31-1379. In the original paper [10], 2θ range is limited (4–50°), so not all experimental peaks could have been accounted. When no crystallographic data on a given polyphosphate was obtainable, as was in the case of samarium, the identification was carried out using information for isostructural europium polyphosphate, $Eu(PO_3)_3$, ICSD files 31-0519 and 34-1005.

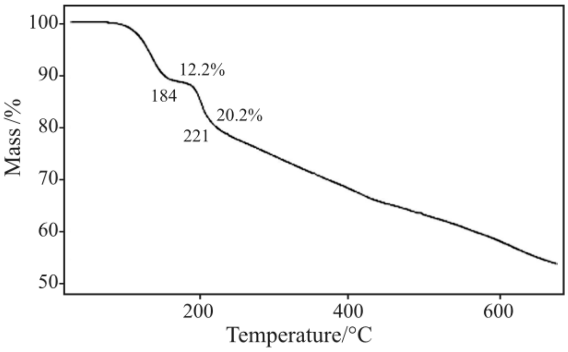

Fig. 7 TG curve simulating preparation of $Cr(PO_3)_3$

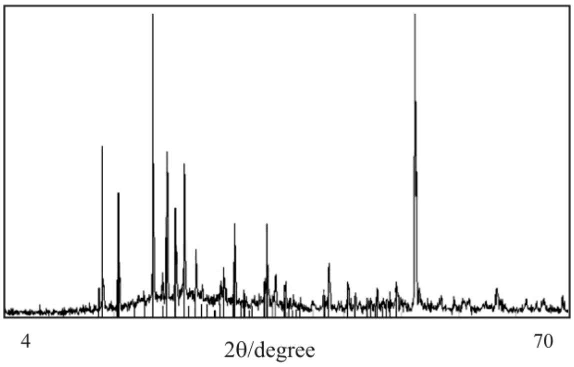

Fig. 8 X-ray powder diffractogram of $Tb(PO_3)_3$

Under the same conditions scandium and gallium form stable tripolyphosphates $ScH_2P_3O_{10}$ and $GaH_2P_3O_{10}$ (files 37-0138 and 77-0704). They are easily qualitatively detected by their low lightness. Finally, $Al(PO_3)_3$ and $Cr(PO_3)_3$, are unstable above 350°C, forming orthophosphates and small quantities of unidentified transitional phases.

As expected, polyphosphates thermal behavior may be considered as a function of ionic radius (i.r.). Actually, rare earth elements from lanthanum (1.06 Å) to lutetium (0.85 Å) and yttrium (0.9 Å) belong in a compact group with common properties. The final differences in their behavior are due rather to a poor and uncontrollable diffusion than to small distinctions in physico-chemical characteristics. However, when polyphosphates precursors are combined together to form a butch for binders, diffusion factors will be the same for all, and hence would not interfere with final adhesion. Tripolyphosphates of the elements with intermediate i.r. – scandium

(0.74 Å), iron (0.64 Å) and gallium (0.62 Å) – are most stable, so their polyphosphates are formed at higher temperatures. These elements can be used as modifiers to ensure adherence in case the metal couples are exposed to excessive heat. Yet aluminum and chromium with i.r. too small (0.53 and 0.52 Å, respectively) are unable to form refractory polyphosphates and should not be used as binders ingredients. It seems that this scheme may be applied for the evaluation of other trivalent ions when looking for modifiers and dopants.

Conclusions

The synthesis of trivalent elements polyphosphates from $Me_2^{III}O_3$ and dibasic ammonium phosphate is a complex process that compulsorily includes an intermediate formation of pentaammonium tripolyphosphate $(NH_4)_5P_3O_{10}$. The latter reacts with $Me_2^{III}O_3$ forming acidic tripolyphosphates $Me^{III}H_2P_3O_{10}$ or their isomers $Me^{III}(PO_3)_3{\cdot}H_2O$, which finally decompose to give $Me^{III}(PO_3)_3$. X-ray diffraction of crystalline samples obtained in static conditions confirms phase compositions supposed on the basis of TG curves. Thermal behavior of the compounds seems to be determined by the elements ionic radii, so this parameter may be used for the evaluation of polyphosphates suitability in materials science practice.

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