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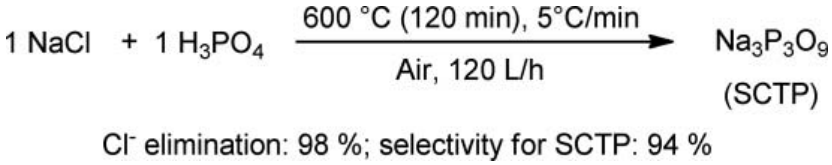
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A NEW ROUTE FOR THE SYNTHESIS OF ALKALI POLYPHOSPHATE FROM ECONOMICAL STARTING MATERIALS: PART II—INFLUENCE OF REACTION CONDITIONS

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GRAPHICAL ABSTRACT



Abstract *Direct synthesis of sodium cyclotriphosphate, $Na_3P_3O_9$ (SCTP), from sodium chloride and orthophosphoric acid as economical starting materials was investigated. Reaction conditions including the heating rate, reaction plateau time, air flow rate, and Na/P molar ratio were found to be key parameters for the elimination of chloride and for the selectivity in SCTP. High yields in SCTP (94–99%) were obtained. The results are very interesting with respect to a potential industrial application for the synthesis of SCTP from point of view of the low cost of the starting materials.*

Keywords Sodium polyphosphate; sodium cyclotriphosphate; sodium chloride; orthophosphoric acid; thermal synthesis

INTRODUCTION

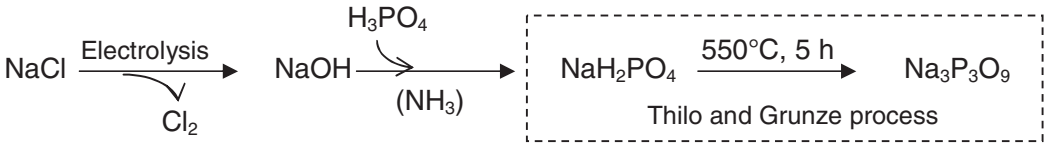
Condensed phosphates are phosphate anions having one or several P-O-P bonds, which are formed by hydrolysis and dehydration reactions of orthophosphate anion under thermal conditions.[1,2] Their formation and structure depend on several parameters of synthesis: reaction temperature, heating rate, reaction time, cooling rate of melts, phosphorus/metal molar ratio, source of orthophosphate, etc.[3,4]

Sodium cyclotriphosphate, $Na_3P_3O_9$ (SCTP), is used in different applications like detergency, food chemistry, water treatment, etc.[1,5–8] Moreover, SCTP is the starting material

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for the preparation of all other metal cyclotriphosphates such as $K_3P_3O_9$, $Ag_3P_3O_9{\cdot}H_2O$, $Mn_3(P_3O_9)_2{\cdot}10\ H_2O$, $Ca_3(P_3O_9)_2{\cdot}10\ H_2O$, $Ba_3(P_3O_9)_2{\cdot}4\ H_2O$, $Tl_3P_3O_9$, $Rb_3P_3O_9{\cdot}H_2O$, $Na_2LiP_3O_9$, $Na_2CsP_3O_9{\cdot}2\ H_2O$, $Ln(Bi)Na_3P_3O_9{\cdot}9\ H_2O$, etc.[9] The actual competing industrial process for the synthesis of SCTP was developed by Thilo and Grunze in 1955.[10–12] Sodium dihydrogen orthophosphate is heated to about 550 °C for 5 h and cooled to room temperature. Pure SCTP is then obtained by a purification step using recrystallization technique. Considering the industrial synthesis of sodium dihydrogen orthophosphate from sodium hydroxide and orthophosphoric acid, we have the following scheme for SCTP industrial synthesis process:



Our previous work shows that SCTP could be obtained from the direct reaction of sodium chloride and orthophosphoric acid at reaction temperature lower than 628 °C.[13] The present study investigates the influence of different synthesis parameters on the conversion of the initial reactants and the selectivity in forming SCTP. In comparison with the Thilo and Grunze process, the proposed process is more economical and ecological as it avoids the electrolysis and neutralization steps.

RESULTS AND DISCUSSION

Influence of the Heating Rate

When the powder of sodium chloride is set in contact with 85 wt% orthophosphoric acid at high temperature, hydrochloric acid is formed and leaves the reaction mixture as vapor. The general reaction between sodium chloride and orthophosphoric acid can be described by the following equation:

$$(85\ \text{wt\%})\ H_3PO_4\ (\text{liquid}) + NaCl(\text{solid}) \xrightarrow{T} Na_aH_bP_cO_d(\text{solid}) + HCl(\text{gas}) + H_2O(\text{gas}) \quad (1)$$

where $Na_aH_bP_cO_d$ is the solid product of the reaction.

As for all thermal processes, the heating rate was first investigated at different reaction temperatures from 300 to 600 °C. The influence of the heating rate on the distribution of chloride and phosphorus-containing species in the solid products, as obtained from ionic chromatography analysis, is shown in Table 1.

No influence of the heating rate on the distribution of chloride, orthophosphate, and pyrophosphate was observed. However, the heating rate had some effects on the formation of cyclotriphosphate anion ($P_3O_9^{3-}$) at 300 and at 400 °C. A slight influence of the heating rate was recognized at 300 °C with higher selectivity for $P_3O_9^{3-}$ at 2 and 5 °C/min than at 10 and 20 °C/min. In fact, the time to reach the reaction temperature of 300 °C at heating rates of 10 °C/min and 20 °C/min starting from ambient temperature was only 28 min and 14 min, respectively. These heating times could be too short for the transformation of initial orthophosphate species and intermediates into $P_3O_9^{3-}$, which explains the low selectivity for $P_3O_9^{3-}$ (4%). On the other hand, the heating rates of 2 °C/min and 5 °C/min required a

Table 1 Influence of the heating rate on the distribution of chloride and phosphorus species in the final solid product. S_{P3O9}: selectivity with respect to $P_3O_9^{3-}$ anion. Reaction conditions: initial quantity of NaCl and 85 wt% orthophosphoric acid: 87.5 mmol, reaction plateau time: 30 min, air flow rate: 120 L/h

T (°C)	Heating rate (°C/min)	Cl^- (mmol)	PO_4^{3-} (mmol)	$P_2O_7^{4-}$ (mmol)	$P_3O_9^{3-}$ (mmol)	S_{P3O9} (%)
300	2	26	27	8	3	10
300	5	23	27	7	4	15
300	10	24	17	9	1	4
300	20	23	18	9	1	4
400	2	7	2	1	22	76
400	5	10	1	1	23	79
400	10	11	2	1	23	78
400	20	12	3	2	17	60
500	2	8	1	trace	23	79
500	5	9	trace	2	23	80
500	10	9	2	1	23	79
500	20	9	1	1	23	79
600	5	3	0	trace	24	84

time of 140 min and 70 min, respectively, to reach 300 °C. So orthophosphate species and intermediates had more time to be converted into $P_3O_9^{3-}$.

At 400 °C, chloride elimination was more effective at 2 °C/min than at other heating rates. Similar selectivity for $P_3O_9^{3-}$ in the range of 76–79% was observed for the heating rate range 2–10 °C/min. A smaller selectivity of 60% for $P_3O_9^{3-}$ was observed at heating rate of 20 °C/min, probably due to the shorter time at this heating rate to reach the reaction temperature, as explained above for the reaction temperature of 300 °C.

At 500 °C, the results were similar for all heating rates with a constant selectivity for $P_3O_9^{3-}$ of 80%. Thus, the reaction at 600 °C was carried out only at the heating rate of 5 °C/min. At 600 °C, the elimination of chloride and the selectivity in $P_3O_9^{3-}$ were higher than those achieved at 300, 400, or 500 °C as observed in previous investigations.[13]

In conclusion, the heating rate influenced mostly the selectivity for $P_3O_9^{3-}$ anion. At three investigated temperatures of 300, 400, and 500 °C, the heating rate of 5 °C/min was the most favorable for the formation of $P_3O_9^{3-}$.

Influence of the Air Flow Rate

The air circulation permits to remove the vapor of water and hydrochloric acid during the reaction and, therefore, influences the performance of the process. Thus, the synthesis was carried out at 350 °C with an air flow rate varying from 30 to 240 L/h. The reaction temperature of 350 °C was chosen to better observe the effect of the air flow rate. The result of this study is presented in Table 2.

At the reaction temperature of 350 °C, no effect of the air flow rate on the elimination of chloride was observed. On the other hand, orthophosphate species and pyrophosphate decreased with increasing air flow rate. In fact, the increase of air flow rate leads to a more effective removal of the gaseous products and so the dehydration of orthophosphate species, pyrophosphate, and eventually other intermediates takes place more readily. At the same time, the selectivity for $P_3O_9^{3-}$ increases from 39 to 77% when the air flow rate is increased

Table 2 Influence of the air flow rate on the distribution of chloride and phosphorus species in the final solid product. S_{P3O9}: selectivity for $P_3O_9^{3-}$ anion. Reaction conditions: temperature: 350 °C, initial NaCl and 85 wt% orthophosphoric acid: 87.5 mmol, reaction plateau time: 30 min

Air flow rate (L/h)	Cl^- (mmol)	PO_4^{3-} (mmol)	$P_2O_7^{4-}$ (mmol)	$P_3O_9^{3-}$ (mmol)	S_{P3O9} (%)
30	10	12	3	11	39
60	10	8	3	22	77
120	10	4	2	23	79
240	10	1	1	23	80

from 30 to 60 L/h. In the range 60–240 L/h, the selectivity for $P_3O_9^{3-}$ increases only slightly from 77 to 80%. This study suggests that the air flow rate should be in range 60–120 L/h. A higher air flow rate is not recommended because of the higher energy consumption in order to keep the reaction temperature unchanged.

Influence of the Reaction Plateau Time

The effect of the reaction plateau time on the elimination of chloride and the distribution of the phosphorus-containing species is shown in Table 3.

Despite the increase of the reaction plateau time up to 1440 min, the content of chloride in the final product was only slightly reduced. Alternatively, the reaction temperature of 300 °C was not sufficient for a total elimination of chloride during a long reaction time (24 h). On the other hand, the reaction plateau time influenced strongly the distribution of phosphorus-containing species and the selectivity for the $P_3O_9^{3-}$ anion. Orthophosphate species nearly disappear after 120 min of reaction time. Pyrophosphate, formed as the first intermediate at the beginning of the reaction also disappears after 120 min. The portion of $P_3O_9^{3-}$ anion strongly increases between 30 and 480 min of reaction plateau time. The highest selectivity for $P_3O_9^{3-}$ was found at 88% after allowing the reaction to proceed for 480 min. However, a longer reaction time (1440 min) resulted in a decrease of the selectivity for $P_3O_9^{3-}$, which is probably due to the transformation of $P_3O_9^{3-}$ into other products. So the most favorable reaction plateau time was found to be 120 min for the elimination of chloride and for the best selectivity with respect to the $P_3O_9^{3-}$ anion.

Table 3 Influence of the reaction plateau time on the distribution of chloride and phosphorus species in the final solid product. S_{P3O9}: selectivity for $P_3O_9^{3-}$ anion. Reaction conditions: initial quantity of NaCl and 85 wt% orthophosphoric acid: 87.5 mmol, air flow rate: 120 L/h, reaction temperature: 300 °C

Reaction plateau time (min)	Cl^- (mmol)	PO_4^{3-} (mmol)	$P_2O_7^{4-}$ (mmol)	$P_3O_9^{3-}$ (mmol)	S_{P3O9} (%)
5	23	28	8	4	15
30	23	27	7	4	15
120	21	4	2	23	79
240	17	1	1	23	79
480	15	1	trace	26	88
1440	15	0	trace	19	65
120*	1	0	0	28	94

*Reaction temperature: 600 °C; air flow rate: 120 L/h, and reaction plateau time: 120 min.

Table 4 Influence of the Na/P molar ratio on the distribution of chloride and phosphorus species in the final solid product. S_{P3O9}: selectivity in $P_3O_9^{3-}$ anion. Reaction conditions: air flow rate: 120 L/h, reaction plateau time: 30 min, $H_3PO_4^{(i)}$: initial quantity of orthophosphoric acid, $NaCl^{(i)}$: initial quantity of NaCl

$H_3PO_4^{(i)}$ (mmol)	$NaCl^{(i)}$ (mmol)	Na/P molar ratio	T (°C)	Cl^- (mmol)	PO_4^{3-} (mmol)	$P_2O_7^{4-}$ (mmol)	$P_3O_9^{3-}$ (mmol)	S_{P3O9} (%)
87.5	175	1/2	300	1	12	11	2	7
			400	trace	3	1	2	6
87.5	87.5	1/1	300	23	27	7	4	15
			400	10	1	1	23	79
175	87.5	2/1	300	101	5	5	8	29
			400	86	1	trace	29	99

From the results obtained above, a synthesis was then carried out at the most favorable conditions found for the Na/P molar ratio of 1/1: reaction plateau time of 120 min, reaction temperature of 600 °C, heating rate of 5 °C/min, and an air flow rate of 120 L/h (Table 3). As expected, the elimination of chloride was nearly total (98%) and a high selectivity for $P_3O_9^{3-}$ of 94% was obtained. This was also the best result obtained with the Na/P molar ratio of 1/1; the solid thus obtained is labeled Syn1.

Influence of the Na/P Molar Ratio

This study was carried out at 300 and 400 °C with Na/P molar ratios of 1/2, 1/1, and 2/1 (Table 4). The result obtained at the molar ratio Na/P = 1/1, which was already shown in Table 1, is also included in Table 4 for comparison.

When an excess of orthophosphoric acid was used (Na/P = 1/2), the chloride elimination rate was nearly total even at 300 °C. Orthophosphate species (PO_4^{3-}) disappear completely and $P_2O_7^{4-}$ and $P_3O_9^{3-}$ anions were found only in small amounts. This means that other intermediates were formed, which were not detected by ionic chromatography. So the excess of orthophosphoric acid is not favorable for the formation of the $P_3O_9^{3-}$ anion.

When an excess of sodium chloride was used (Na/P = 2/1), a great amount of chloride remained in the final product. At 300 °C, PO_4^{3-} and $P_2O_7^{4-}$ were still present and the selectivity for the $P_3O_9^{3-}$ anion reached only 29%. At 400 °C, PO_4^{3-} was nearly totally converted into $P_3O_9^{3-}$ anion (99% of selectivity) and a half of the initial amount of chloride was consumed. The solid product obtained with 99% of selectivity with respect to the $P_3O_9^{3-}$ anion is labeled Syn2.

In conclusion, an equimolar Na/P ratio (Na/P = 1/1) or an excess of sodium chloride (Na/P > 1/1) is required to obtain a high selectivity for $P_3O_9^{3-}$.

Mass Balance

For all experiments, the mass balance for elemental chlorine, sodium, and phosphorus was established. ICP-AES analysis showed that all initial sodium and phosphorus were found in the final solid product. At the same time, the analysis of the gaseous products trapped in the wash bottle showed the presence of only chlorine in form of hydrochloric acid, which was easily condensed from the gas output of the reactor. The total quantity

of chlorine in the gaseous and solid products reached in all cases the initial quantity of chlorine in the NaCl used.

Characterization of the Solid Product

By varying the reaction conditions, high selectivity for the $P_3O_9^{3-}$ anion up to 99% was obtained, as showed by ionic chromatography analysis. However, additional characterization is necessary to identify the corresponding product.

Characterization by XRD. All solid products were analyzed by XRD technique. The results show that $P_3O_9^{3-}$ anion is present mainly as $Na_3P_3O_9$ (SCTP), but in some cases small amounts of $Na_2HP_3O_9$ could be detected. The compound $Na_2HP_3O_9$ was only observed when the selectivity for $P_3O_9^{3-}$ was high and the chloride elimination rate was low, resulting in a deficiency of sodium for the formation of SCTP. For example, in Table 3 within the reaction plateau time range from 120 to 480 min $Na_2HP_3O_9$ was present in the solid products because the quantity of sodium (in mmol) liberated from the elimination of chloride was much smaller than the quantity of orthophosphates (in mmol) transformed into $P_3O_9^{3-}$ anion. In addition, the reaction temperature of 300 °C might also not have been sufficient to remove the last hydrogen atom of $P_3O_9^{3-}$ ring and substitute it by sodium atom.[14]

Figure 1 shows the XRD patterns of the two solid products (Syn1 and Syn2) having the best selectivity for $P_3O_9^{3-}$ for the Na/P molar ratio of 1/1 or 2/1 in comparison with that

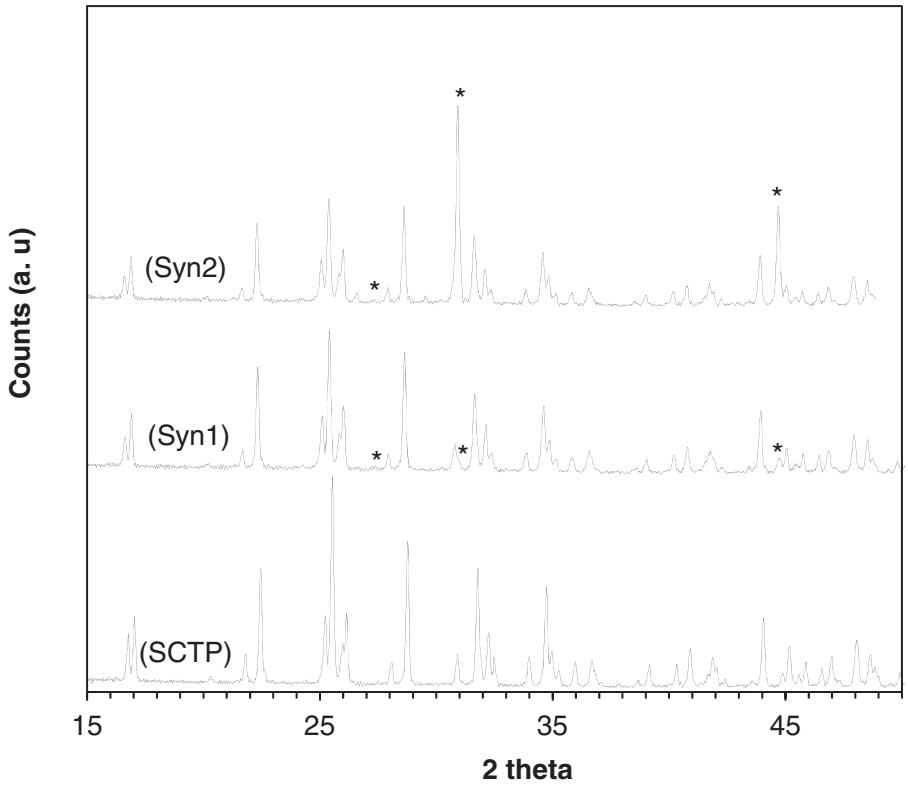


Figure 1 (SCTP): XRD pattern of pure SCTP. (Syn1): XRD pattern of the solid product formed at 600 °C and a Na/P molar ratio of 1/1 with 98% chloride elimination rate and 94% of selectivity for the $P_3O_9^{3-}$ anion (Table 3). (Syn2): XRD pattern of the solid product formed at 400 °C and a Na/P molar ratio of 2/1 with 99% of selectivity for $P_3O_9^{3-}$ anion (Table 4). (*): peak positions of the NaCl diffraction in 2θ range from 15 to 50°.

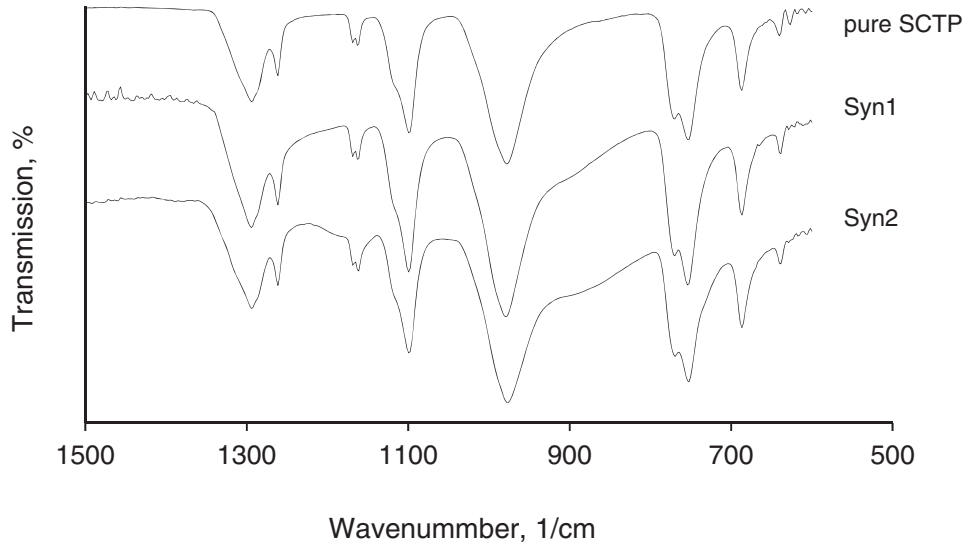


Figure 2 IR spectra of (STM): pure STM; (Syn1): solid product formed at 600 °C and a Na/P molar ratio of 1/1 with 98% chloride elimination rate and 94% of selectivity for the $P_3O_9^{3-}$ anion (Table 3); (Syn2): solid product formed at 400 °C and a Na/P molar ratio of 2/1 with 99% of selectivity for the $P_3O_9^{3-}$ anion (Table 4).

of pure SCTP. Both products, Syn1 and Syn2, did not contain $Na_2HP_3O_9$ as byproduct. XRD patterns of the product Syn1 and pure SCTP are very similar. NaCl was practically not detected in Syn1 according to the almost complete elimination of chlorine (98%). For the product Syn2, all peaks could be attributed to SCTP and NaCl. In fact, half of the NaCl remained in Syn2 because of the excess of NaCl in the synthesis using the Na/P molar ratio of 2/1.

IR Analysis. Figure 2 compares the IR spectra of pure SCTP with the spectra of the two solid products Syn1 and Syn2.

Both solid products synthesized showed IR spectra similar to that of pure SCTP, and display characteristic bands in the range of 650–1400 cm^{-1}.[15–17] No other bands were observed in the range 1400–4000 cm^{-1}. Note that the remaining NaCl does not show an IR signal. These results confirm again that the SCTP synthesized is well crystallized.

CONCLUSIONS

A new route for the direct synthesis of SCTP from sodium chloride and orthophosphoric acid as economical starting materials was developed. The reaction temperature, heating rate, air flow rate, reaction plateau time, and Na/P molar ratio were found to be important parameters for the elimination of chloride and the selectivity with respect to SCTP. Complete elimination of chloride and high yield of SCTP could be obtained under the following conditions:

- Moderate heating rate of 5 °C/min and reaction temperature of 600 °C.
- Air flow rate of at least 60 L/h permitting an effective removal of the gaseous products.
- Reaction plateau time of about 120 min.
- Na/P molar ratio of 1/1 or 2/1.

Starting from a Na/P molar ratio of 1/1, the best result was obtained with 98% of chloride elimination and 94% of selectivity for SCTP (reaction conditions: temperature of 600 °C, heating rate of 5 °C/min, air flow rate of 120 L/h, and reaction plateau time of 120 min). Increase of the molar ratio Na/P to 2/1 results in a complete transformation of the

initial orthophosphoric acid into SCTP at only 400 °C. A mixture of pure SCTP and NaCl was obtained. These results are technically and economically very interesting in comparison with the actual competing industrial process for the fabrication of SCTP. Hydrochloric acid was the only product in gas phase, which could be condensed and recovered in liquid form as pure chemical product.

Future investigations will focus on the purification of the solid product to obtain pure SCTP, for example, by recrystallization. The reactor engineering aspects of the process should be also considered, for example, a reactor equipped with a stirring system, for the improvement of the performance of the process.

EXPERIMENTAL

Fine powder of sodium chloride from Acros Organics (99.5%) with a volume-mean diameter of 375 μm and phosphoric acid (85 wt% pure grade) from Merck were used as starting reactants. Pure SCTP (99%) was purchased from Sigma-Aldrich. The experimental setup was described elsewhere.[13] For the reaction, the quartz reactor was loaded with sodium chloride powder and 85 wt% orthophosphoric acid at room temperature. The reactor was then heated to the reaction temperature and kept at this temperature between 5 min and 24 h. According to our previous work, all experiments were carried out at a temperature lower than 625 °C to avoid the transformation of SCTP in glass amorphous products.[13] After this plateau time, the reactor was freely cooled down to room temperature. During the reaction, an air circulation at constant flow rate was applied to remove the gaseous products formed. The gaseous products were trapped into a wash bottle containing an aqueous solution of potassium hydroxide.

The solid product was crushed into fine powder prior to all analyses and characterizations. ICP-AES (inductive coupled plasma atomic emission spectroscopy) analysis was carried out with a HORIBA Jobin Yvon Ultima 2 instrument for quantification of sodium and phosphorus. Chloride (Cl^-), orthophosphate (PO_4^{3-}), pyrophosphate ($P_2O_7^{4-}$), and cyclotriphosphate ($P_3O_9^{3-}$) anions were analyzed with a Dionex ionic chromatography apparatus equipped with a Dionex IonPac AS 19 (4 × 250 mm) column, a Dionex P/N 061830 conductivity detector, and a Dionex ICS-3000 EG eluant generator. Ultra-pure water was used as mobile phase, eluted at a rate of 1 mL/min.

From the results of ionic chromatography analysis, the selectivity for the $P_3O_9^{3-}$ anion (S_{P3O9}) was calculated as follows: $S_{P3O9} = 100 \times {n_P}^{P3O9}/{n_P}^{i}$ where ${n_P}^{P3O9}$ was the quantity (mole) of phosphorus converted in $P_3O_9^{3-}$ anion and ${n_P}^{i}$ was the initial quantity (mole) of phosphorus introduced in the reactor.

IR (infra-red) spectra were measured with a Shimadzu FTIR 8400S spectrometer using a sensitive pyroelectric detector with an L-alanine-doped deuterated triglycine sulfate (DLATGS) element. Solid powder samples were directly measured in the wave number range 500–4000 cm^{-1}. XRD (X-ray diffraction) measurements were carried out using a Phillips Panalytical X'pert Pro MPD diffractometer with a Cu Kα (1.543 Å) radiation source.

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