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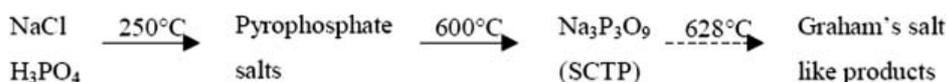
A NEW ROUTE FOR THE SYNTHESIS OF ALKALI POLYPHOSPHATE FROM ECONOMICAL STARTING MATERIALS: PREPARATION AND CHARACTERIZATION OF SODIUM CYCLOTRIPHOSPHATE

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GRAPHICAL ABSTRACT



Abstract Thermal synthesis of sodium cyclotriphosphate (SCTP) – $\text{Na}_3\text{P}_3\text{O}_9$ was investigated in the temperature range of 150 °C to 750 °C using sodium chloride (NaCl) and 85 wt% orthophosphoric acid (H_3PO_4) as economical starting materials. Reaction temperature had a crucial impact on the chloride elimination rate and the formation of SCTP. The best result was obtained at 600 °C with 96% of elimination of the initial chloride as hydrochloric acid and 84% of selectivity in SCTP. At lower temperatures, residual chloride contents were high. At higher temperatures (650 °C and 750 °C), SCTP was melted and transformed into glassy products.

Keywords Alkali polyphosphate; sodium cyclotriphosphate; thermal synthesis

INTRODUCTION

Alkali polyphosphates, formed from the condensation of orthophosphates, are used in various fields such as water treatment, metal surface treatment, detergent, food additives, fuel cells, ceramic materials, etc.^{1–8} For example, in multi-stages flash sea water distillation alkali polyphosphates were found to be good anti-scale agents.^{9–11} At low concentration, alkali polyphosphates are used as inhibitors for soluble copper corrosion control to prevent the leaching of copper from potable water distribution system.^{12,13} Steel corrosion in similar conditions of sea water was reduced by addition of small amounts of alkali polyphosphates in the presence of divalent cations, such as Ca, Mg, Zn, and dissolved oxygen thanks to the

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formation of thin film between polyphosphates and metal cations and thereby inhibits the electrochemical processes that lead to corrosion.¹⁰⁻¹⁴

Sodium cyclotriphosphate (SCTP) is an important polyphosphate since it is used in different applications as mentioned above. In addition, SCTP is used as starting material for the preparation of all other metal cyclotriphosphates, such as $K_3P_3O_9$, $Ag_3P_3O_9 \cdot H_2O$, $Na_2LiP_3O_9$, $Mn_3(P_3O_9)_2 \cdot 10 H_2O$, $Ca_3(P_3O_9)_2 \cdot 10H_2O$, $Ba_3(P_3O_9)_2 \cdot 4H_2O$, $Ln(Bi)Na_3P_3O_9 \cdot 9H_2O$, $Tl_3P_3O_9$, etc.¹⁵ Actually SCTP is industrially synthesized by a thermal route (500 °C, 5 h) using sodium dihydrogen phosphate (NaH_2PO_4) as reactant which is a relatively expensive product.¹⁶⁻¹⁸

Here, we report a new route for the synthesis of SCTP starting from sodium chloride ($NaCl$) and orthophosphoric acid (H_3PO_4). The results obtained are of interest for a potential industrial application from point of view of the availability and low cost of the starting materials used.

RESULTS AND DISCUSSION

Influence of the Reaction Temperature

When solid sodium chloride powder is brought in contact with 85 wt% H_3PO_4 at a Na/P molar ratio of 1/1 a supersaturated solution of sodium chloride results because the quantity of water initially present in 85 wt% H_3PO_4 is much smaller than that required to dissolve all the sodium chloride. Under this condition, we can predict that hydrochloric acid could be formed in solution because of the present of both H^+ and Cl^- ions. Under thermal conditions, hydrochloric acid could evolve from the reaction mixture as gas. Simultaneously, water will evaporate also. So, the general reaction between sodium chloride and H_3PO_4 can be written as follows:

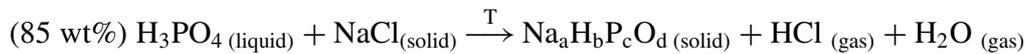


Table 1 shows the chloride elimination rate and the distribution of species in the solid products as a function of reaction temperature between 150 °C and 750 °C. We obtained

Table 1 Influence of the reaction temperature on the distribution of the species in the solid products. Reaction conditions: initial $NaCl$ and H_3PO_4 : 87.5 mmol, volume-mean diameter of $NaCl$ powder: 375 μm , reaction plateau time: 30 min, air flow rate: 120 L/h

T (°C)	Cl^- (mmol)	X_{Cl} (%)	PO_4^{3-} (mmol)	$P_2O_7^{4-}$ (mmol)	$P_3O_9^{3-}$ (mmol)	P_{balance} (mmol)	$S_{P_3O_9}$ (%)	Observation
150	80	9	88	trace	0	88	0	Pasty
200	66	25	68	10	trace	88	3	Pasty
250	43	51	40	17	1	77	3	Pasty
300	23	73	27	7	4	53	15	Pasty
350	10	85	4	2	23	77	79	Opaque
400	10	88	1	1	23	72	79	Opaque
450	10	89	2	1	23	73	79	Opaque
500	9	90	trace	2	23	73	80	Opaque
550	8	91	0	trace	23	69	80	Opaque
600	3	96	0	trace	24	72	84	Opaque
650	3	97	0	trace	2	6	6	Transparent
750	1	99	0	trace	1	3	3	Transparent

either pasty or solid products in the temperature range 150 °C–300 °C or 350 °C–750 °C, respectively. The solid products were opaque between 350 °C and 600 °C and transparent between 650 °C and 750 °C. It seems that the reaction temperatures of 650 °C and 750 °C lead to a melt, indicated by the perfect homogeneity of the solid products.

The reaction temperature had an important influence on the chloride elimination rate which varied progressively from 9% to 99%. The elimination of chloride explained the appearance of the solid products. Between 150 °C and 300 °C, the chloride elimination rate changed from 9% to 73%. This means that high quantity of initial H₃PO₄ remained after the reaction which caused the pasty consistency of the final product. No further characterization was performed for these pasty products. On the other hand, solid products were formed between 350 °C and 750 °C, thanks to the successive increase of chloride elimination rate, up to nearly total.

At 150 °C, the amount of orthophosphate (PO₄³⁻) was nearly unchanged and only trace of pyrophosphate (P₂O₇⁴⁻) was detected. A dehydration of PO₄³⁻ occurred already at this temperature. With the increase of the reaction temperature, PO₄³⁻ was rapidly converted into intermediates and its disappearance was nearly total at 400 °C. P₂O₇⁴⁻ was formed as the first intermediate with the highest amount of 17 mmol at 250 °C, corresponding to the transformation of 34 mmol of PO₄³⁻ (initial quantity of H₃PO₄ used was 87.5 mmol). At higher reaction temperature, P₂O₇⁴⁻ was then transformed into other intermediates. This transformation was nearly complete at 350 °C. Cyclotriphosphate (P₃O₉³⁻) was found to be the main product, with selectivity (S_{P₃O₉}) varying from 79% at 350 °C to 84% at 600 °C.

Analysis of the gaseous products trapped in a wash bottle showed that only chloride was detected in form of HCl. No trace of sodium or phosphorus was detected. The quantification of chloride in the gaseous phase and in the solid product permitted to regain the initial quantity of chloride introduced in the reactor.

Total phosphorus (P_{balance}) was calculated from the quantified phosphorus containing products (PO₄³⁻, P₂O₇⁴⁻, and P₃O₉³⁻). At 150 °C and 200 °C, P_{balance} reached the initial quantity of phosphorus introduced in the reactor (called also P_{initial}:87.5 mmol). At higher temperature from 250 °C to 750 °C, P_{balance} was smaller than P_{initial}. This difference must be due to some intermediates which were not identified in this temperature range. In fact, besides the three identified phosphorus compounds mentioned above, ionic chromatography analysis showed also one or several other small peaks that could not be identified. As example, Figure 1 shows the ionic chromatography analysis of the solid product formed at 400 °C which shows two unknown peaks eluted after P₃O₉³⁻.

Phosphorus deficit (the difference with P_{initial} and P_{balance}) was small between 250 °C and 600 °C where the selectivity in P₃O₉³⁻ was high. Exceptionally at 650 °C and 750 °C, great phosphorus deficits were observed. This phenomenon was certainly due to a transformation of P₃O₉³⁻ into other products.

Characterization of the Solid Product

Simultaneous Thermogravimetry and Differential Scanning Calorimetry Analysis (TGA-DSC). Figure 2 shows TGA-DSC analysis of the solid product formed at 350 °C. The first weight loss of 3.5% (25 °C–400 °C) could be attributed to the dehydration of orthophosphate and pyrophosphate species. The second weight loss (400 °C–610 °C) could be due to the reaction between remaining chlorides (15% in this case) with phosphorus-containing species to form gaseous HCl (so the elimination of chloride). After this second weight loss, the product containing essentially P₃O₉³⁻ (at 600 °C)

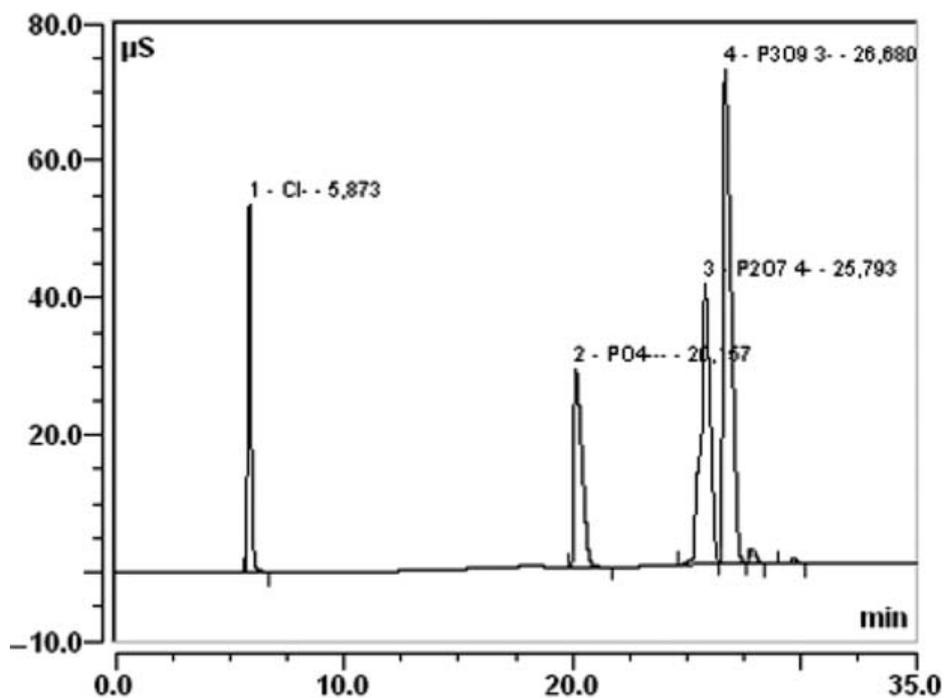


Figure 1 Example of ionic chromatography analysis of the solid product formed at 400 °C: the two peaks eluted after $P_3O_9^{3-}$ were not identified.

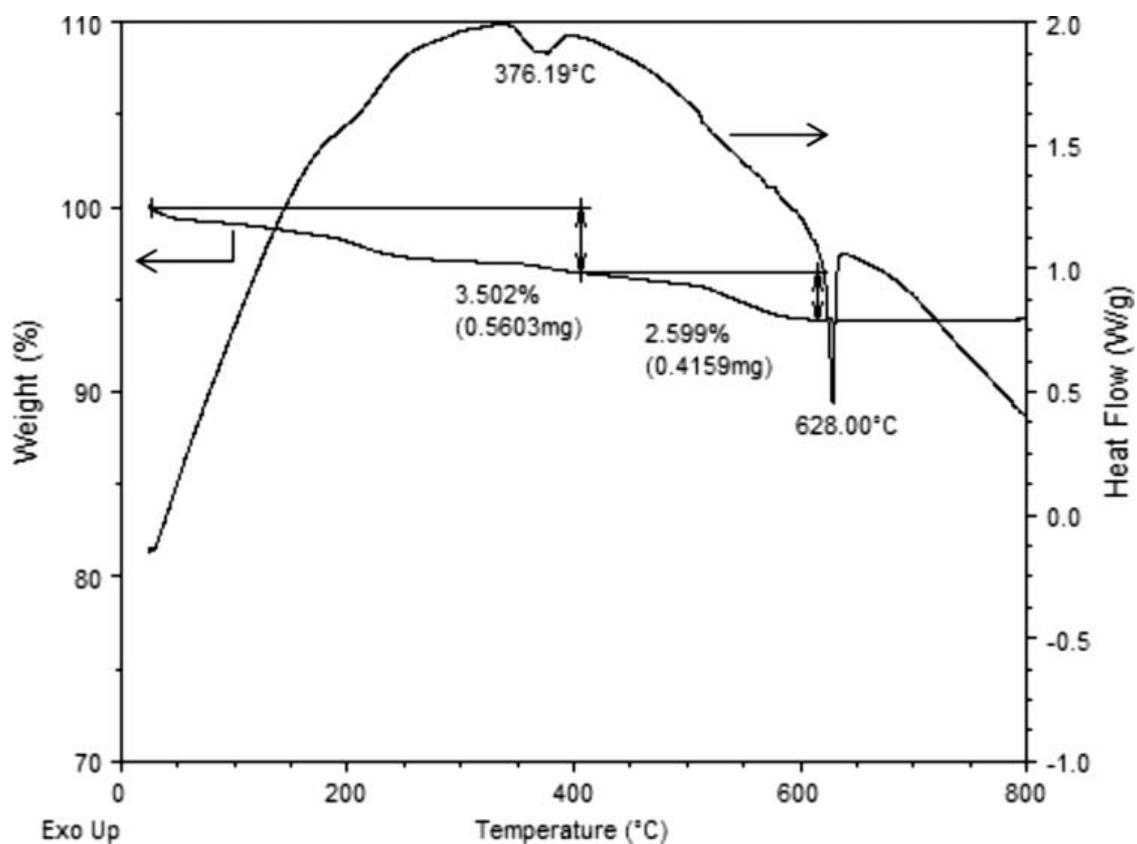


Figure 2 ATG-DSC analysis of the solid product formed at 350 °C.

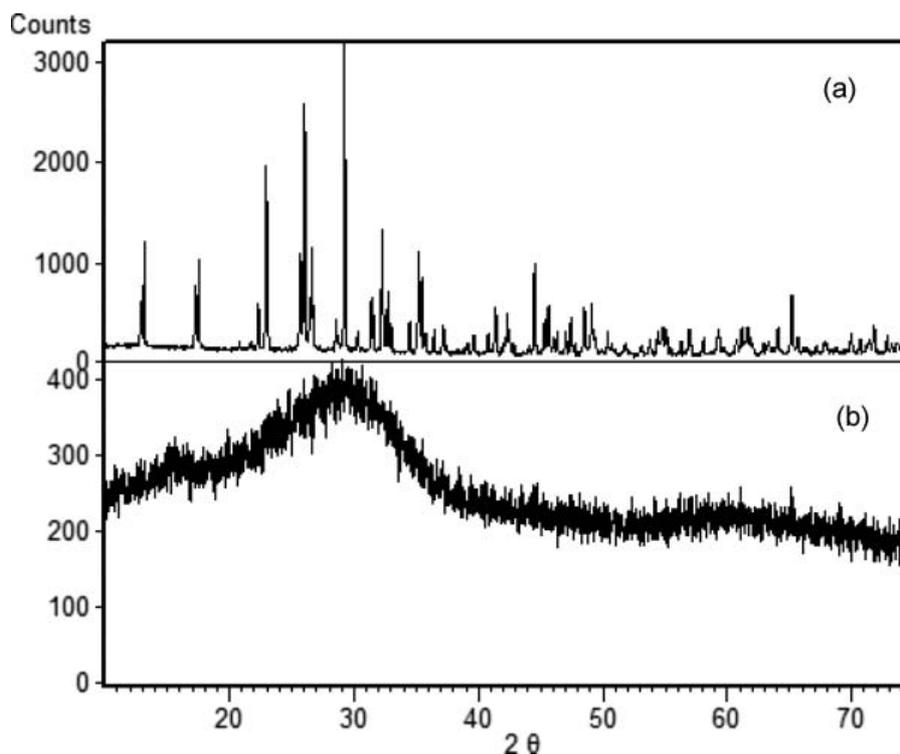


Figure 3 XRD patterns of the solid products formed at 600 °C (a) and 650 °C (b).

melted in accord with the endothermic peak at 628 °C. No weight change was observed after melting of the solid. Melting at 628 °C was also observed for all other solid products formed in the temperature range 400 °C–600 °C.

X-ray Diffraction (XRD). Figure 3 compares the XRD patterns of two products formed at 600 °C and 650 °C.

The product formed at 600 °C was well crystallized. Most of the peaks could be attributed to SCTP and NaCl. This means that $P_3O_9^{3-}$ quantified in Table 1 exists only in SCTP form. Three peaks with low intensity (2θ position: 21.9; 30.3; 39.1) were not identified and are probably due to the principal peaks of unknown intermediates, formed at low contents. Similar results were observed for the solid products formed in the temperature range 350 °C–600 °C. According to the results of the ionic chromatography analysis, a difference was found in the intensity of the peaks for NaCl (decrease from 350 °C to 600 °C) and SCTP (increase from 350 °C to 600 °C).

On the other hand, the product formed at 650 °C was amorphous. In fact, melting of the solid product at 628 °C, observed in Figure 2, resulted in the formation of a glassy product or Graham's salt-like products.¹⁹ This latter is a mixture of different long-chain polyphosphates and was described as an amorphous product. The same result was obtained with the solid product formed at 750 °C. So, the reaction temperature must be limited to 600 °C to avoid the formation of amorphous products.

Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM-EDX).

The change of the reaction temperature from 350 °C to 750 °C led to a change of the chlorine elimination rate, degree of dehydration and composition of the products formed. Accordingly, some morphological changes were observed as showed in Figure 4. All SEM micrographs were at the same scale. The largest difference in these products was the homogeneity of particle appearance, which increased with increasing reaction temperature.

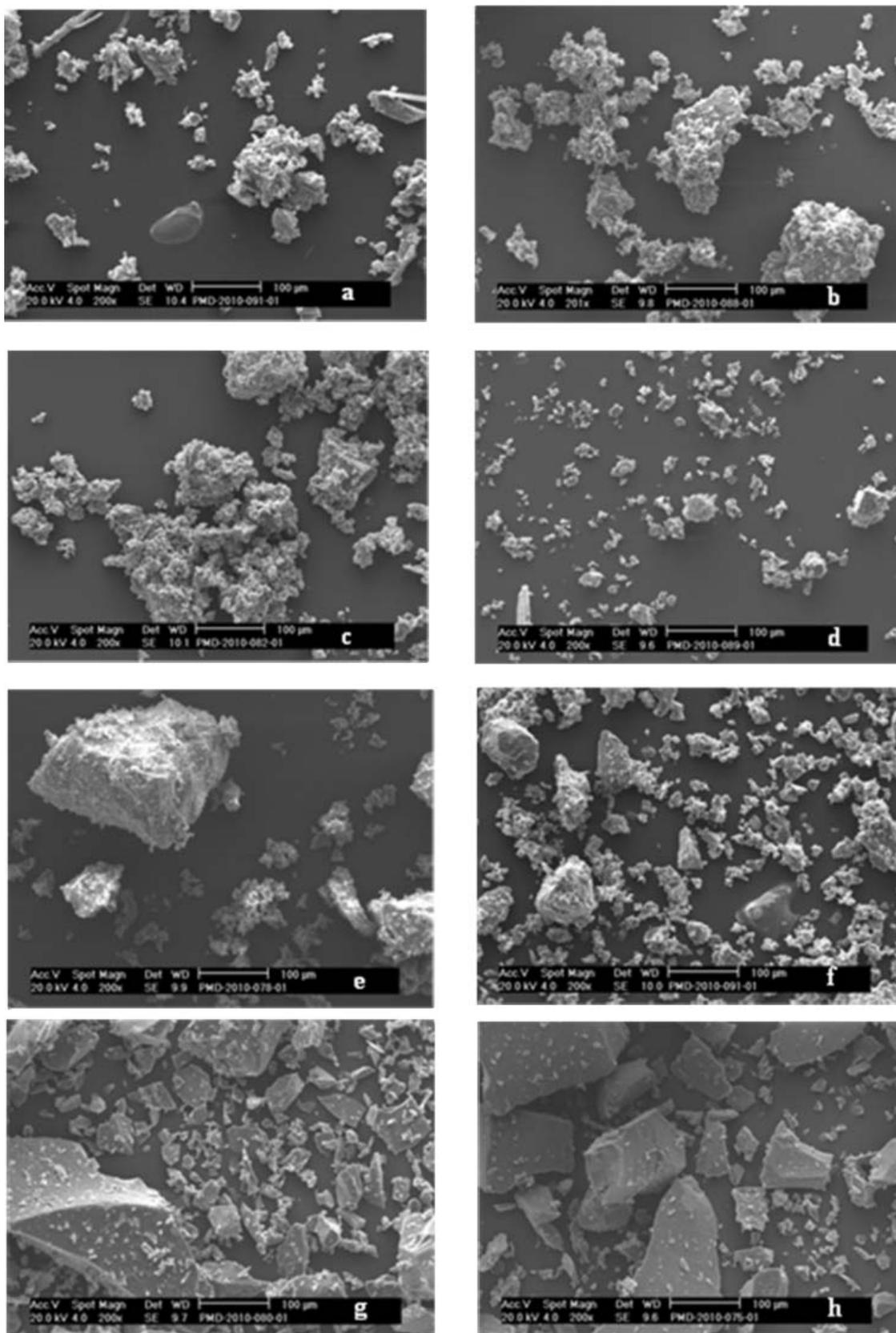


Figure 4 SEM micrographs of the solid products formed at 350 °C to 750 °C: (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C, (e) 550 °C, (f) 600 °C, (g) 650 °C, and (h) 750 °C.

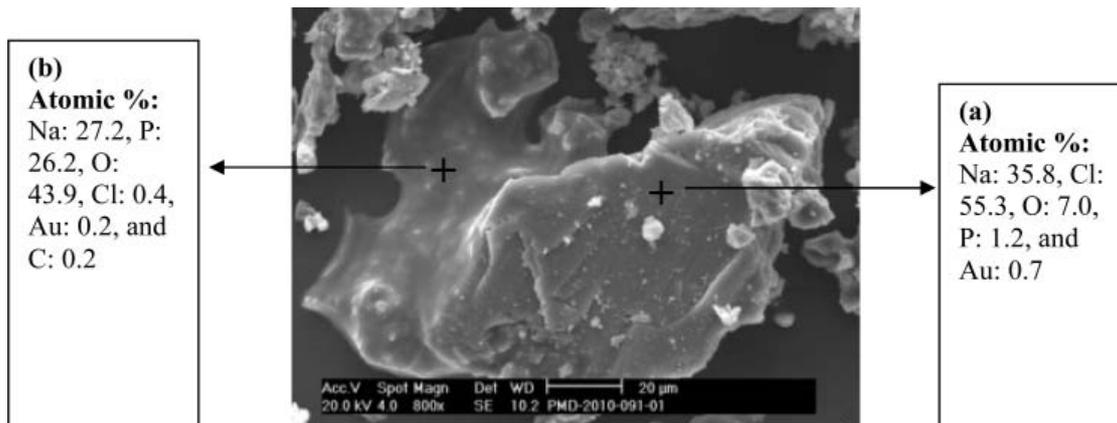


Figure 5 Example of EDX analysis on the glossy (a) and light crust (b) surfaces of the same particle from the product formed at 600 °C.

At 350 °C (micrograph a), most particles were similar with a gray glossy surface covered partially by light crust. Besides, there were also some particles which had a totally glossy surface. At higher reaction temperatures, there were no more any totally glossy particles. The surface of the particles covered by light crust increased with increasing reaction temperature up to 600 °C. At 650 °C and 750 °C, a perfect homogeneity of particle surface was observed, explained by the melting of these products at 628 °C as demonstrated by TGA-DSC results.

EDX analysis was then performed on all solid products. For the solids which had non homogenous appearance (products formed from 350 °C to 600 °C), sodium and chlorine were detected as two major elements on glossy surfaces that must correspond to NaCl remaining after reaction. On the other hand, all EDX analyses of light crust's surface showed the presence of sodium, phosphorus, and oxygen as major elements. Chlorine was frequently present on the light crust's surface but its content decreased with increasing reaction temperature. So, the light crust corresponded to the solid product of the reaction. It grows and sticks directly on the surface of NaCl particles. As an example, Figure 5 presents EDX analysis on glossy and light crust surfaces of the same particle of the solid product formed at 600 °C. Note that the presence of C in EDX results was due to the CO₂ present in air during the analysis and the presence of Au was due to the metallization for SEM sample preparation.

The result of SEM-EDX analysis revealed also that when a particle of sodium chloride is totally wrapped in light crust (or product of the reaction), it could not be in contact with the H₃PO₄ and the reaction slows up. So, the particle size of NaCl powder could be an important parameter of the reaction.

CONCLUSION

SCTP can be conveniently prepared in a one step thermal process by heating sodium chloride and H₃PO₄ as economical starting materials. It can be claimed that this synthesis represents also a smaller ecological footprint because it avoids the use of a strong base in comparison with the competing industrial process. Hydrochloric acid is the by-product of the reaction and could be recovered by condensation.

Reaction temperature was found to be a crucial parameter in the formation of the desired product (SCTP). The most favorable reaction temperature was at 600 °C with 96% of chloride elimination rate and 84% of selectivity in SCTP. Lower temperatures led to important remains of chloride residues while higher temperatures led to the transformation of SCTP into a Graham's salt-like product after melting at 628 °C.

EXPERIMENTAL

Reactor

A quartz reactor consisting of a cylinder-shaped tube with gas input and output, a 65 mL crucible where the reaction takes place and a stick for keeping the crucible fixed was used. The reactor was heated by a vertical furnace with defined temperature program.

Fine powder of sodium chloride from Acros Organics (volume-mean diameter of 375 μm) and H_3PO_4 (85 wt% pure grade) from Merck were used as received without further modification. For the reaction, 5.1 g of sodium chloride and 10.1 g of 85 wt% H_3PO_4 were introduced into the crucible at room temperature, corresponding to a 1/1 Na/P molar ratio. The reactor was then heated to the reaction temperature (between 150 °C and 750 °C) and kept at this temperature for 30 min. After this temperature plateau, the reactor was freely cooled down to room temperature. During the reaction, an air circulation at constant flow rate of 120 L/h was applied. Output gas was trapped into a wash bottle containing pure water or an aqueous potassium hydroxide solution.

The concentration of sodium and phosphorus in solution was measured by ICP-AES (inductive coupled plasma atomic emission spectroscopy) using a HORIBA Jobin Yvon Ultima 2. The concentration of different anions (Cl^- , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, and $\text{P}_3\text{O}_9^{3-}$) in solution was analyzed using a Dionex ionic chromatography apparatus equipped with a Dionex P/N 061830 conductivity detector and a Dionex IonPac AS 19 (4 \times 250 mm) column. The mobile phase was constituted by ultra-pure water eluted at a rate of 1 mL/min and the pH was regulated and kept constant at 13 by a Dionex ICS-3000 EG eluant generator. The anions listed above were identified by comparison of their retention times with those of authentic samples.

TGA-DSC analysis was carried out in a TA Instruments SDTQ600 analyzer. It measures simultaneously the heat flow and weight changes associated with transitions and reactions in materials over the temperature range from ambient temperature to 800 °C under air atmosphere (100 mL/min). About 10 mg of the sample were used for each measurement with a heating rate of 5 °C/min. XRD data for the solids was collected using a Phillips Panalytical X'pert Pro MPD diffractometer with a $\text{Cu K}\alpha$ (1.543 Å) radiation source and a nickel film which suppressed the $\text{Cu K}\beta$ ray. SEM-EDX measurement was performed on a Philips XL30 ESEM apparatus (FEI Company). Metallization of SEM-EDX sample was carried out with metallic gold in a SC 7640 Sputter Coater (Quorum Technologies).

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