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Synthesis and Infra-Red (IR) Characterization of Silica, Alumina and Phosphate Frame work

A graduation research project
submitted to the Department of Chemistry in partial fulfillment of the
requirements for the completion of the degree of Bachelor of Science in
Chemistry

by

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Under Supervision

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I have great honor to be part of this wonderful educational community, which help me to learn Science at high level education and training. I wish all of you, the Department and Professors all success in the future.

Abstract

In this work, we conducted several reactions to prepare metal phosphate salts. We used two methods are reported in the literature. The first method is to react the phosphoric acid with sodium hydroxide to obtain monosodium phosphate. While, sodium carbonate was reacted with phosphoric acid to obtain disodium phosphate in the second method.

The metal-phosphate salt was reacted with silica gel, which has terminal hydroxyl groups in another condensation reaction to incorporate sodium-phosphate on the silica surface. The silica-metal-phosphate was then reacted with aluminum chloride to obtain the SAP final product.

Each obtained compound were characterized by IR and compared with the IR spectrum of the readymade salt or the starting materials.

Introduction

Metal phosphate compounds, and specially sodium phosphates are playing major roles in various industries. Sodium phosphate mono and di-hydrates are widely applied in the food industries as emulsifiers, texturizer, thickening agent, neutralizing agent, nutrient and leavening agents.^{1&2} It is also used in medicine, chemical industry, water treatment and other fields.³ These compounds have also some other application in fuel and detergent additives as well.⁴

Recently, phosphate, aluminum, iron, chrome and other elements are incorporated in different silica framework for catalytic application. Different applications have been reported in the literature for these compounds in more precise for catalytic reactions. Some of these framework catalytic systems commonly contain silica, aluminum, and phosphorous (SAP). These compositions have been used as modified supports for the catalyst. For instance, alumina and phosphate are playing major roles on silica supports for catalysis for ethylene polymerization.⁵ They have been used to prepare various types of Zeolites as well, which are captured major attention of catalytic industrial applications.⁶ Accordingly, we are trying different composition of SAP for similar catalytic studies. However, we are trying different new approach to prepare these compounds for specific application and in more controllable framework.

In this work, we are trying to reach our goals by preparing different composition and ratios of SAP using different raw materials and methodology as well. Low cost, simple preparative way, high yield, and more controlled structure product are essential factor in our work. Therefore, we use very basic materials such as sodium hydroxide, sodium or cesium carbonate and phosphoric acid to produce metal phosphate salts. These different salts will be incorporated with aluminum chloride and silica to yield the SAP final product.

Reflux with Dean-Stark apparatus was applied on when all these condensation reaction are completed for immediate remove of all generated water from the reaction medium. Soxhlet Extraction Apparatus was also used to purify the product in ethanol.

Experimental Part

All chemicals were used as available with no further treatment or purification. Phosphoric acid is 98% received from Qorpak, sodium hydroxide pellets are manufactured by BDH. Sodium carbonate anhydrous are used as received from Fisher Scientific. Methanol, ethanol and isobutanol provided by LOBAL Chemie were used as received with no further drying. Acetone synthesis grade and toluene analytical grade were received from Scharlau. Hydrated silica gel grade of W-955 from Grace-Davison was used without any pretreatment. All IR spectra were obtained from powder samples using Bruker IR.

Experiment 1:

Preparation of mono-basic sodiumphosphate from NaOH:

In a round bottom flask, 0.25 mol of NaOH was dissolved in iso-butanol and methanol. After vigorous stirring, 0.25 mol of phosphoric acid was added slowly to the base solution, Equation 1. Immediately, white powder suspension in the solvent is observed. The addition was continued under stirring at room temperature. The reaction left to stir for overnight. The dean-stark apparatus provided with condenser was assembled on the reaction flask as shown in Figure 1. The reaction heated up to about 150 °C in order to remove the free obtained water from the reaction medium. The reaction kept to reflux until no drops of water were condensed in the dean-stark flask. The reaction was filtered through medium porous frits under vacuum, washed thoroughly by acetone and dried to obtain a clear white color powder.

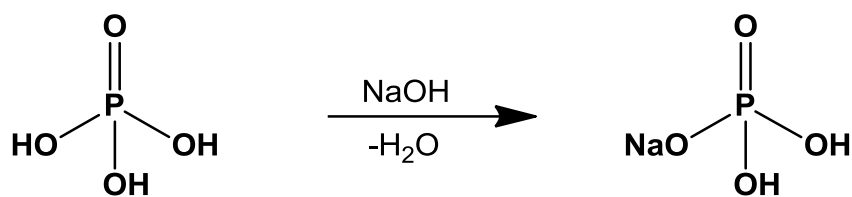


Figure 1: Preparation of mono basic sodiumphosphate using Dean-Satrk apparatus

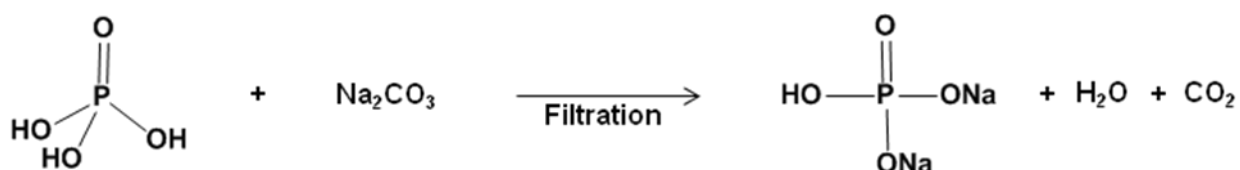
Experiment 2:

Preparation of di-basic sodiumphosphate from Na_2CO_3 :

Amount of 0.19 mol of Na_2CO_3 was dissolved in 100 ml of methanol and toluene in a round bottom flask. Phosphoric acid (0.19 mole) was added in portions under continuous stirring at room temperature, Equation 2. Immediately, white powder suspension in the solvent was observed with bubbles and water formation. The addition was continued under stirring at room temperature. The reaction left to stir until no more bubbles are observed. The reaction left to stir for 2 hours more, before dean-stark apparatus reflux was applied on the reaction to remove the free obtained water from the reaction medium. The reaction kept to reflux until no drops of water were condensed in the dean-stark flask. The solvent was removed using rotary evaporator (Roto-vap) to obtain white free flow powder. It was washed thoroughly by acetone and dried for characterization.



Equation 1: Chemical reaction of phosphoric and sodium hydroxide



Equation 2: Chemical reaction of phosphoric and sodium hydroxide

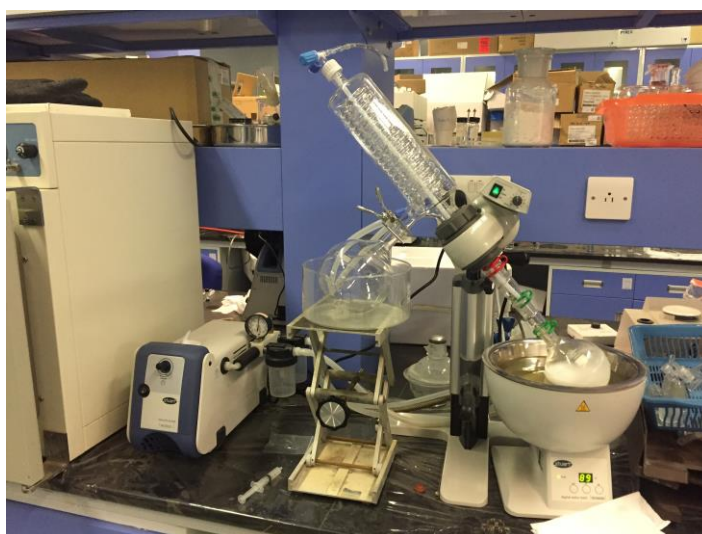


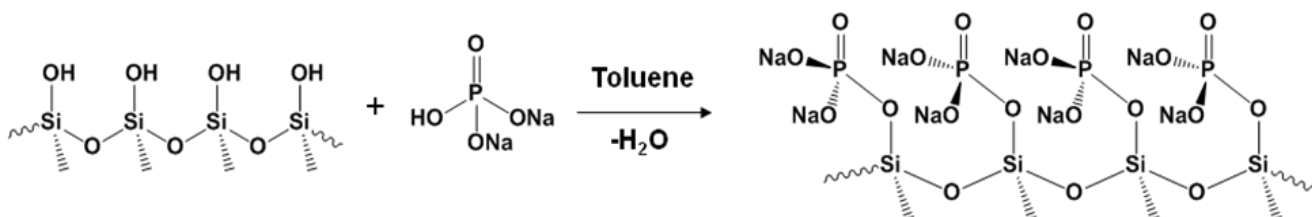
Figure 2: Drying the sodium phosphate by Roto-Vap under vacuum

For further purification, the obtained product was placed on the Soxhlet Extraction Apparatus and reflux in ethanol. The reflux applied for 3 hours before the product removed and washed by acetone and dried.

Experiment 3:

Reaction of di-basic sodium phosphate and Silica:

In a round bottom flask provided with Dean-Stark apparatus and condenser, 5 g of silica was placed with 0.18 mole (42 g) of di-basic sodium phosphate and toluene. The reaction left to stir and reflux for 4 hours under continuous remove of the obtained water. The product was filtered and thoroughly washed with acetone. Fine free flow white powder was obtained according to Equation 3.

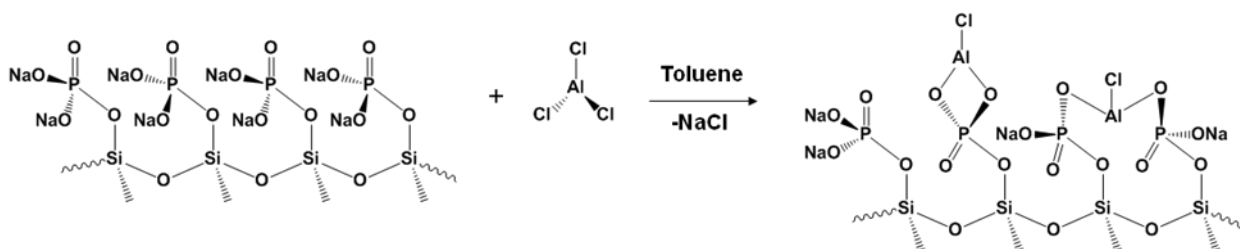


Equation 3: Reaction of di-basic sodium phosphate and Silica

Experiment 4:

Reaction of silica-phosphate product of Ex. 3 with AlCl₃:

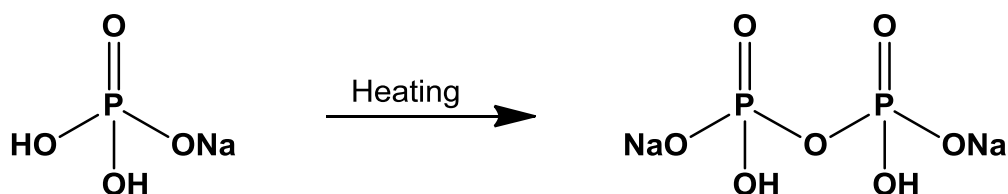
In a round bottom flask, 0.18 mole of AlCl₃ was added to the suspension of silica-phosphate in toluene, according to Equation 4. The reaction was gently refluxed for 4 hours to obtain white powder. The product was filtered and washed by acetone. According, the under continuous remove of the obtained water. The product was filtered and thoroughly washed with acetone. Fine free flow white powder was obtained.



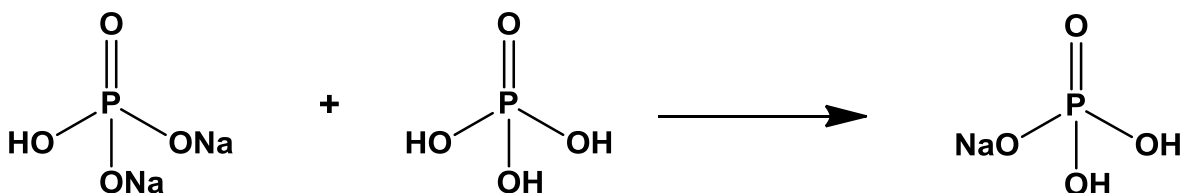
Equation 4: Reaction of silica-phosphate product of Ex. 3 with AlCl₃:

Results and Discussion

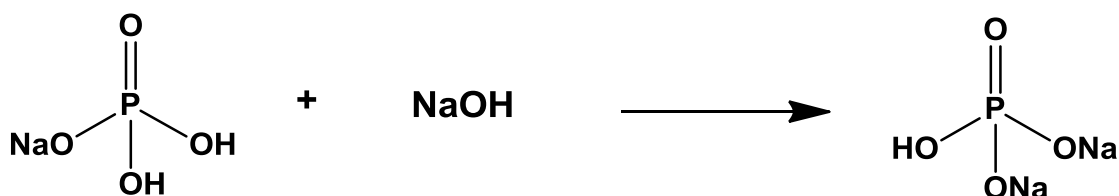
The sodium phosphate has been prepared according to different reaction and starting materials. In the first reaction straight forward acid-base reaction was followed to obtain di-basic sodium phosphate as illustrated previously in Equation 1. By heating the reaction to remove further water, sodium phosphate dimer can be obtained as shown in Equation 5. Further treatment of disodium phosphate with phosphoric acid or monosodium phosphate with sodium hydroxide will reach the equilibrium to give monosodium and disodium phosphate respectively as shown in Equation 6 & 7.



Equation 5: Heating up of monosodium phosphate to produce dimer-sodium phosphate



Equation 6: Equilibrium reaction of disodium phosphate with phosphoric acid to produce monosodium phosphate



Equation 7: Equilibrium reaction of monosodium phosphate with sodium hydroxide to produce disodium phosphate

These reactions have been carried out in order to prepare the both mono and disodium phosphate. The products of experiment 1 and 2 have been characterized by IR. As shown in Figure 3, a broad peak at the range of 3200-3600 cm^{-1} of the hydroxyl group of water coordinated to the product. Another broad peak is shown in the range of 2550-2700 cm^{-1} representing the phosphonic acid ($\text{O}=\text{PO}-\text{H}$), at 1100-1200 and 570 cm^{-1} represents the phosphine oxide $\text{P}=\text{O}$ and phosphate $\text{P}-\text{O}$.⁷

The broad peaks at 1300-1500 and 3200-3600 cm^{-1} which are representing OH groups were disappeared after purification of product 2 as shown in Figure 4.

The melting point test indicates that the products these reactions are dimer or oligomer of phosphate. Our critical observation of the melting point test of these products showed marginal change (melted material) at the range of 90 & 260 $^{\circ}\text{C}$, which are melting point of mono and disodium phosphate respectively. But the major material does not melt until 400 $^{\circ}\text{C}$, the maximum temperature of the instrument. It has been reported that the melting point of dimer phosphate is higher than 600 $^{\circ}\text{C}$.⁸ further investigation for melting points of the produced compounds will be conducted using Differential Scanning calorimetry , DSC.

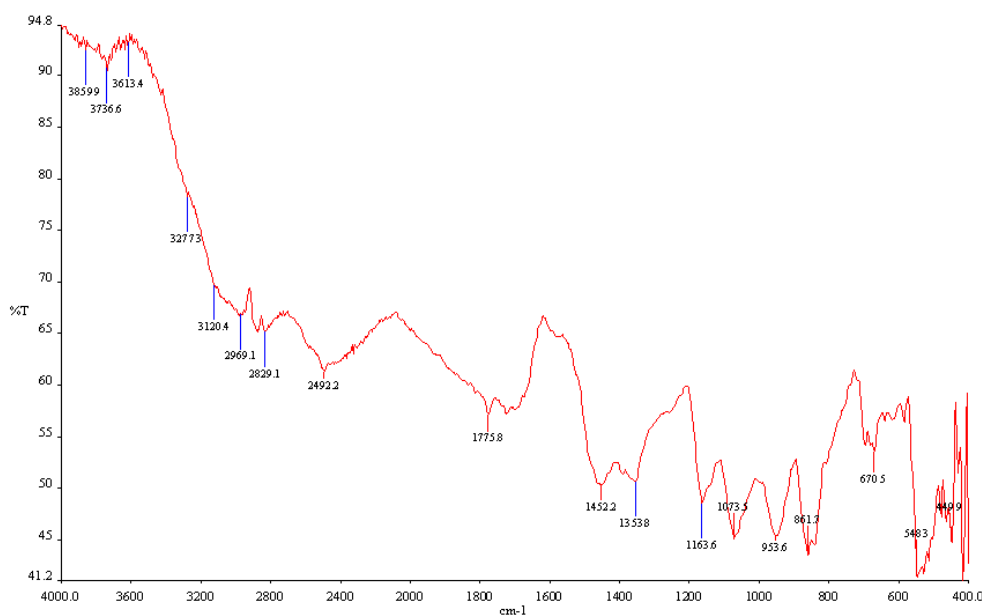
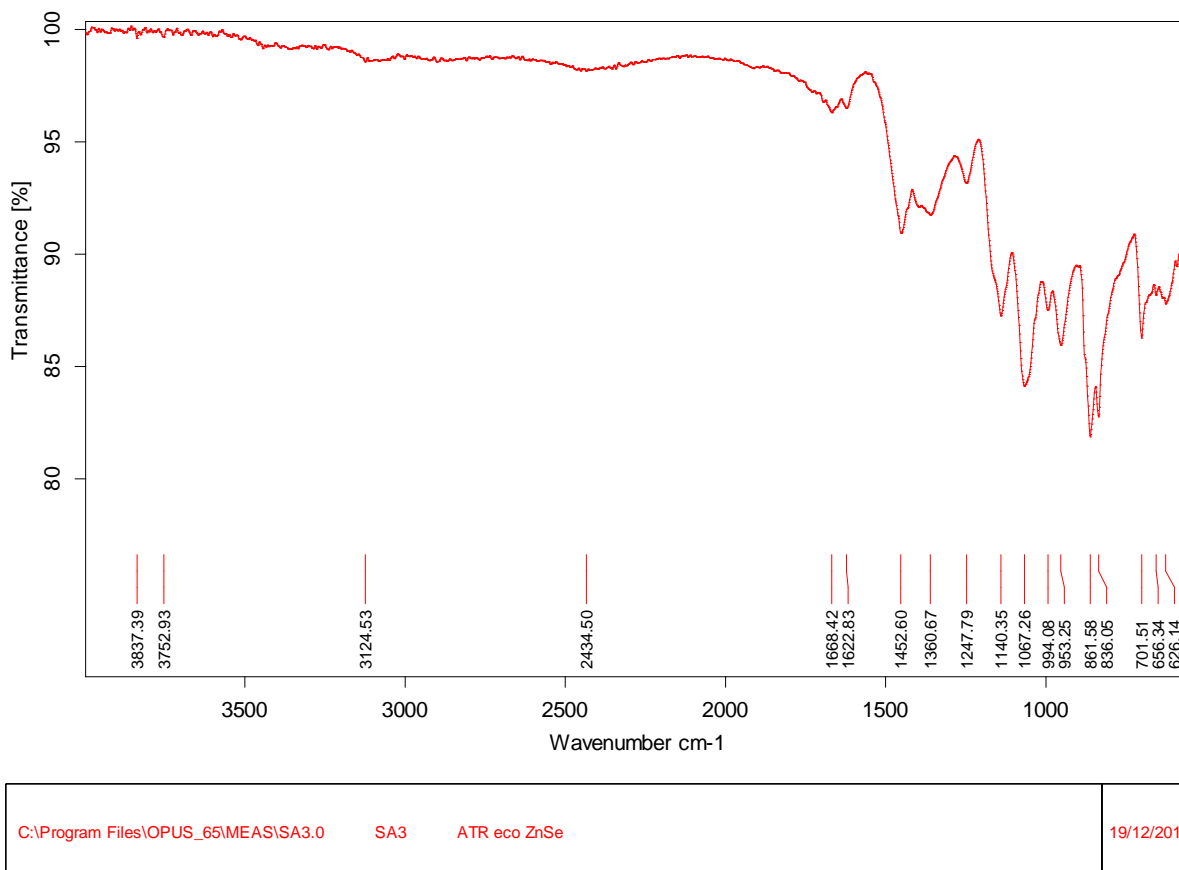


Figure 3: The IR spectrum of product obtained in Ex. 2.



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Figure 4: IR spectrum of the Purified Product 2.

The reaction of phosphate with silica produced white fine powder. The IR spectrum of the produced compound has shown broad peaks at both characteristic range of phosphate. However, clear indication of the two components reaction has been observed as a reduction on the intensity of the OH peak at 3500 cm^{-1} of the silica. Although, no clear evidences of the incorporation between the two components, however, the broadness in the peak at $1000\text{-}1200\text{ cm}^{-1}$ is a good indication of the overlap of the two character peaks of PO_4 and O-Si-O at 1097 & 1106 respectively as shown in Figure 5.

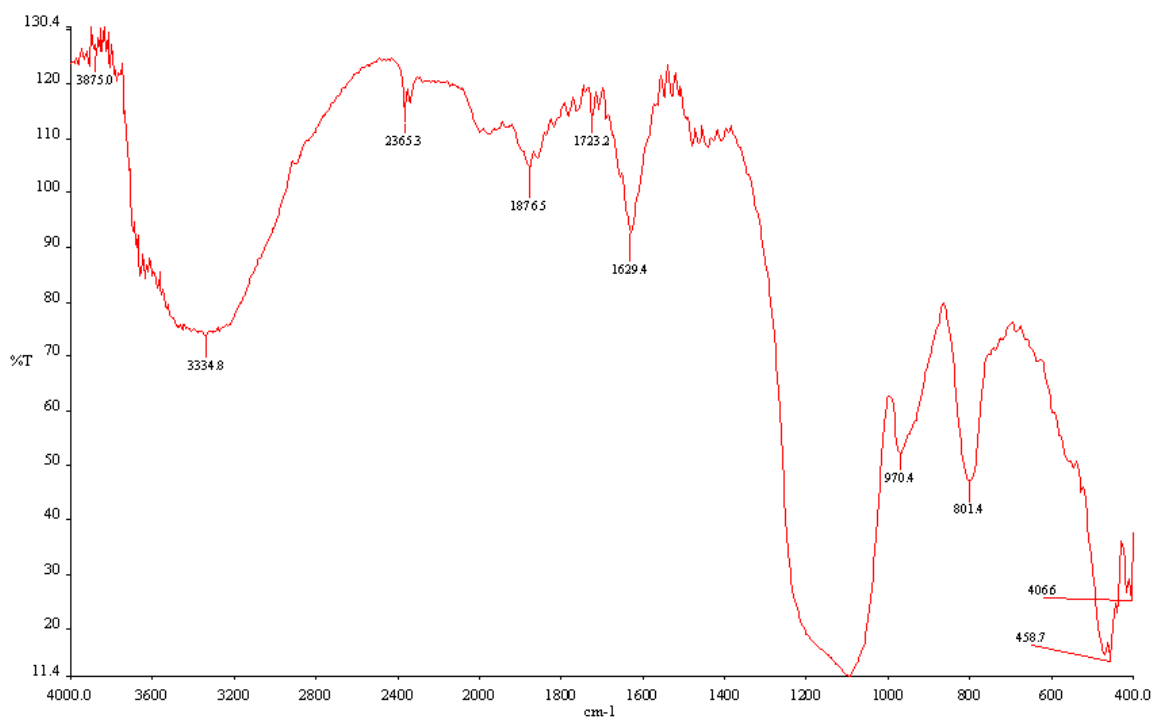


Figure 5: IR spectrum of Experiment 4.

Conclusion

The sodiumphosphate was prepared from experiment 1, experiment 2 according to reaction in equation 1, equation 2 to gives mono-basic sodiumphosphate and di-basic sodiumphosphate respectively, then reaction of di-basic sodiumphosphate with silica in equation 3 to gives silica sodiumphosphate which reacts with aluminum chloride to gives the SAP in equation 4.

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