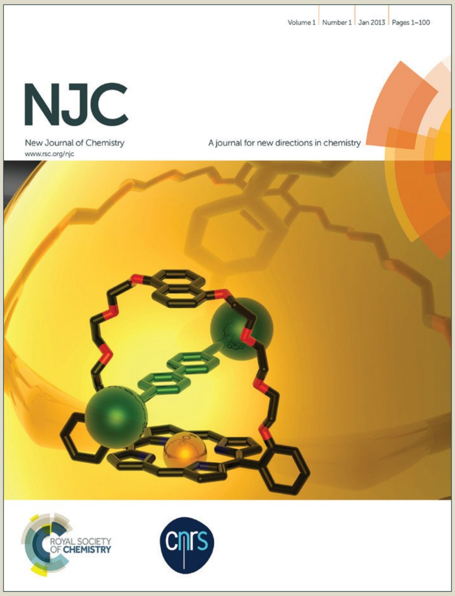
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ARTICLE

Synthesis of Zeolite A using kaolin from Ethiopia and its application for detergents

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Most commercial manufacturers of soap and detergents in developing countries and few developed countries are still using environmentally unfriendly phosphate based materials like sodium tripolyphosphate as detergent builders. Detergents that contain phosphorus contribute to the eutrophication of fresh waters. To surmount this problem, many detergent manufacturers are currently using zeolite A as the builder material which has proved to be a better substitute for phosphorus additives. Despite its remarkable potential, the high cost of zeolite A has limited its effective use in detergents. In this work detergent-grade zeolite A has been synthesized from the Ethiopian kaolin collected from the southern part of the country with the molar gel composition of Na_2O: Al_2O_3: $2SiO_2$: $37H_2O$. Two routes are surveyed for the synthesis of the zeolite A: alkali fusion using raw kaolin, and conventional hydrothermal synthesis. The resulting zeolite A samples are studied by X ray diffraction (XRD), Scanning Electron Microscopy (SEM), chemical analysis (ICP) and Thermogravymetry (TGA). Moreover, the cation exchange capacity (CEC) >310 mg of $CaCO_3$/gm as well as average particle size of 3 µmof zeolite A is found to be satisfactory to be used as a detergent builder. This study also focused on evaluating its potential use as detergent by analyzing some physicochemical properties like foam height, pH value, moisture content and alcohol insolubility of the formulated detergent using our synthetic zeolite A. The result showed that the synthesized detergent has comparable detergency to commercial brands of powder detergents.

Introduction

Laundry detergents are compositionally made of at least six groups of components: surfactants, builders, enzymes, bleaching agents, fillers and other minor additives such as dispersing agents, fabric softening clay, dye-transfer inhibiting ingredient, and optical brighteners. Among these components, builders take the share of almost 30%. In detergents, builders constitute about 6-25 wt% of liquid detergents and about 20-55 wt % of powder detergent formulations. Thus, builders play a significant role in the detergents market[1]. Sodium tripolyphosphate (STPP) has been the most commonly used detergent builder. The job of phosphates is to sequester water hardening alkaline earth metal ions, calcium and magnesium, in order to favour solubilising, emulsifying and suspending action of surfactants[2]. However, in the 1980s STPP was banned in the USA and Western Europe due to eutrophication, excessive growth of algae and fungi, in water bodies. This led to an intensive search for the development of acceptable substitutes[3]. The introduction of ion exchange materials and zeolites as detergent builders led to the gradual movement away from phosphate based materials[4,5]. The high cation exchange capacity and special particle morphology of zeolite A makes it a viable alternative as a detergent builder. Over the past 20 years, the trend towards compact detergents increased the demand for zeolite A. Zeolite A is now a builder leading to compact and super compact detergents[6]. This strong versatility has expanded the applications of zeolite A reaching 73 % of the total production of synthetic zeolites, ranking it as an important inorganic chemical[7]. Besides, it is environmentally safe with almost zero loading of harmful effect on the environment[8]. Zeolite A, LTA (Linde Type A) or 4A is a synthetic sodium aluminosilicate, a low silica zeolite with Si/Al = 1 represented by the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$. It has cubic crystal structure with a lattice parameter of 12.32 Å. Zeolite A

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is characterized by a 3-dimensional network consisting of cubic α-cages, placed in the centers of the edges of a cube in the truncated octahedral and β-cage (sodalite cage) linked by double 4-ring (D4R). These α-cages connect the β-cages, creating a three-dimensional structure having pores of size 4.2 Å. Each corner of the cube (α-cage) is occupied by the truncated octahedra (β-cage) enclosing a cavity with a free diameter of 6.6 Å. The centre of the unit cell is a large cavity, which has a free diameter of 11.4 Å. This particular porosity allows for shape selectivity in acid catalysis, specifically in the conversion of n-paraffins and olefins to smaller chain alkanes[9]. Zeolite A is also widely used in wastewater treatment, including the removal of radioactive ions[10]. Although, the commercial production of detergent-grade zeolite A is mainly conducted using the aluminosilicate hydrogel route using sodium silicate and sodium aluminate[11], its use as builder in detergents requires a competitive price with regard to phosphates and other possible sequestering agents. In order to overcome this challenge, many investigations are still devoted to the synthesis of detergent grade zeolite A from inexpensive raw materials. Among these cheaper raw materials: clay minerals, coal ashes, natural zeolites, municipal solid wastes and industrial sludge have been tested[12, 13]. With these naturally available raw materials, kaolin which has Si/Al ratio of nearly 1 similar to zeolite A has been used as alternative cheap raw material for the synthesis of zeolite A[14]. The synthesis of zeolite A from kaolin involves two basic steps: metakaolinization, which is the calcination of the raw kaolin at high temperature to change chemically stable kaolin into a very reactive but amorphous material, metakaolin, and hydrothermal treatment of the calcined to yield the crystalline zeolite A[15]. The synthesis of zeolite A from kaolin source started in the 1970s by the hydrothermal reaction of dehydroxylated kaolin with sodium hydroxide solution[16]. During the past four decades, there have been relevant studies and patents reported in this area trying to minimize the synthesis cost with good quality detergent grade, pure zeolite A[17-20]. Among various studies conducted, apart from the conventional hydrothermal method of zeolite A synthesis, alkali fusion followed by hydrothermal synthesis has been used to obtain single crystals of zeolite A. This method enhances the dissolution of the Al_2O_3 and SiO_2 from the starting raw kaolin and avoids the use of alkaline solution. In this work, we investigated the transformation of kaolin from Ethiopia into zeolite A by two different methods: (1) alkaline fusion followed by hydrothermal reaction which involved the direct use of raw kaolin without any pre-treatment and (2) conventional hydrothermal synthesis which involved the use of both raw and purified kaolin. Besides to the comparison of the two synthesis methods in terms of quality of the final zeolite A, in this paper we mainly focused on the application of these synthetic materials as detergent builder.

Experimental

The raw kaolin sample was collected from Hawassa ceramic factory which is located in the southern part of Ethiopia. For the purification of the raw kaolin, mechanical methods such as separation and sedimentation were employed for the removal of quartz, and ultrasonic suspension followed by magnetic separation for the removal of iron species. Analytical grade NaOH pellets was purchased from Sigma Aldrich. Commercial Zeolite A was purchased from Industrias Químicas Del Ebro (Spain) for the comparative studies.

Alkali fusion and conventional hydrothermal synthesis of zeolite A

In the application of this method, the raw kaolin was dry-mixed with the base in the form of NaOH pellet. The synthesis was as follows: 1.25 g of the raw kaolin was dry-mixed with 1.5 g of NaOH (solid) for 30 min followed by calcination at 600 °C for 1 h in a muffle furnace. Then the fused product was ground in a mortar and mixed with 12.5 ml of the ultra pure distilled water and stirred (500 rpm) at 50 °C for 1 h for gel formation. The gel formed was aged under static condition (0, 1, 3 and 6 h) at room temperature (RT). For the conventional hydrothermal synthesis, raw and purified kaolin were tested. In this case, the activation of chemically inert kaolin was performed by taking 5 g of both raw and purified kaolin in a separate crucible and calcining it at 600 °C for 3 h in a muffle furnace. Then the alkaline treatment was done with 3 M NaOH with stirring (500 rpm) at 50 °C for 1 h for the complete homogenization of the reaction mixture. The gel formed undergoes aging at room temperature under static condition similar to the alkali fusion synthesis method. The molar gel composition for both methods was:

$$Na_2O: Al_2O_3: 2SiO_2: 37H_2O$$

Crystallization for both synthesis routes was carried out by hydrothermal method in water bath under static condition for 3 h at 100 ^{o}C. Once the time was reached, the bottles were quenched in cold water to stop the reaction. The reaction mixtures with pH 13 were filtered and washed with distilled water to remove excess alkali until the pH of the filtrate fell below 10. Then, the samples were oven dried overnight at 80 °C. The final products from the conventional hydrothermal method with the raw kaolin have been labelled as R-3M-3G-3h, the one with the purified kaolin as P-3M-3G-3h and the alkali fusion product is named F-3M-3G-3h.

Characterization of the synthesized zeolite A

Powder X-ray diffraction (XRD) patterns were collected with a Philips X'PERT diffractometer equipped with an X'Celerator detector and using Cu, Kα radiation. The percentage of crystallinity of the synthesized zeolite A was calculated by comparing the sum of peak intensity of the most five intense peaks of the synthesized zeolite A (d_{442} at 21.67°, d_{622} at 23.99°, d_{642} at 27.11°, d_{820} at 29.94° and d_{664} at 34.18°) and the commercial zeolite A[18]. Inductively Coupled Plasma Optical Emission Spectrometry, (ICP-OES) (Optima 3300 DV model) was used to determine chemical weight percent composition of the samples. The morphology was studied by Scanning Electron Microscopy using a NOVA NANO SEM 230 (FEI). Thermal stability of the kaolin and synthesized zeolite A was carried out in air, with a Perkin-Elmer TGA 7 instrument in the temperature range of 20-900 °C at a heating rate of 20 °C/min. The Cation Exchange Capacity (CEC) of the Na-form of synthesized samples of zeolite A has been studied using a GLP 22 multimeter Ca ion selective electrode. For this test, 0.5 g of zeolite A is first dried at 110 °C for 1 h. Then, it was cooled down to room temperature in a desiccator, weighed again and poured into a beaker containing 500 ml of 0.005 M $CaCl_2 \cdot 6H_2O$. The removal of Ca^{2+} ion from the solution was measured with initial water hardness of 500 mg $CaCO_3$/L, which is considered as very hard water. The mixture obtained is vigorously stirred at room temperature for 15 min. The zeolite is then filtered off and the residual Ca^{2+} concentration is measured in the filtrate using Ca ion selective electrode.

Formulation of powder detergent

Sodium sulphate, linear alkylbenzene(C12) sulphonate (LABSA), zeolite A, sodium tripolyphosphate (STTP), sodium silicate, soda ash, were mixed and homogenized in a mixing unit. The formulation of 25 g of detergent contains 55 % sodium sulphate, 15 % LABSA, 8 % sodium silicate, 7 % soda ash and the remaining 15 % is formed by either pure zeolite or zeolite A:STPP in 50:50. For this particular formulation, esthetical value additives such as optical brightener, perfumes, preservatives, active enzymes and stabilizer have not been used. In addition, a commercial powder detergent having sodium aluminosilicate as a builder was tested for comparison. The three zeolite A samples synthesized from Ethiopian kaolin were compared with a commercial zeolite A. In this study we have tried to substitute STTP from 50 to 100 % by Zeolite A in the detergent formulation composition. Based upon the type of synthetic zeolite A used for the formulation, the detergent formulated is abbreviated as: detergent synthesized with commercial zeolite A (DZAC), detergent made of synthesized zeolite A by alkali fusion method (DZAF), detergent made of synthesized zeolite A from raw kaolin (DZAR) and detergent made of synthesized zeolite A from purified kaolin (DZAP).

Characterization of the formulated detergent

The formulated detergent sample was then tested using various physicochemical parameters such as moisture content, foam height, pH measurement and alcohol and water insolubility test, which is adapted from Ethiopian Standard for Soaps and Detergent[19]. The same tests were also conducted on the known commercial powder detergent brand and the results of their comparative evaluation are presented. Foam height measurement was done by preparing 1 % detergent solution. 1 g of the detergent is dissolved in 99 ml of real hard water having moderate hardness (120 mg $CaCO_3$/L,). Then 10 ml of the prepared solution was taken and shacked very well using 100 ml measuring cylinder with a glass stopper until the detergent is completely dissolved and forms foam. The foam height was measured after 10 minutes stability of the foam. The pH of the 1 % detergent solution was measured using pH meter at 25 °C following the calibration of the instrument. For the moisture and volatile content, 5 g of detergent sample was weighed, and dried to constant mass in an oven at 105 ±2°C. This was done until constant mass is attained when successive heating for one-hour period shows less than 5 mg difference. The % moisture content was calculated using the following equation:

$$\%\ \text{Moisture} = \frac{\text{Initial weight – Final weight of the sample}}{\text{Initial weight of the sample}} \times 100$$

Insoluble matter in alcohol refers in this scenario to inorganic salts, such as phosphates, sulphates, silicates and carbonates, which are usually present in non-soapy detergent preparations. This was done by weighing 5 g of the detergent into a beaker, and digested with 50 mL of ethanol, followed by heating on a steam bath for about 2 minutes. Any hard lump was broken down with a glass rod flattened at one end. The solid matter was then allowed to settle and decanted through a sintered glass filter funnel. The alcoholic digestion was repeated in a similar manner with five further consecutive 30 mL portions of boiling ethanol. Each extract was filtered in turn through the same sintered glass funnel and the residue was washed several times with hot ethanol to remove all the alcohol soluble matter. Finally, the sintered glass funnel was dried with the residue at a temperature of 105 ±2 °C until a constant weight is obtained. The insoluble matter in alcohol is determined using an equation:

$$\text{\% Mater insoluble in alcohol} = \frac{\text{Mass insoluble in alcohol}}{\text{Initialmass in gram}} \text{x100}$$

For water insoluble matter analysis, 5 g of detergent sample was weighed and digested with 200 ml of freshly boiled water until sample is completely dissolved. Then, the solution was filtered through the filter paper dried at 105 ^{o}C and mass recorded. The residue was washed several times with hot water. And the filtrate and the residue were dried t for 3 h at 105 ±2 °C. Finally, the water insoluble matter was calculated using the equation below.

$$\text{\% Mater insoluble in water=} \frac{\text{Mass insoluble in water in gram}}{\text{Initial mass in gram}} \text{x100}$$

Results and discussion

Purification of the raw kaolin

Purification of the raw kaolin was done in order to remove mainly quartz, identified by the intense peak at 24.6°. After sedimentation and decantation we were able to increase the crystallinity in the sample from 60 to 70 %. Further treatment by sonication and magnetic separation was tried in an attempt to remove Fe species present in the sample. The elemental and phase composition analysis result is summarized in table 1. The ICP results confirmed that the clay is mainly composed of kaolinite and minor quartz and other impurities including Fe. After purification, a notable reduction in the Fe content along with the Si content can be observed, due to the elimination of certain amount of quartz, leading to a Si/Al ratio closer to 1, which is required to the crystallization of zeolite A.

Table 1 Chemical composition (wt %) of kaolin from Ethiopian raw (R) and purified (P).

Oxides	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**Si/Al**
Raw	54.7	34.0	0.6	2.1	1.4
Purified	42.2	36.0	0.3	1.3	1.0

Minerals	**Kaolinite**	**Quartz**	**LoI**
Raw	67	27	12.9
Purified	77	19	12.9

LoI = Loss on ignition

Synthesis and characterization of zeolite A

Given the need to activate the kaolin prior the hydrothermal synthesis, we surveyed alkali fusion followed by hydrothermal treatment in order to maximize the amount of quartz and aluminosilicate to be converted into the zeolite. Besides, using alkali fusion, we could avoid any purification of the starting raw material. Figure 1 shows the X ray diffraction patterns of the three samples: conventional hydrothermal method with the raw kaolin (R-3M-3G-3h), the one with the purified kaolin (P-3M-3G-3h) and the alkali fusion product (F-3M-3G-3h). Three of them fit well to the profile of zeolite A[20] although it is possible to follow the changes in the characteristic peak of quartz at 2θ of 26.6°. In the profiles of the samples prepared using the conventional hydrothermal method both from raw and purified kaolin sources (fig. 1a and fig. 1b) the peak of quartz is more intense. Whereas in the XRD profile of the alkali fused product (fig. 1c) this peak is negligible. This feature of the alkali fusion method compared with the conventional method confirms the high efficiency of the alkali fusion technique in optimizing the incorporation of silicon from kaolin and quartz into the framework of the zeolite A. The result obtained is in good agreement with the report of Ríos et al[21], in which they compared the conventional hydrothermal method with the alkali fusion for the synthesis of zeolite A. Apart from comparing the XRD profiles of the synthetic products, the percent crystallinity (% C_{XRD}) has been calculated in reference to the commercial zeolite A. High crystallinity is one of the major requirements for detergent grade zeolite A, which indicates the purity of the material. The Indian standard zeolite detergent grade specification protocol shows the minimum crystallinity requirement of zeolite for detergent application is in the range of 77.5 to 79.5 percent by mass[22]. According to this method, the percentage of crystallinity attained for zeolite A by alkali fusion and the conventional hydrothermal synthesis (raw and purified) is summarized in table 2. The table includes as well the crystallinity data attained using different gel aging (0, 1, 3 and 6 h).

Table 2 Percent crystallinity (% C_{XRD}) of synthetic zeolite A

Synthetic Zeolite A	**0 h**	**1 h**	**3 h**	**6 h**
Alkali fusion	82	87	91	81
Conventional (Raw)	78	79	80	83
Conventional (Purified)	80	81	90	87

In general, the alkali fusion method gives better crystallinity compared to the synthetic products prepared with conventional hydrothermal method (raw and purified). In the synthesis conditions surveyed, i.e., with different aging time, the alkali fusion method, which did not involve any purification, gave better crystallinity results while in the case of the conventional method of synthesis, the purification of the starting kaolin is required to improve the crystallinity, and yet the presence of impurities like quartz remains a drawback.

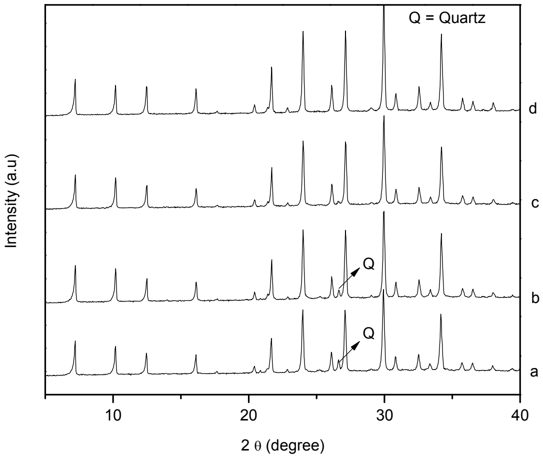

Fig. 1 XRD pattern of synthetic zeolite A: (a) R-3M-3G-3h, (b) P-3M-3G-3h (c) F-3M-3G-3h and (d) zeolite A commercial

In addition to good crystallinity, achieving appropriate morphology and crystal size of zeolite A for detergent application is also very important. Incrustation of textiles can be reduced using the appropriate morphology and crystal size. Zeolite A cubic crystals with sharp edges can be knotted in textile fibres. In contrast, cubes with rounded corners and edges tend to decrease incrustation on textile materials[23]. For zeolite to be used as a detergent grade builder, the optimal range for particle size is 1–10 µm. Crystal sizes smaller than 1 µm may be retained in the textile fibre and damage it, while particles over 10 µm in size cause unacceptable deposition in textile materials, fabric and machine parts[24]. In order to obtain zeolite A with appropriate crystal size and morphology, the gel formed in the alkali fusion method was allowed to age for 1, 3 and 6h at room temperature and compared with no aging at all. From the SEM micrographs (fig. 2), we could conclude that optimum cubic shaped crystals of zeolite A with rounded edges showing average particle size of 3 µm was obtained using 3 h gel aging (F-3M-3G-3h) while the sample prepared without gel aging (F-3M-0G-3h) exhibited large cubic crystal of zeolite A with sharp edges, which is not suitable in detergent application as a detergent builder. Furthermore, sample F-3M-3G-3h resulted in the highest crystallinity (91%) as collected in table 2.

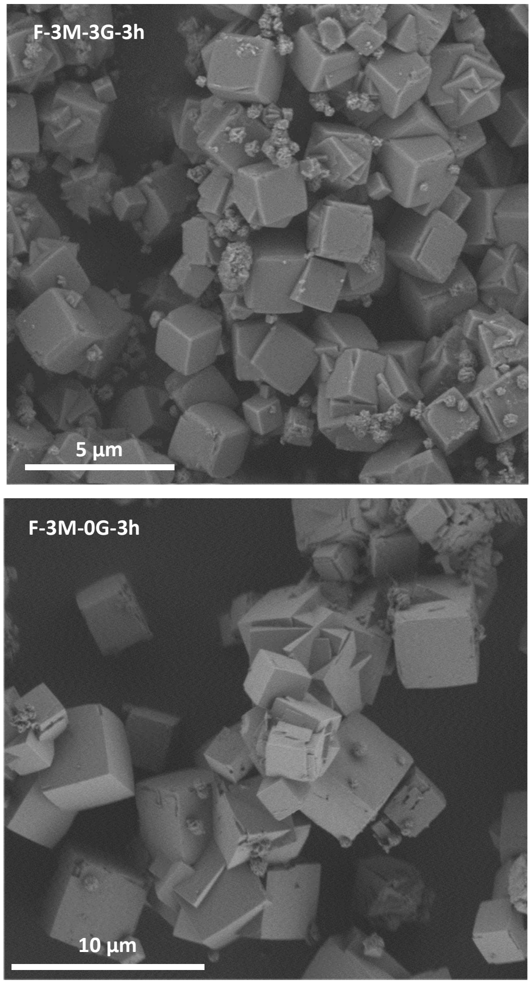

Fig. 2 SEM micrographs of the alkali fusion synthesized zeolite A.

In the case of conventional hydrothermal synthesis, the size of cubic crystal of zeolite A varies within the sample and from sample to sample, indicating a continuous crystallization process through the whole range of time and different generations of crystals. The SEM results obtained by alkali fusion method using 3h gel aging time are in good agreement with the conventional hydrothermal synthesis with purified kaolin under similar synthesis conditions[18]. Therefore, from both synthesis methods, we observed the significance of reaction gel aging on the crystallinity and crystal shape. These results are in agreement with the report of Kosanovic*et al*[25],which stated that the morphological characteristic of the crystallized zeolite A depend on the synthesis condition of the reaction mixture. According to ICP elemental analysis collected in table 3, all detergent-grade zeolites are characterized by high aluminium content, whereby a Si/Al ratio = 1 or virtually 1 is achieved. This in turn results in a maximum content of Na^+ ions, which are necessary to neutralize the zeolite framework. Since Na^+ ions are able to move in the zeolite pores, they can easily be exchanged for calcium ions, and sometimes other ions[26].

Table3 ICP elemental analysis result of synthesized zeolite A

Zeolite A	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	Si/Al
ZA-C	33	28.0	17.4	0.02	1.0
F-3M-3G-3h	27.4	25.0	14.3	0.9	1.0
P-3M-3G-3h	29.4	24.4	13.4	0.9	1.0

ZA-C, Commercial zeolite A

Regarding the thermal behaviour of the synthetic zeolite A, it exhibited total water loss of 20 % at 400 °C (fig. 3)

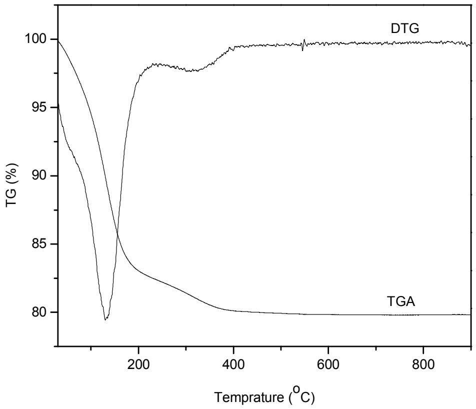

Fig. 3 Thermogravimetric analysis (TGA/DTG) of F-3M-3G-3h

This behaviour confirms the potential for detergent builders since they are typically sold in a hydrated form in which the weight of the hydrated zeolite is approximately 20-22 % water[27].

The main requisite used for the application of zeolite A in detergent formulation is its cation exchange capacity. It is believed that the potential application of zeolite samples as a detergent builder could be addressed from the performance of removing Ca^{2+} and Mg^{2+} ions from hard waters[5]. A builder material possessing higher cation exchange capacity is supposed to excel in water softening, which ultimately results in foaming by reducing surface tension between dirt particles and fabric. The theoretical calcium binding capacity of zeolite A is 352 mg $CaCO_3$/g anhydrous zeolite A. Owing to the presence of other competing ions like sodium or potassium, in the practical detergent washing scenario, this level of calcium cannot be achieved and thus calcium binding capacities of ≥160 mg $CaCO_3$/g is considered good for detergent application[28]. The cation exchange capacity result obtained is directly related with the crystallinity and particle size of the synthetic materials. Our synthetic products obtained by the alkali fusion method (F-3M-3G-3h) exhibited maximum calcium exchange capacity (CEC) of 310 mg $CaCO_3$/g which is comparable with the commercial zeolite A having the CEC of 320 mg $CaCO_3$/g that can be attributed to its higher crystallinity (91 %). Zeolite A from the conventional hydrothermal synthesis method (R-3M-3G-3h and P-3M-3G-3h) also exhibited the CEC of 290 and 295 mg $CaCO_3$/g which is sufficient for detergent application.

Analysis of the formulated detergent

The formulated detergent sample was analysed using various physicochemical parameters such as foam height and pH measurement, moisture and volatile matter content and alcohol and water insolubility. The same tests were also conducted on one well-known commercial powder detergent brand and the results of their comparative evaluation are presented.

A foam height test was used to determine how much foam the detergent can produce. Two compositions were tested: 50 % substitution STPP by Zeolite A, followed by 100 % zeolite A in the formulation. We have used the foam height of the commercial powder detergent as standard. The results obtained are depicted in Figure 4.

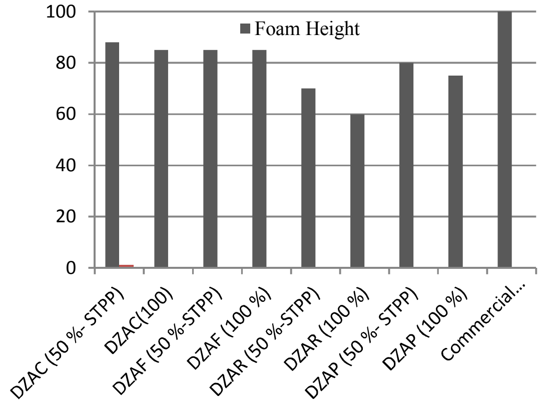

Fig. 4: Foam height of 1 % detergent solution of synthetic zeolite A in comparison with the commercial powder detergents.

From the graph it is possible to see that the 50 % STTP substitution exhibited almost the same height with 100 % STPP substitution by zeolite A. The foam height analysis result is comparable with the foam height of the commercial powder detergent. This promising value exhibited by the formulated detergent based on our synthetic zeolite A builders can be attributed to its higher CEC of 310, 295 and 290 mg $CaCO_3$/g anhydrous zeolite A forF-3M-3G-3, P-3M-3G-3hand R-3M-3G-3h, respectively. It is also possible to observe from the graph that the detergent made of synthetic zeolite A synthesised by alkali fusion (DZAF) exhibited the same foam height in both 50 and 100 % substitution and also the same height with detergent made of commercial zeolite A (DZAC) which can be attributed to the higher crystallinity of the material.

It is also possible to observe that the detergent made of synthetic zeolite from the raw kaolin (DZAR) exhibited the lower foam height compared to the one made with the purified kaolin (DZAP); this could be due to the presence of impurities in the raw kaolin. The pH requirement for 1% aqueous solution of industrial detergent determined at 25 °C shall be not less than 9 and more than 11. In the formulated detergent, pH was 9.8 for DZAF, 10.2 in DZAP and DZAR, and 10.1 for the commercial detergent. Thus, the value measured for powder detergent formulated with our synthetic zeolite A is in good agreement with the specification range and also with the commercial powder detergent.

The moisture content test was carried out on the detergent samples made with 100 % of synthetic zeolite (Table 4). The maximum moisture and volatile components content requirement of any commercial synthetic detergent is 13 % by mass. From the analysis result there is remarkable difference between our zeolite A based detergent and commercial detergent that could be due to the absence of some ingredients and fillers in our zeolite based detergent.

Table 4 Moisture content, alcohol and water insolubility analysis result of zeolite A based detergent and the commercial detergent.

Detergent type	Moisture content (%)	Alcohol insolubility (%)	Water insolubility (%)
DZAF	2.6	85.0	10
DZAR	2.3	81.0	17
DZAP	2.4	83.0	13
DZAC	2.2	81.0	11
Commercial detergent	4.0	77.0	6

The result of alcohol and water insoluble matter analysis of synthetic zeolite A based detergent and commercial powder detergent is also summarized in table 4. Here we have tried to investigate the stability of inorganic salts, such as phosphates, sulphates, silicates and carbonates, which are insoluble in alcohol. This has been done by extracting the material with 99.9 %ethanol. The maximum alcohol insoluble matter requirement for industrial detergent powder is 80 % by mass. From the result it is possible to see that our synthetic zeolite A based detergent lie in the higher value of the permitted range although these results could be tuned by varying the specific formulation used to build the detergents Regardless of this, the obtained results are in good agreement with the commercial sample and indicate the possibility to use these synthetic zeolites fro detergent formulation. From the alcohol insolubility analysis result, the 15 % mass loss corresponds to the alcohol soluble component of the detergent, which could be the surfactant linear alkyl benzene sulphonic acid (LABSA). The remaining 85 %, which is insoluble in alcohol corresponds to the inorganic ingredients: aluminosilicate, sulphate and carbonates.

Appropriate solubility of detergent in water is one of the requirements in washing. The maximum insoluble matter in water should not exceed more than 5-10 % by mass. The water insolubility analysis result (table 4) shows that our synthetic zeolite Abased detergent lies in higher ranges, probably due to the chosen formulation. Nevertheless, the results obtained by the sample prepared by alkali fusion shows good results, due to the fact that by this method, the obtained zeolite is highly crystalline with almost no presence of impurities.

Conclusion

The synthesis of zeolite A using kaolin from Ethiopia by two different methods have been reported. The first method involves the alkali fusion followed by hydrothermal synthesis and the second method involved the conventional hydrothermal synthesis. The first method is in principle more cost effective in terms of time and energy for the chemical activation of kaolin. Moreover, the purification of the starting raw kaolin is avoided. The zeolite A product obtained by alkali fusion is better in terms of its quality as well as in its efficiency in detergent application. In the second method (conventional hydrothermal synthesis), synthesis was carried out with both raw and purified kaolin. Despite the fact that purified kaolin yields better quality zeolite A, the raw kaolin was also promising one. The synthetic zeolite A is efficiently used as a builder in detergent by substituting the environmentally unfriendly phosphate based material sodium tripolyphosphate (STPP). This has been done by formulating powder detergent with our synthetic zeolite substituting the STPP from 50 to 100 %. The result showed that zeolite A based detergent perform almost similar with the commercial powder detergent composed of sodium aluminosilicate as a detergent builder.

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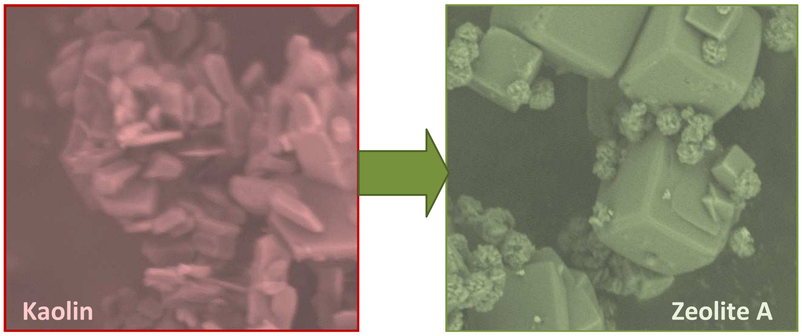
References

1. A. Davidson and B. M. Milwidsky Synthetic Detergents, 6th Edition; Publisher: G. Godwin, 1978 ISBN 10: 047099312X / ISBN 13: 9780470993125.
2. Y. Yu, J. Zhao and A. E. Bayly, *Chinese Journal of Chemical Engineering*, 2008, **16**, 517-527.
3. M. M. Crutchfield, *Journal of American Oil Chemistry Society*, 1978, **55**, 58-65.
4. D. Bajpai and V. K. Tyagi, *Journal of Oleo Science*, 2007, **56**, 327-340.
5. V. N. E. Avenue, *ZEODET*, 2000.
6. B. S. Sekhon and M. Sangha, *Resonance*, 2004, **9**, 35-45.
7. S. H. Park, J.-K. Yang, J.-H. Kim, C.-B. Chung and G. Seo, *Green Chemistry*, 2015, **17**, 3571-3578.
8. K. S. Hui and C. Y. Chao, *Journal of Hazardous Materials*, 2006, **137**, 401-409.
9. T. Bein, *Chemistry of Materials*, 1996, **8**, 1636-1653.
10. K. Yoshida, K. Toyoura, K. Matsunaga, A. Nakahira, H. Kurata, Y. H. Ikuhara and Y. Sasaki *Scientific Reports,* 2013, **3**, 2457.
11. J. Z. Ihab H. Farag, *IRACST – Engineering Science and Technology An International Journal* 2012, **2**, 188-194.
12. D. Novembre, B. Di Sabatino, D. Gimeno and C. Pace, *Clay Minerals*, 2011, **46**, 339-354.
13. L. Bieseki, F. G. Penha and S. B. C. Pergher, *Materials Research*, 2013, **16**, 38-43.
14. Q. Miao, Z. Zhou, J. Yang, J. Lu, S. Yan and J. Wang, *Frontiers of Chemical Engineering in China*, 2009, **3**, 8-11.
15. S. Chandrasekhar, *Clay Minerals*, 1996, **31**, 253-261.
16. M. Murat, A. Amokrane, J. P. Bastide and L. Montanaro, *Clay Minerals*, 1992, **27**, 119-130.
17. E. Costa, A. De Lucas, M. A. Uguina and J. C. Ruiz, *Industrial & Engineering Chemistry Research*, 1988, **27**, 1291-1296.
18. L. Ayele, J. Pérez-Pariente, Y. Chebude and I. Díaz, *Microporous and Mesoporous Materials*, 2015, **215**, 29-36.
19. *Compulsory Ethiopian Standard (CES 105), 1st edition. Published by Ethiopian Standards Agency ICS: 71.100.40,*2013.

20. M. M. J. Treacy and J. B. Higgins, in *Collection of Simulated XRD Powder Patterns for Zeolites (fifth)*, eds. M. M. J. Treacy and J. B. Higgins, Elsevier Science B.V., Amsterdam, 2007, pp. 18-19.

21. C. A. Ríos, C. D. Williams and M. A. Fullen, *Applied Clay Science*, 2009, **42**, 446-454.
22. Indian standard zeolite detergent grade-specification (IS 15267). 2003.
23. G. García, W. Aguilar-Mamani, I. Carabante, S. Cabrera, J. Hedlund and J. Mouzon, *Journal of Alloys and Compounds*, 2015, **619**, 771-777.
24. C. Fruijtier-Pölloth, *Archives in Toxicology*, 2009, **83**, 23-35.
25. S. Bosnar, J. Bronić, Đ. Brlek and B. Subotić, *Microporous and Mesoporous Materials*, 2011, **142**, 389-397.
26. A. Mayoral, T. Carey, P. A. Anderson, A. Lubk and I. Diaz, *Angewandte Chemie International Edition* 2011, **50**, 11230-11233.
27. B. B. D. Georgiev, I. Markovska, Y. Hristov, *Journal of Chemical Technology and Metallurgy*, 2013, **48**, 168-173.
28. R. J. H. D. J. Micco, *U.S. Patent 2003/0050219 A1*.

Zeolite A synthesized from raw Ethiopian kaolin via alkali fusion with 91% crystallinity and CEC >310 mg of $CaCO_3$/g.


Kaolin
Zeolite A