SBA-15 synthesis from sodium silicate prepared with sand and sodium hydroxide

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Abstract

In the industry, sodium carbonate is used to prepare sodium silicate; however, this process generates great volumes of CO₂. In this work, sodium hydroxide has been proposed to prepare sodium silicate using natural sand. Two experimental variables were considered, sodium hydroxide concentration and temperature to prepare sodium silicate. Results show the formation of sodium silicate with a NaOH:sand ratio = 1.1 at 550 °C. Moreover, an economical revision was achieved to compare costs of sodium silicate with sodium hydroxide and sodium carbonate. The use of sodium hydroxide permits to decrease CO₂ emissions generated in the decomposition of sodium carbonate. Additionally, the sodium silicate prepared herein was used to synthesize a zeolite type material, SBA-15. SBA-15 obtained has similar characteristics than the commercial mesoporous material. The use of sodium silicate prepared with non-pure sand for preparing mesoporous materials is an economical and friendly environmental alternative.

1. Introduction

Santa Barbara Amorphous type Material-15 (SBA-15) has attracted the attention from its properties in comparison with other porous materials; for example, the wall thickness and its ordered mesoporous. SBA mesoporous family can be used in drug delivery and catalysis with excellent performance. Several studies [1–13] confirm the presence of different structures as cubic cage Im3m, cubic Pm3m (or others), the three-dimensional hexagonal P63/mmc cage structure, a honeycomb hexagonal p6mm structure, and lamellar (LR) and possibly continuous L3 sponge mesophases that belong to SBA mesoporous materials. Zhao et al [1] reported SBA-11 material showed a surface area of 1070 m² g⁻¹ and a pore size of 2.5 nm while the SBA-15 exhibited a surface area of 1040 m² g⁻¹ and a pore size of 4.6–30 nm. The applications of porous materials in areas as biorefineries, biodiesel production or biogas purification, among others is important to increase the efficiency in those processes. Several studies have been carried out to synthesize SBA-15 with the same properties [5–8, 10, 13]. However, in order to minimize costs, various silicon sources, organic and inorganic, including industrial waste have been used with promising results [13–21].

The use of extracted silicon from sand results in a reactive silicon [15]. Basic fusion is the most used technique to form sodium silicate and, consequently, SBA-15. The modification of silicon minerals with soda has been implemented. However, there is not any information about sodium silicate preparation. In this work, the synthesis of SBA-15 using sodium silicate prepared from sand is demonstrated. Klimova et al [22] synthesized SBA-15 following a factorial design to determine the effect of principal experimental factors in the hydrothermal synthesis. The authors considered textural properties as surface area, pore size, total pore volume, micropore area, among others, obtaining a material with high surface area, 800 m² g⁻¹. The experimental factors were the aging temperature, hydrothermal temperature and the hydrothermal synthesis time. In the present study, sodium silicate with sand and NaOH was obtained from a systematic study. The sodium silicate prepared was used in the synthesis of SBA-15 material following a procedure according to Klimova et al [22]. Moreover, tetraethyl-orthosilicate (TEOS) and commercial sodium silicate were evaluated to obtain SBA-15 material.
2. Materials and methods

SBA-15 synthesis was achieved using TEOS and sodium silicate. TEOS and Pluronic 123 were purchased by Merck. Commercial sodium silicate was obtained from SIDES A.S.A. de C.V. Sand sample was obtained from Queretaro, Mexico. Sand was characterized by XRD and SEM-EDS to know the minerals and the elemental composition, respectively. For XRD and SEM analysis, a Bruker D8 Advance and Jeol JSM 6500 LV with a Bruker XFlash6110 EDS equipments were used, respectively.

In order to obtain sodium silicate alkaline fusion process was implemented. Several NaOH:solid mass ratio and temperatures were evaluated considering the reaction 1:

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]

In accord to stoichiometry, a NaOH:sand 1.33 mass ratio considered the 100% of SiO2 in the sand; however, other oxides must be treated according to EDS analysis. Table 1 summarizes the preparation conditions of fusion product.

Fusion product obtained in the experiments was placed in water to dissolve the solid (5 g l\(^{-1}\)) to determine the extraction of silicon, aluminum and iron. Liquid was analyzed by ICP-MS technique. Moreover, electrical conductivity was measured in each lixiviated experiment.

SBA-15 was synthesized by the hydrothermal method in acid medium. Pluronic P123 and silicon source were placed in a 2 M solution of HCl with a molar formula of 1TEOS:0.017P123:5.95HCl:171H\(_2\)O. The mixture was keeping for 20 h at T1 at 35 and 60 °C. Then, the solution was placed in a steel autoclave for t2 (24 and 48 h) and T2 (60 and 80 °C). Samples were washed and dried at 110 °C for 12 h. Subsequently, the powder was calcined at 300 °C for 30 min and 550 °C for 6 h. SBA-15 samples were characterized by XRD, SEM and BET analysis. XRD measurements were achieved in a Bruker D8 Advance at low angles. SEM-EDS analysis was implemented in a Jeol 6500LV equipment with EDS Bruker X Flash6110 EDS equipments were used, respectively.

2. Results

3.1. Preparation of sodium silicate

Figure 1 shows the XRD pattern of sand with signals of quartz and amorphous halo. Moreover, signals of feldspar appear in the pattern indicating the possible presence of calcium, sodium and potassium minerals; iron oxides signals are not observed. Amorphous halo shows the possibility to release silicon to synthesize SBA-15 material considering that vitreous or amorphous material are reactant to form zeolite type materials [23–26].

Elemental analysis of sand (table 2 and figure 2) shows a predominance of silicon useful to prepare sodium silicate and, subsequently, SBA-15 material.

Sand has a Si/Al ratio of 4.7 considered adequate to synthesize a siliceous mesoporous material. Before the preparation of SBA-15, the sand is treated by alkaline fusion with NaOH at different NaOH:sand mass ratios and temperatures. According to silicon available, more of 50% of sand would react with sodium hydroxide to form...
sodium silicate. Moreover, in this work the elimination of iron or other impurities was not implemented considering the possible high costs and the generated liquid effluent.

Alkaline fusion had the objective to form sodium silicate from sand to use it in the synthesis of SBA-15 material. Five NaOH:sand mass ratio and three temperatures were evaluated and to permit the reaction with the impurities present in sand. Figures 3(a)–(c) shows the XRD pattern of sodium silicate prepared using sand and NaOH.

In all of the cases, signals of sodium silicate are appreciated inclusively, when a NaOH:sand ratio used is similar to stoichiometry indicating that the impurities present in sand do not affect the sodium silicate preparation. Moreover, the formation of sodium aluminosilicate is expected; however, signals in the XRD pattern are not appreciated due to high presence of sodium silicate. This result guarantee the maximum release of silicon in water to form the SBA-15 material. The minimum energy and reactants consumption are considered in order to choose the optimal conditions for preparing sodium silicate. A minimum consumption of NaOH and the low temperature evaluated are preferred. The NaOH:sand ratio of 1.1 would be chosen with a thermal treatment at 550 °C. Theoretically, a reaction from external to internal particle of sand with NaOH occurs promoting the fractional formation of sodium silicate. As consequence, only a section of the particle sand

![Figure 1. XRD pattern of sand used for the synthesis of SBA-15. Q, quartz; F, feldspar.](image)

![Figure 2. EDS spectrum of sand.](image)

### Table 2. Elemental analysis (EDS) of sand.

| % w/w | O   | Si  | C   | Al  | K   | Na  | Ca  | Mg  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Sand  | 50.2| 31.9| 4.1 | 6.7 | 5.5 | 1.3 | 0.8 | 0.6 | 0.6 |
would be useful to form sodium silicate being negative if the objective is to use the maximum content of the silicon from sand. Formation of sodium silicate is not only verified with the thermodynamic; kinetic aspect must be considered to complete the process. In spite of, the evaluated temperatures are very closing to consider an important change in the thermodynamic parameters. The calculated enthalpies of formation of sodium silicate at 550, 650 and 750 °C, are $-117.865$, $-115.835$ and $-113.805$ kJ mole$^{-1}$, respectively. Moreover, in this work only one fusion time is evaluated (1 h) because a long time in this step means high costs in the overall process of formation of the SBA-15 material. Additionally, the excess of NaOH is expressed as NaOH:sand mass ratio pointed in the figures 4(a)–(c). Results of experimental section of fusion of sand at 550, 650 and 750 °C indicate that the temperature has not a significant effect to silicon, aluminum and iron lixiviated. Figure 4 shows the

![Figure 3](image_url)

**Figure 3.** XRD pattern of sodium silicate prepared with sand, (a) sodium silicate prepared at 550 °C, (b) sodium silicate prepared at 650 °C, (c) sodium silicate prepared at 750 °C, S, commercial sodium silicate; (a): NaOH:sand ratio of 1.1; (b): NaOH:sand ratio of 1.2; (c): NaOH:sand ratio of 1.3; (d): NaOH:sand ratio of 1.4; (e): NaOH:sand ratio of 1.5.
results of Si, Al and Fe released in water from sand; moreover, electrical conductivity is measured in each sample to determine the efficacy in the formation of sodium silicate from the extraction of silicon from sand.

In the case of sodium silicate produced at 650 °C, the products have low crystallinity. In the figure 3(b), the signals have low intensity indicating the presence of amorphous material or a small particle size. This is more evident when the NaOH:sand mass ratio increases from 1.2 to 1.5. Possibly, the kinetic affects the formation of sodium silicate particles. With high NaOH: sand mass ratio an excess of NaOH do not react. This excess means a decreasing of crystalline signals of sodium silicate. However, this is not appreciated in the figures 3(a) and (c). In this case, all of the NaOH reacts to form sodium silicate and other compounds that are not identified.

In the case of silicon released, NaOH:sand mass ratio has a significance difference in 1.1–1.2 values while a high values there is not a difference. Maximum silicon lixiviated reaches 1400 mg l⁻¹ with a dose of 5 g l⁻¹ (NaOH:sand mass ratio of 1.2). These values mean an extraction of 280 mg g⁻¹ of silicon that is almost the 100% of total silicon in the sand, according to the elemental analysis achieved by the EDS technique. In order to correlate this parameter with the silicon extraction and the NaOH:sand mass ratio, the conductivity is measured (figure 5).

There are empirical correlations between the conductivity of prepared solutions and the silicon extraction from sand. At high temperature, the silicon extraction is superior due to endothermic reaction of formation of sodium silicate. Considering that, the synthesis of SBA-15 material is achieved in an acid medium, the minimum presence of residual alkali is ideal to prepare sodium silicate. That is, the minimum NaOH:sand mass ratio is selected. This conjecture is verified in the figure 5(b); the silicon extraction is maximized with the low NaOH: sand ratio.

3.2. Economical and technical aspect in the preparation of sodium silicate

Fawer et al [26] achieved the Life Cycle Inventories for the production of sodium silicate. The authors evaluate five different process including a solid-state case. In this process pure sand reacts with sodium carbonate at 1400 °C generating 1.066 Ton of CO₂ by Ton of sodium silicate prepared. This process generates 0.36 ton of CO₂ from the decomposition of sodium carbonate in the reaction with SiO₂; that is, 0.706 Ton of CO₂ are generated.
by fuel consumption. Moreover, Silicates Manufacturing Company elaborates sodium silicate by a furnace process using sand fused with Na$_2$CO$_3$ at 1000 °C [27]. Evidently, the process applied in the present work to elaborate sodium silicate generates low CO$_2$ emissions. The sodium carbonate is more economical than sodium hydroxide; then, the difference is significant. A review in internet demonstrates the price in the global market (Table 3).

Figure 5. Silicon extraction, from sand treated at different NaOH:sand ratio and temperatures, and conductivity of solutions prepared with the fusion product.

Table 3. Prices of sodium hydroxide and carbonate from Alibaba.com (5th, July 2019).

| Sodium hydroxide, US$ | Sodium carbonate, US$ |
|-----------------------|-----------------------|
| 300–400               | 180–250               |
| 450–490               | 180–230               |
| 545–550               | 190–230               |
| 350–450               | 230–450               |
| 330–400               | 250–400               |
| 320–380               | 210–290               |
| 350–400               | 230–600               |
| 425.38                | 268.95                |
| 86.08                 | 97.37                 |
| Statistical interval (95%) | 380–462 | 237–300 |
However, with a novel technology, Du et al [28] estimate a production cost of sodium hydroxide of US$250.1 that is similar to the price of the sodium carbonate presented in the table 3. This technology could decrease the cost of NaOH to prepare sodium silicate and zeolite type materials.

3.3. Preparation of SBA-15 material
Temperature of 550°C is chosen to obtain the sodium metasilicate and consequently the SBA-15 material. That condition permits to release the maximum aluminum content in the sand while the iron is minimum under the mentioned parameters. NaOH:sand mass ratio of 1.1 and 550°C are chosen to prepare the sodium silicate from sand. The second step is the mesoporous material synthesis by hydrothermal method incorporating Pluronic 123 in acid medium. Table 4 shows the results in the synthesis of SBA-15 material using TEOS, commercial and prepared sodium silicate herein.

A great surface area value is obtained when TEOS is used to synthesizing the SBA-15 material. Figure 6 shows the nitrogen adsorption/desorption isotherm. Representative isotherms of mesoporous material are showed in the figure 6 for explaining the porosity character of SBA-15. The isotherm has the typical form of the mesoporous material with a microporous proportion at low values of relative pressure while the mesoporous filling begin at 0.4 of P/Po. The desorption hysteresis of SBA-15 T and CS materials belong to the typical mesoporous material while the SBA-15 SP micro/mesoporous character. This material shows a great majority of microporous character with a low contribution of mesoporosity. However, its surface area is greater than original sand. This behavior is attributed at the particle size and the formation of small particle of SBA-15 material.

The EDS analysis of sand and different SBA-15 material obtained are showed in the figure 7. The predominance of Si and Al in all of the SBA-15 materials prepared is evident. The Si/Al molar ratio to SBA-15 prepared with TEOS, sodium silicate commercial and sodium silicate prepared herein is 62.62, 19.63 and 18.52, respectively. In the figure 8 the SEM images of mesoporous materials prepared is shown.

Typical particles of SBA-15 are obtained using TEOS with a size approximately of 2 μm while with commercial sodium silicate small particles are formed. Considering that the parameters in the synthesis are the same, it is clear the effect of the silicon source to form the SBA-15 material. When the sodium silicate synthesized from sand is used to form the SBA-15, particles of heterogeneous morphology are appreciated; moreover, some

| Sample   | T1 (°C) | T2 (°C) | t1 (h) | t2 (h) | Surface area (m² g⁻¹) | Porous size (nm) |
|----------|---------|---------|--------|--------|-----------------------|-----------------|
| SBA-15 T | 35      | 80      | 20     | 24     | 659.9                 | 3.19            |
| SBA-15 SC| 35      | 80      | 20     | 24     | 283.7                 | 7.87            |
| SBA-15 SP| 35      | 80      | 20     | 24     | 306.56                | 14.01           |

Figure 6. Nitrogen adsorption/desorption isotherm of SBA-15 materials synthesized. T: TEOS; SC: sodium silicate commercial; SP: sodium silicate prepared in this work.
typical structures of SBA-15 material are formed. In this last case, the interparticle porosity contributed to mesoporosity \cite{29}. Particles of size $<500$ nm are observed generating the surface area in the total material.

4. Conclusions

A systematically study to prepare sodium silicate from sand was achieved considering as experimental factors the dose of sodium hydroxide and the temperature in the fusion process. Natural source of sand with a typical composition was used to prepare sodium silicate that could be used as effective source of silicon in other chemical process. Sodium silicate preparation using sodium hydroxide and sand is an economical and environmental option to decrease the CO$_2$ emissions. Results show that the sodium silicate is useful to prepare a SBA-15 type material with a great surface area being a total ecofriendly process. Inclusively, other zeolite type materials could be prepared using the sodium silicate prepared herein.

Figure 7. EDS spectrum of SBA-15 samples synthesized using (a) TEOS, (b) sodium silicate commercial, (c) sodium silicate prepared in this work.
**Figure 8.** SEM images of SBA-15 materials synthesized. (a) SBA-15 synthesized with TEOS; (b) SBA-15 synthesized with commercial sodium silicate; (c) and (d) SBA-15 synthesized with prepared sodium silicate.

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