Synthesis and Characterization of the Nano Particle Crystals of Sodalite Zeolite from agricultural waste

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ARTICLE INFO

Article History:
Received: 24/08/2017
Accepted: 10/09/2017
Published: 23/1/2018

Keywords:
Zeolite sodalite
Rice husk ash
hydrothermal synthesis
Characterization.

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ABSTRACT

In this study, zeolite sodalite was synthesized from rice husk ash (RHA) by a simple conventional hydrothermal method using different time 1, 2, 3 and 4h. The best time for synthesizing is 4h. Rice husk (RH) was used as a source silicate to produce nanozeolite. The RHA silicate was obtained by combusting the RH at 700°C for 6h. Sodalite nanocrystals with crystallite sizes ranging from 35 to 44 nm have been synthesized from a sodium aluminosilicate solution at low temperature. A physical property of nanosized sodalite crystals were characterized by FTIR, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) method. BET was used to determine the average pore size distribution, pore volume and surface area. The results obtained from BET method proved that the average pore size in the mesoporous ranges, therefore it can be suitable for using in adsorption ion exchange and catalyst applications.

1. INTRODUCTION

In general, amorphous silica is prepared using silicon alkoxide raw materials; such as tetramethyloethersilicate(TMOS),tetraethylorthosilicate (TEOS) and polyethoxydisiloxane (PEDS), etc (Radin, et al., 2005; Anderssson, et al., 2004). However, such precursors are fairly expensive (Tang, and Wang, 2004). Thus alternative low cost amorphous silica precursors are required to substitute alkoxides. In that respect, a cheap source of amorphous silica of bio-origin would be the (RAH). Although RHA contains the small amount of other metallic impurities; it may be safely used in the physiological environment as it is originated from biomass. However, due to the high silica (SiO2) content in this material (>90%), carbon and other metal discover, the disposal of RHA has become a problem. Because of this reason, RHA had become an interesting material to study since it is abundance and cost free (Tzong-Horn and Chun-Chen, 2011).
Zeolites are microporous crystalline aluminosilicates, compositionally similar to clay minerals, but the conflict in their well-defined three-dimensional microporous shape. Aluminum, silicon, and oxygen are devised in a consistent structure of $[\text{SiO}_4]^{-}$ and $[\text{AlO}_4]^{-}$ tetrahedral units that form a structural framework with systematic pores form of tunnels, channels, or cavities of about 0.1-2 nm diameter running through the material (Zaarour, et al., 2014). Zeolites have been used as ion-exchange and molecular sieves in the separation and shifting transfer of gases and solvents. In inclusion, zeolites have the ability to act as a catalyst for chemical reactions which take place within the internal cavities (Pal and Bhaumik, 2013). An essential grade of reactions is that catalyzed by hydrogen-exchanged zeolites, whose structural framework-hurdle protons give rise to very high acidity. Due to this quality, zeolites have been used as a catalyst in petrochemistry and fine-chemical industry because of their large surface area, large adsorption capacity, giant thermal and hydrothermal stabilities, strong acid sites within their defined micropores, and their structure selectivity in catalysis (Hums, 2017). Hydroxysodalite $\text{Na}_6 [\text{AlSiO}_4]_6 (\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (SOD) as well as zeolites X, Y (FAU) and zeolite A (LTA) belong to the class of zeolites which have the common characteristic of $\beta$-cages (sodalite units) as common building unit. Although it is well-known that sodalite can be ideally formed by direct attachment of sodalite units, there is still a constant interest to study the process of SOD synthesis. Sodalite can be successfully synthesized starting the crystallization either from gels (Jin, et al., 2008). In multiple catalytic applications, the main disadvantage of zeolites is their complex pore and channel structure in the molecular size scope from 0.3 to 1.5 nm. Thus, large molecules cannot react effectively over these microporous materials because of the limitation of their small pore sizes (Huang, et al., 1995). To solve the dispersal problems of client species in zeolites, mesoporous materials with adaptable huge pore sizes, example, MCM-41 and SBA-15, have been successively created (Qin, et al., 2013). The mesoporous a material, as defined by IUPAC nomenclature, is material with pore of free diameters in the range of 2-50 nm (Liu, et al., 2008). These materials can defeat the pore size constraint of microporous zeolites and allow the diffusion of lager molecules (Petushkov, et al., 2011). As the compared with conventional zeolites, these mesoporous materials revealed insufficient hydrothermal stability and acidity, which limits their use as catalysts in a wide range of industrial processes and reactions. In order to overcome the limitations of single micro- or mesoporous materials and to combine the advantages of these two types of molecular sieves, various attempts to synthesize mesoporous aluminosilicate materials with improved framework crystalinity have been devoted to synthesize nanosized zeolite with ultra large pore zeolites and hierarchical mesoporous zeolite.

2. MATERIALS AND METHODS

2.1. Preparation of Rice Husk Ash Silica

Rice husk (RH) was collected from a local rice mill. Unwanted fine dust materials were removed through air-blowing separation technique and then washed properly to remove the physically adhered impurities using tap water. After successive washing, RH was dried in an air-circulated oven at 100 ± 2 °C for 12 h to get clean and dry RH. The cleaned RH was burned at 700 °C for 6 h in air to get the rice husk ash (RHA). The ash was brownish in colour and termed brown ash (BA). To get impurity free ash, cleaned husk was acid leached using 3N HCl (Panreac.Spain, 37%).
solutions under boiling condition for 1 h followed by thorough washing with warm distilled water to remove acid. The husk was then dried and burned following same procedure stated above for BA. The ash thus obtained was whitish in color and designated as WA. (Nur, 2001).

2.2. Materials and Preparation of the Synthesis Mixtures

Sodium aluminate (Fluka Company, 93%), WA as a source of silica, sodium hydroxide (Aldrich 99%), and distilled water were used in the synthesis. Typically, an aluminosilicate gel containing 5.0 g of NaOH, 2.5 g of NaAlO2, 3.45 g WA of extracted silica, and 50.0 g of H2O was adopted. First, a 500 mL polupropylene bottle containing prepared sodium aluminate solution and (WA) as the silicate sources were slowly mixed with prepared aluminate solution at 45°C and then directly motion in shaker at the desired temperature for hydrothermal crystallization. Hydrothermal crystallization was conducted at 55°C for 4h in a shaker with a rotation rate of 300 rpm and then aged for 8h. The powdered products were returned with centrifugation, washed with DI water until pH < 8, and then dried at 60°C over night for further characterization (Mahdi and Abdolreza, 2011).

2.3. Characterization

Characterization of sodalite zeolite formed was carried out by X-Ray Diffractometer (Siemens D5000) with radiation sources Cu Kα that has λ=0.154 nm at 40 kV and current of 10 mA. The diffractogram was scanned in the degree of 20 at the range of 5 - 50 with the step size of 0.05. The crystal size of the zeolite was calculated theoretically using Debye-Scherrer equation (1) at angle 20, around 14.099°, 24.448°, which are the major diffraction peaks of sodalite crystals (Pan, et al., 2009).

\[ t = \frac{0.9λ}{β \cos θ} \]  \hspace{1cm} (1)

Where \( t \) is average in crystal size (nm), \( B \) is a Scherrer’s constant (0.9), \( λ \) is the wavelength of X-rays (nm), and \( θ \) is Bragg angle (i.e. the angle of the peak maximum). \( β \) is the full width at half-maximum (FWHM) of the broad peak after correction for intrinsic instrumental line broadening and must be in radians.

The content of tetrahedral TO4 (T = Si or Al) bonding is discovered by using, FTIR (Perkin Elmer spectrum one). The spectrum was explained for zeolite framework structure at wavelength between 400-1500 cm-1. The (BET) method was used to determine the surface area of synthesized zeolite (Micromeritics 2010 V3.01G analyzer). The morphology of nanosodalite was elucidated using, FESEM and TEM (JEOL).

3. RESULTS AND DISCUSSION

The XRD of sodalite formation using WA silica was presented in Figure 1.

![Figure 1: XRD patterns of (a) reference sample and (b) synthesized sodalite zeolite using WA silica as silica source.](image-url)
14.099°, 24.448°, 31.100°, 34.875° and 42.988° with that of the standard for a sodalite [JCPDS 81-0705]. These peaks similarity to the plane d[110], d[211], d[310], d[222] and d[330]. In Figure 1, which shows the samples synthesized using WA silica as silica source, pure sodalite was observed to form within 4 h of crystallization time. Diffraction peaks showing the probability of the crystal to exist in nano size. The crystallize size of sodalite formed was calculated using Debye- Sherrer equation as shown in Table 1.

Table 1- Analysis physical properties of the synthesized zeolite sample

| Zeolite Sample | FESEM (nm) | TEM (nm) | XRD (nm) |
|----------------|-----------|----------|----------|
| Sodalite       | 40-50     | 40       | 35 and 44 |

The size of sodalite formed was in the range of 35- 44 nm regardless the silica sources used, indicating that sodalite sample obtained in the synthesis are in the nano-sized range. The formation of small size of zeolite was the result of the conditions that favors nucleation instead of growth (Charles, et al., 2008).

IR spectrum of sodalite sample in Figure 2 shows broad band of asymmetric stretching of T-O-T (T=Si or Al) bond was viewed around ~1019 cm-1 which indicates the formation of Si-O-Al bond. A slightly broad peak around ~868 cm-1 show the existence of silanol group (Si-OH) bending mode which incorporated with silicon atom linked with hydroxyl group in the framework. The vibration of T-O-T symmetric stretching mode was observed around 730 cm-1 to 560 cm-1 and a small peak around 469 cm-1 indicating the formation of T-O bending vibration in the sodalite framework (Barthomeuf, 2013).

The morphology of the nanosodalite from WA is shown in Figure 3 and 4 FESEM and TEM image respectively was recorded for the as synthesized nanozeolite sample was shown in Figure 3.

Figure (2): FTIR spectra of synthesized sodalite zeolite using WA silica as silica source

Figure (3): FESEM image of synthesized sodalite zeolite using WA silica as silica source

Figure (4): TEM image of synthesized sodalite zeolite using WA silica as silica source
Figure 3 and 4 FESEM and TEM image respectively was recorded for the as synthesized nanozeolite sample is shown in Figure 3 which clearly indicates that the particle size of nano-sodalite is ultrafine and within a range of 40-50 nm which is consistent with the results calculated from the XRD pattern. While TEM image in Figure 4 indicates that the products are 40 nm aggregates of sodalite nanocrystals with crystallite sizes ranging from 35 to 44 nm (Wright, 2008).

Surface area and pore size distribution in Figure 5 and 6 shows the BET plot of the prepared sodalite. The sodalite nanocrystals were characterised using N2 adsorption/desorption to determine their pore volume (Pv) and surface area (Flanigen, et al., 2009). The synthesized zeolite exhibited type-IV adsorption isotherm, which indicates the presence of mesopores (Shi, et al., 2006). Pore size distribution of the synthesized zeolite is shown in Figure 6. The pore was around 22.87 nm, i.e. in the mesoporous range. The result shows that in Table 2. The large external surface of the resulted sodalite further supports that sodalite nanocrystals have small crystallite size.

Table 2: Nitrogen adsorption-desorption data synthesized zeolite sample

| Zeolite sample | BET surface area \( \text{m}^2\text{g}^{-1} \) | P\( \text{v} \) (mL g\(^{-1}\)) | Average pore size distribution (nm) |
|---------------|-------------------------------|----------------|----------------------------------|
| Sodalite      | 271.33                        | 0.10           | 22.87                            |

Figure 5: N2 adsorption/Desorption isotherm of synthesized sodalite zeolite using WA silica as silica source
4. CONCLUSIONS

The results procured from this study demonstrated the reactivity of rice husk ash (RHA) as a source of silica in the synthesis of nanozeolite also; the effect of time and conditions of crystallization on the properties of the final product was scrutinized. The results reveal that the crystallization time plays a very important role in the sodalite phase. The purity, crystalinity and morphology of the final products varied considerably depending on the crystallization time. It was detected that nanosodalite formed from RHA was in nanosized zeolite particles. Nanosized sodalite of RHA formed at 4h. The average size using Debye-Scherrer equation shows the size in the range of 35-44 nm. Image from FESEM and TEM analysis shows the formation of nanosodalite from RHA in the arrangement of worm-like morphology with an average size of around 40-50 nm and 40 nm respectively. To best of our knowledge, this research on the hydrothermal synthesis of nanozeolite with rice husk as a source of extracted silica. Our environmentally friendly process reduces the costs of synthesis effectively through utilization of inexpensive raw materials and also by circumvents consumption of costly chemical sources as template.

Conflict of Interest

The Author acknowledges to ALS laboratory in Spain and Ibnu sina institute sor fundamental science studies-University of UTM/Malaysia.

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