



## Original Research Paper

# Synthesis of hydroxysodalite zeolite by alkali-activation of basalt powder rich in calc-plagioclase



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## ABSTRACT

Hydroxysodalite (H-SOD) microcrystalline particles were synthesized from basalt powder rich in calcic-plagioclase (anorthite) by alkali activation at 80 °C/24 h. Sodium hydroxide (NaOH) solution was used as alkaline activator. The reactivity of the natural solid precursor basalt was studied using differential scanning calorimetry (DSC), and a maximum reaction enthalpy of ( $-\Delta H$ ) of 170 J/g was obtained. The chemical, mineralogical, and textural properties were obtained by using X-ray powder diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and  $N_2$ -adsorption-desorption measurements. The synthesized material has a specific BET surface area of  $20.5 \text{ m}^2 \text{ g}^{-1}$  approximately 200 times higher than raw basalt material ( $0.1 \text{ m}^2 \text{ g}^{-1}$ ). The compressive strength of basalt based H-SOD/sand composite samples cured at 80 °C for 24 h upon using different amounts of the activator (NaOH) was evaluated under dry and saturated conditions. The dry samples with NaOH/basalt mass ratio of 0.12 have reached a compressive strength of 57 MPa. Wet samples, on the other hand, showed a compressive strength of 25 MPa after seven days of soaking in water and four episodes of wetting and drying. The present work illustrates that crystalline H-SOD could be synthesized from cheap basalt powder precursor.

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## 1. Introduction

Hydroxysodalite (H-SOD) is a crystalline aluminosilicate that belongs to zeolites of numerous micro and meso uniform channels [1]. This unique channel-like structure is responsible for high selectivity of adsorption [2–5], ion-exchange [6–10], molecular sieve [11], and catalytic activities [12,13]. In the last decades, the global industrial demand for natural zeolites has increased dramatically to become about 2.8 MT/year [14]. Different attempts were made to meet the huge demands of natural zeolites by producing synthetic zeolites via simulating hydrothermal reactions for natural zeolite formation [15]. Synthetic zeolites have higher purity, crystallinity, larger pore size and uniformity of particle sizes than most of the known natural zeolites [16]. Zeolites are usually synthesized by conventional hydrothermal alkali-activation of com-

mercial sources of aluminum and silicon such as sodium aluminates and sodium metasilicate [17–19]. Recent research on zeolite synthesis has focused on low cost sources such as clays [20–24], volcanic ash [25], and industrial wastes such as fly ash [26–28] and coal gangue [29]. The structure and composition of produced zeolites are mainly determined by the Si/Al ratio. Zeolites with low Si/Al ratio ( $\text{Si}/\text{Al} \leq 5$ ) are classified as zeolites-A (LTA), X (FAU) and hydroxysodalite (H-SOD), whereas zeolites with high Si/Al ratio ( $\text{Si}/\text{Al} > 5$ ) are classified as zeolite-beta (BEA), ZSM-11 (MEL), and ZSM-5(MFI) [30].

The small aperture size (2.2–2.8 Å) and hydrophilic nature of H-SOD powder have made it one of most used zeolite for the separation of small molecules from gas or liquid mixtures, hydrogen storage and as catalyst [18,31–33]. The pioneering work of Borchert and Keidel [34] was the first attempt to synthesis H-SOD powder by alkali-activation of kaolinite. They classified the final products as poor sodium H-SOD [ $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ ], basic-H-SOD [ $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$ ], and rich sodium H-SOD [ $\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{25}(\text{OH})_2$ ]. The actual hosted water content in the  $\beta$ -cages of H-SOD was not clarified [34]. Hassan and others [35] found that the compositions the

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basic H-SOD range between  $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$ . Felsche and Luger [36] studied the crystal structure of basic and poor sodium H-SOD using thermogravimetry, infrared and X-ray diffraction heating experiments. They reported two H-SOD end member series  $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot n\text{H}_2\text{O}$ , where  $0 < n \leq 4$  (basic series), and  $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot n\text{H}_2\text{O}$ , where  $0 < n \leq 8$  (poor series).

Basalt is a volcanic basic igneous rock that covers about 70% of the earth surface. It is considered as a high-potential industrial raw material due to its large scale availability, high homogeneity, low impurities, high chemical stability, recyclability and non-toxic reactivity with water and air [37]. Basalt is composed of calcic-plagioclase and augite ( $\text{CaMgFeSi}_2\text{O}_6$ , calcic-plagioclase refers to crystals that contain more anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) than albite ( $\text{NaAlSi}_3\text{O}_8$ ) in molar term. Basalt is essentially composed of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in addition to other oxides such as  $\text{Fe}_2\text{O}_3$ , FeO, CaO and MgO [38]. The relatively high silica and alumina content of basalt enable its use as an inexpensive raw material for the synthesis of zeolite-like materials.

In our previous work [23] we presented data on the reaction stoichiometry of producing hydroxysodalite by alkali-activation of well crystalline and untreated kaolinite-rich clay. The kaolinite based hydroxysodalite was found to be in the tetrahydrate phase with a Na/Al ratio of 8/6. In this paper we concentrate on synthesizing hydroxysodalite powder at low temperature and pressure from calcic-plagioclase (the essential component of basalt). The use of basalt as precursor to synthesize H-SOD powder by alkali-activation and to the best of our knowledge is described for the first time. The effect of different NaOH/basalt mass ratios on the reaction enthalpy, morphology and thermal properties of the synthesized basalt based H-SOD has been investigated. The mechanical strength and durability have also been evaluated on composite specimens made of a mixture of basalt based H-SOD and quartz sand.

## 2. Materials and methods

Calcic-plagioclase rich basalt raw material was used as a starting material for synthesis of H-SOD. A 2000 kg gross sample of Jordanian basalt (JB) was collected from Harrat Ash Shaam volcanic plateau in Jordan. The Plateau basalt composition was studied by Mehyar and co-workers, the volcanic field thickness of this plateau ranges from 100 m to 1800 m in an area that spreads from Syria to Saudi Arabia [39]. The major oxides (wt.%) were found to be  $\text{SiO}_2$  (40–43%),  $\text{Al}_2\text{O}_3$  (12–15%),  $\text{Fe}_2\text{O}_3$  (11–13%), CaO (10–12%), MgO (9–10%) and  $\text{TiO}_2$  (2–3%). The essential mineral components were found to be plagioclase, clinopyroxene, olivine and magnetite [39].

The sample was crushed by cone crusher (TRIO model TC36) equipped with micro filters. Nearly 98% of the particles in the sample were found to have a diameter less than 60  $\mu\text{m}$  when determined according to the standard sieving analysis [40]. The powdered basalt sample was dried at 105 °C for 24 h. NaOH solutions with different concentrations were prepared by dissolving NaOH pellets (Merck, 98.0%) in deionized water in a capped plastic bottle. Deionized water with an electrical conductivity  $\leq 2.8 \mu\text{S}/\text{cm}$  was obtained by using a Milli-Q10 integral water purification system. Sodium hydroxide solutions were left to cool down to ambient temperature.

Two groups of basalt based H-SOD samples were synthesized in this work. The first group (group A) was synthesized by alkali-activation of basalt powder with different ratios of NaOH and was characterized for their reactivity, chemical, mineralogical, morphological and surface area, as described in Table 1 (JB1 to JB5). For the reactivity study, the samples were analyzed immediately after mixing, whereas for the other analyses, the samples

were cured at 80 °C for 24 h, then crushed and sieved down to a diameter  $\leq 250 \mu\text{m}$ . The second group (group B) target was evaluation of mechanical strength and durability of H-SOD powder on composite specimens made from basalt based H-SOD and quartz sand. Quartz sand was used as a filler to enhance the mixture workability that is needed for specimen molding and demolding, improving pore structure and reducing cracking on drying [41]. The quartz sand was supplied by S.C.R. Sibelco, Belgium with 99.5% purity and mean particle size ( $D_{50}$ ) of 260  $\mu\text{m}$ . The weight ratios of sand/basalt and water/basalt were fixed to be 0.25 and 0.14 respectively, being the highest ratios that provided enough workability and stability for molding and demolding of the composite specimens. All starting materials were mixed in a planetary mixer (Hobart A200) for 15 min at 198 rpm. The final mixture was divided to nine portions (about 50 g each) and molded immediately in a stainless steel cylindrical mould (25 mm i.d.  $\times$  150 mm height) using a hydraulic press at a 15 MPa pressure. The dimensions of the specimens after hydraulic pressure were nearly 25  $\times$  50 mm. The demolded specimens were cured in an oven (Heraeus model TU100/150) for one day at 80 °C to avoid the high vapor pressure which may disrupt the specimens. The cured specimens were divided into three groups of three specimens each and then treated using the same procedure described in our earlier work [23,24]. This procedure is summarized in Fig. 1. Four series of cylindrical specimens as described in Table 1 (JB6 to JB10) were prepared using different weight ratios of NaOH/basalt for mechanical strength and durability studies. The reported strength values are the average of three specimens for similar composition and treated at the same conditions.

The reactivity of basalt powder during alkali-activation process was investigated by measuring the reaction enthalpy ( $\Delta H$ ) using differential scanning calorimeter (Mettler Toledo DSC822E). The measurements were carried out on a 30 mg fresh paste sample immediately after mixing the basalt powder with the NaOH solution. The DSC curves were recorded from 30 °C to 290 °C at a heating rate of 5 °C  $\text{min}^{-1}$ . The sample was heated linearly inside a hermetically sealed gold plated stainless steel pan. The measurement baseline was obtained by applying the same thermal program to a preheated sample. The reported results represent the average of duplicate samples.

The chemical and mineral composition of the basalt powder and basalt based H-SOD was performed on fused pellets using Shimadzu Lab Center XRF-1800 sequential X-ray fluorescence spectrometer (XRF) equipped with Rh anode X-ray tube. Samples mineralogy was determined by X-ray diffraction (XR) analysis using a Shimadzu MAXima X XRD-7000 diffractometer with a ( $\text{Cu K}\alpha$ -radiation  $\lambda = 1.54 \text{ \AA}$ , 40 kV, 40 mA at a  $2\theta$  range 2–70° with scan rate of 2 deg/min, step scan size 0.02, and receiving slit of 0.3 mm). The infrared spectra were obtained by using a Thermo Scientific Nicolet spectrometer (IS50R), coupled with attenuated total reflectance diamond crystal unit (Thermo Scientific Smart iTR). Spectra were collected from 4000 to 650  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  and averaged over 32 scans. The thermal stability and dehydration of basalt based H-SOD were investigated by thermogravimetric analysis (TGA), using a NETZSCH (STA 409 PG/PC thermal analyzer). About 35 mg was heated from 50 °C to 1000 °C at 10 °C  $\text{min}^{-1}$  under nitrogen gas atmosphere. The morphology of the basalt based H-SOD was investigated by scanning electron microscope (FEI Inspect, F50/FEG) coupled with a Bruker AXS EDS system. The SEM images were collected at  $6 \cdot 10^{-4}$  Pa and with 30 kV accelerating voltage. The SEM imaging was conducted on platinum-coated specimens using Quorum-Emitech K550X sputter coater.

The specific surface areas and texture properties of basalt based H-SOD was determined by a  $\text{N}_2$  adsorption-desorption analyzer (NOVA Quantachrome – 4200e, USA). All samples were

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