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Ultrasonic assisted synthesis of Bikitaite zeolite: A potential material for hydrogen storage application

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ABSTRACT

Li containing Bikitaite zeolite has been synthesized by an ultrasound-assisted method and used as a potential material for hydrogen storage application. The Sonication energy was varied from 150 W to 250 W and irradiation time from 3 h to 6 h. The Bikitaite nanoparticles were characterized by X-ray diffraction (XRD), infrared (IR) spectral analysis, and field-emission scanning electron microscopy (FESEM) thermo-gravimetrical analysis and differential thermal analysis (TGA, DTA). XRD and IR results showed that phase pure, nano crystalline Bikitaite zeolites were started forming after 3 h irradiation and 72 h of aging with a sonication energy of 150 W and nano crystalline Bikitaite zeolite with prominent peaks were obtained after 6 h irradiation of 250 W sonic energy. The Brunauer–Emmett–Teller (BET) surface area of the powder by N_2 adsorption–desorption measurements was found to be 209 m^2/g. The TEM micrograph and elemental analysis showed that desired atomic ratio of the zeolite was obtained after 6 h irradiation. For comparison, sonochemical method, followed by the hydrothermal method, with same initial sol composition was studied. The effect of ultrasonic energy and irradiation time showed that with increasing sonication energy, and sonication time phase formation was almost completed. The FESEM images revealed that 50 nm zeolite crystals were formed at room temperature. However, agglomerated particles having woollen ball like structure was obtained by sonochemical method followed by hydrothermal treatment at 100 °C for 24 h. The hydrogen adsorption capacity of Bikitaite zeolite with different Li content, has been investigated. Experimental results indicated that the hydrogen adsorption capacities were dominantly related to their surface areas as well as total pore volume of the zeolite. The hydrogen adsorption capacity of 143.2 c.c/g was obtained at 77 K and ambient pressure of (0.11 MPa) for the Bikitaite zeolite with 100% Li, which was higher than the reported values for other zeolites. To the best of our knowledge, there is no report on the synthesis of a Bikitaite zeolite by sonochemical method for H_2 storage.

1. Introduction

Now-a-days hydrogen has been considered as next generation clean fuel for its high energy content and clean burning emission [1]. Safe and high energy density storage of hydrogen is a challenge for its efficient use as a fuel. Hydrogen can be stored by chemisorptions (chemical bonding with metals) and physisorption (physical adsorption) process. The physisorption of hydrogen on various porous materials like zeolites, mesoporous silica materials, carbonaceous materials, metal-organic frameworks (MOFs) etc. have been studied intensely for hydrogen storage applications [2–10]. Zeolites as hydrogen storage materials are investigated broadly and it is found that as small molecules such as molecular hydrogen can be easily absorbed into a flexible network of zeolites [3–5].

Zeolites belong to a most prominent class of microporous materials which have been used commercially in many applications in catalysis and gas separation. Recently, zeolites have also been considered as potential sorbents for hydrogen storage. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms to form an open crystal lattice. The negative charge created by the substitution of an AlO_4 tetrahedron for a SiO_4 tetrahedron is balanced by exchangeable cations. The cations, which take part in the charge balance of zeolitic structure, play a very important role in determining the adsorption and gas-separation properties of zeolites. For strong binding of H_2 in zeolite pores, charge balance by light alkali metal cations such as Li^+, Na^+, Mg^{2+}

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into the porous framework of zeolite increases the binding energy for hydrogen adsorption [11–13]. Among the alkali metal cations, lithium ion is more promising due to its low atomic weight and high affinity towards hydrogen by charge induced dipole interactions [14]. On the other hand, the pore structure of zeolites, offers a high internal surface area, which is a useful attribute for the physisorption of hydrogen.

One of the potential advantages of using zeolites as hydrogen storage materials is their thermal and chemical stability. According to literature various groups are involved in the study of Hydrogen storage in various types of zeolites since the 1970's, with initial research focused on room and high temperature, and at high pressure adsorption of hydrogen in zeolite cages [15,16]. The kinetic diameter of the hydrogen molecule is 2.89 Å, so it can access to void spaces in zeolites. To enhance the hydrogen storage capacity of porous materials, different methods have been studied by different research group. Karikkethu et al. synthesized the metal organic framework, with Lithium doping for enhanced hydrogen uptake [10]. In comparison with zeolites, metal organic framework shows difficulties in synthesis, low thermal stability and high preparation cost. Recently, zeolites have also been considered as potential sorbents for hydrogen storage. They are of interest because of their, high bulk density, and adjustable composition.

Based on the above discussion, in the present study, we attempt to synthesize Bikitaite (Li-containing zeolites) for hydrogen storage application.

Small pore (diameter 0.28–0.37 nm) sized zeolite Bikitaite (BIK) has been studied for various applications and most notably has shown excellent performance in H_2 gas separations from other light gases like CO_2, N_2, CH_4 etc. [17]. However, to the best of our knowledge, there have been few reports on the synthesis of Li-zeolites for hydrogen storage.

From literature, zeolites can be synthesized from various precursor materials and methods [18,19]. Sathupunya et al. synthesized Lithium zeolite from clay at a crystallization temperature of 85 °C [20]. Murayama et al. synthesized it from sodium silicate solution by microwave treatment [18].

The most commonly used method to synthesis zeolite Bikitaite is hydrothermal synthesis and also by microwave heating. (Generally, the zeolite synthesis is performed in the temperature range of 90–200 °C for periods of time between several hours to several weeks [21]. Drysdale et al. synthesized BIK zeolite between temperature range 300–350 °C in a sealed gold capsule within 5–30 days [22].

During the past decade "soft" chemistry is commonly used for the preparation of solid state compounds. In this method, low temperature and environmentally friendly preparation procedures are used. Recently, successful attempts to decrease the crystallization temperature in the synthesis of microporous zeolite-type materials have been made [23,24]. From economical and environmental point, the low temperature synthesis opens a new route for synthesis by chemical reactions. For preparation of nano materials, sonochemical methods can lead to homogeneous nucleation and a substantial reduction in crystallization time at room temperature compared to conventional chemical methods [25,26].

Sonochemistry is the application of ultrasound to chemical reactions and processes. Ultrasound seems to influence the physicochemical phenomena related to nucleation and crystal growth, occurring during crystallization [27].

In this work, we have reported the synthesis of Li substituted alumino silicate zeolite Bikitaite zeolite nano crystals at room temperature in short crystallization time by sonochemical method. Further, ultrasonic irradiations have been used along with hydrothermal treatment for synthesis of zeolite nano crystals. A substantial reduction of the formation time of zeolite within 3 h, combined with full conversion of the sol into Bikitaite zeolite at 100 °C and room-temperature would make such synthesis very useful for zeolite. The effects of sonication and combined sonication and hydrothermal method on zeolite synthesis were characterized by phase identification, crystallinity, morphology, particle size distribution etc. H_2 adsorption capacity of the developed materials suited at cryogenic temperature and room temperature. The highest H_2 adsorption capacity for pure Li zeolite reached up to 1.3 wt% which is more than the reported value.

2. Experimental

The chemical reagents used are colloidal silica (Ludox AS-30% Sigma Aldrich), LiOH flakes (Merck, India), boehmite and distilled water. Two reactant mixtures were prepared respectively by suspending measured amount of colloidal silica and Lithium hydroxide in deionized water (DI water) in a glass beaker (mixture 1). A stirring bar was immersed into the solution and stirred with a magnetic stirrer (SCHOTT Instruments GmbH, Mainz, Germany) at 200 rpm for 30 min. In another mixture (mixture 2), measured amount of boehmite was mixed with 5 wt% of aqueous solution of Lithium hydroxide. Boehmite was dissolved in Lithium hydroxide solution by warming it at 90 °C. Then it was cooled to room temperature and mixed slowly to mixture 1 with constant and vigorous stirring, the mixture turned into a milky white sol. The initial mixture was stirred for 1 h. All these procedures were carried out at room temperature. The resulting mixture was sonicated for 3 h. The ultrasound equipment (UIP1500 hd HIELSCHER Ultrasound Technology) which produces acoustic waves at frequency of 20 kHz [28]. The energy input of sonication was varied from 150 W to 250 W followed by aging for 72 h. The molar composition of the sol used for the synthesis was 10 Li_2O:0.5 Al_2O_3:2.5 SiO_2:600 H_2O.

The sonicated mixture was poured into Teflon-lined stainless steel autoclave. Hydrothermal crystallization was continued under autogenous pressure in a hot air oven at 100 °C for 24 h. After synthesis, the zeolite powders were washed thoroughly with deionized water until the pH of the washing liquid became neutral and then dried at room temperature for further characterization.

For comparison, the different Bikitaite samples were synthesized by hydrothermal process similar to above mentioned condition without sonication treatment. The molar composition of the initial sol was same as that used in case of sonochemical synthesis. Crystallization was carried out in oven at 100 °C. The powdered products were recovered through centrifugation, washed with DI water until pH < 8.

3. Characterization

The Crystalline structure of the as synthesized powder was determined by X-ray diffraction pattern in the 2θ range of 0–60 were collected at ambient temperature. XRD was carried out on a Philips 1710 diffractometer using CuK_α radiation ($\alpha = 1.541$ Å).

The FTIR spectra of the BIK zeolite crystals were recorded in the diffuse reflectance mode using a Nicholet 380 FTIR spectrophotometer for detecting characteristics vibration bond.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed in static air using the thermogravimetric analyzer (NETZSCH STA 409 C F3 Jupiter, Germany). The samples were heated at a rate of 10 °C min^{-1} under air flow.

Microstructure and morphology of the zeolite crystals were examined using Scanning electron microscopy (FESEM: model Leo, S430i, U.K.). Elemental analyses of the samples were conducted by energy dispersive X-ray spectrometer (EDXS) attached to a Cambridge Stereo scan S440 microscope.