One pot non-emulsion based hydrothermal synthesis of urchin-shaped hydroxy sodalite using waste coal fly ash

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Urchin-shaped hydroxy sodalite particles have been synthesized by one pot non-emulsion based hydrothermal conversion of coal fly ash at 100 °C for 96 h in the absence of any surfactants. Crystallization behavior of the particles has been studied by X-ray diffraction, and the characteristic vibration bands of hydroxy sodalite were confirmed by FTIR spectroscopy. BET surface area of the particles are found to be 193, 197, 82 and 44 $m^2 g^{-1}$ for the reaction time of 24 h, 48 h, 72 h and 96 h, respectively. FESEM images revealed that the thread-ball-like particles are converted into urchin-shaped hydroxy sodalite with increasing reaction time from 24 h to 96 h at 100 °C. The elemental analysis of the product studied by EDX indicates the Si/Al and Na/Al ratios of 1.28 and 1.03, respectively which is close to the stoichiometric composition of hydroxy sodalite.

A large quantity of coal fly ash, a waste by-product is generated from electric power plant throughout the world. Efficient disposal of coal fly ash is a major concern worldwide due to its harmful effects on environment[1,2]. Utilization of fly ash in cement industry, brick construction materials, road pavements, etc., is widely known. However, the use of fly ash for the synthesis of zeolite is a promising way of value addition to the waste industrial by-product in terms of environmentally friendly and economically viability[3]. Due to uniform pore size and large surface area, zeolites are important materials for a wide range of applications such as ion exchanger, molecular sieves, catalysts, adsorbents and gas/liquid separation materials[4].

Synthesis of zeolite from coal fly ash has been reported by many authors[5]. Hollman *et al.*[6] reported the conversion of coal fly ash into NaA, NaX and NaP zeolites by two-step process. In this process silicon was extracted by alkaline attack of fly ash followed by adjusting Si/Al ratio with the addition of Al sources. Rayalu *et al.*[7] studied the effect of fusion reaction parameters for the preparation of NaY zeolite from fly ash. Ojha *et al.*[8] synthesized zeolite X from coal fly ash by alkali fusion followed by hydrothermal treatment. In recent time, Sangita *et al.*[9] synthesized zeolite from fly ash by adopting two methods: silica extraction method and fusion method.

Hydroxy sodalite is crystalline aluminosilicate and hydrophilic in nature. It belongs to the group of clathrasils made of cubic array of β-cages and has a structure similar to sodalite. With a six-member oxygen aperture, it has a kinetic diameter of 2.65 Å[10]. Due to its small diameter, it provides access to various molecules like He (~2.6 Å), H_2O (~2.7 Å) and NH_3 (~2.5 Å), making it a potential membrane material in separation of small molecules. It addition, hydroxy sodalite finds wide applications in semiconductor, hydrogen storage, hydrogen separation, catalysts and pigment occlusion materials[11]. We have earlier reported the synthesis of hydroxy sodalite from the agro-waste material, rice husk ash[12]. We have also reported emulsion-derived synthesis of urchin-shaped hydroxy sodalite using Span 80 as surfactant[13].

In the present work, we have synthesized urchin-shaped hydroxy sodalite particles by one pot non-emulsion based hydrothermal conversion of coal fly ash at 100 °C for 96 h in the absence of any surfactants. The present method is important in terms of low cost as well as environmentally friendly process.

Experimental

Coal fly ash was obtained from a thermal power plant in West Bengal, India. The raw fly ash samples were calcined at 800 °C for 1 h to remove unburnt carbon and other volatile materials present in the fly ash. Sodium hydroxide (GR, Merck, India) and deionized water were used for the experiments.

In a typical experiment, 10 g of fly ash was added into 86 mL of 1.66 *M* sodium hydroxide in a Teflon-lined autoclave, maintaining the molar composition of 6Na_2O:4.4 SiO_2:1Al_2O_3:200 H_2O. The slurry thus prepared was aged at 100 °C for 24 h, 48 h, 72 h and 96 h under static condition. After the reaction under hydrothermal condition, the resulting solid masses were washed with distilled water repeatedly until pH

of the washed liquid was almost neutral. Finally, the samples were dried at 80 °C for 6 h.

The chemical composition of fly ash was determined by X-ray fluorescence (XRF) analysis (PANalytical, model Axios, Almelo, Netherlands). The thermal behavior of the samples was studied by differential thermal analysis (DTA) and thermogravimetry (TG) (Netzsch STA 449C, Germany) from 30–800 °C in air atmosphere at the heating rate of 10 °C min^{-1}. The crystal phases of the particles were identified using powder diffraction technique using a Philips X'Pert Pro XRD (model PW 3050/60) with Ni-filtered Cu-K$_\alpha$ radiation (λ = 0.15418 nm), operating at 40 kV and 30 mA. The characteristic vibration bands of the particles were confirmed by FTIR (Spectrum two, Perkin Elmer) by KBr pellet method at a resolution of 4 cm^{-1} and scan rate of 100 spectra s^{-1}. Nitrogen adsorption-desorption measurements were made at 77 K with a Quantachrome (ASIQ MP) instrument. The samples were outgassed in vacuum at 200 °C for 4 h, prior to the measurement. The total surface area was determined by the BET method. The total pore volume was estimated from the amount of nitrogen adsorbed at the relative pressure (*p/po*) of ~ 0.99. The Barrett-Joyner-Halenda (BJH) method was employed to calculate the pore size distribution in the mesopore range. The morphology of the synthesized particles was examined by FESEM (model Zeiss, Supra^{TM} 35VP, Oberkochen, Germany) operating with an accelerating voltage of 10 kV, and elemental analysis of the synthesized products was determined by energy dispersive X-ray (EDX) analysis.

Results and discussion

The chemical composition (wt%) of fly ash was determined as: Na_2O (0.36%), MgO (1.04), Al_2O_3 (24.38), SiO_2 (63.58), P_2O_5 (0.65), SO_3 (0.11), K_2O (2.08), CaO (1.63), TiO_2 (1.32), Fe_2O_3 (4.80), SrO (0.02), ZrO_2 (0.03). Figure 1 shows (a) XRD, (b) FTIR and (c) FESEM image of fly ash. The XRD peak of fly ash shows the crystallization of α-quartz phase (JCPDS File No. 5-490) corresponding to the *hkl* values of (100) and (101) at 2θ of 20.9 and 26.8, respectively. FTIR spectra of fly ash indicate four prominent absorption bands at 466, 551, 791 and 1079 cm^{-1} (Fig. 1b). The signals at 1079 and 791 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of SiO_4 tetrahedra, respectively and that at 466 cm^{-1} to the Si-O bending mode of α-quartz[14]. The absorption band at 551 cm^{-1} was due

to Al-O vibration[15]. The FESEM micrograph of fly ash indicates irregular shape of the particles along with some spherical particles of size range 1-4 µm (Fig. 1c). During cooling of exhaust gas, the fused materials from the power plant solidified into spherical glassy particles.

XRD patterns of the samples synthesized at 100 °C for 24 h, 48 h, 72 h and 96 h (Fig. 2a) show the crystallization of hydroxy sodalite (JCPDS File No. 11-401) in all the samples along with the existence of α-quartz phase (JCPDS File No. 5-490). It is interesting that crystallization of hydroxy sodalite increases with increase in reaction temperature. To
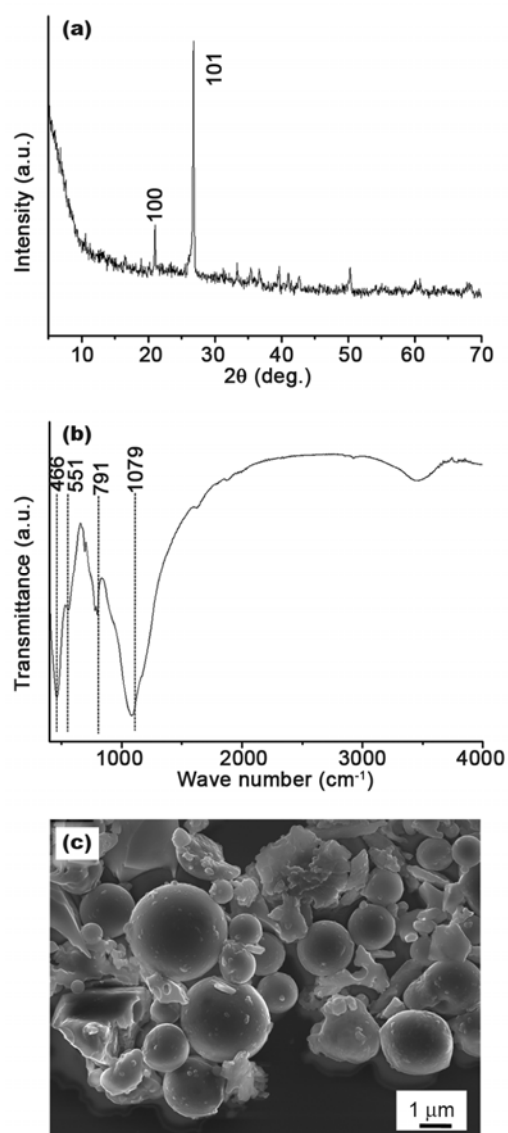

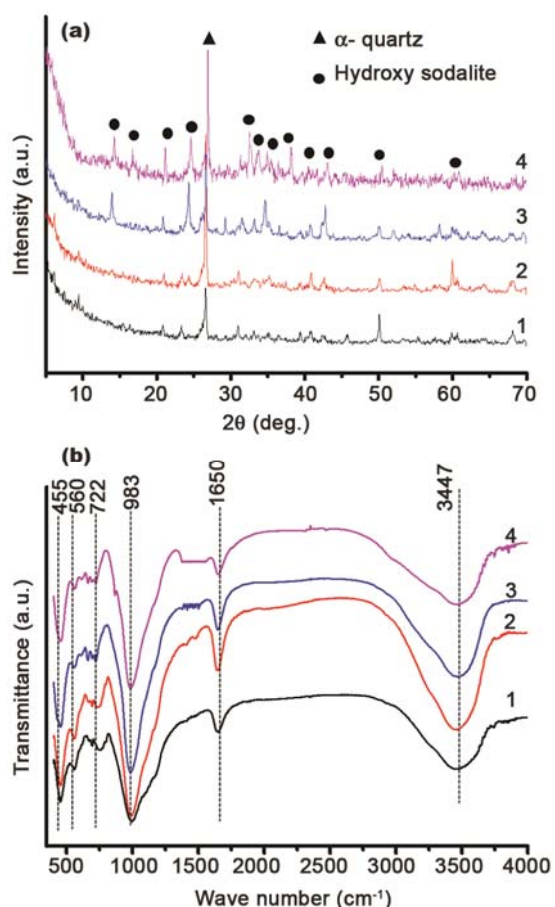Fig. 1 — (a) XRD, (b) FTIR and (c) FESEM image of coal fly ash.

Fig. 2 — (a) XRD and (b) FTIR spectra of hydroxy sodalite synthesized from coal fly ash at 100 °C for (1) 24 h, (2) 48 h, (3) 72 h and (4) 96 h reaction time.

investigate the vibrational characteristics of the bonds found in the samples, FTIR spectra were recorded (Fig. 2b). The characteristic absorption bands of hydroxy sodalite[16] were found for the reaction time of 24 h, 48 h, 72 h and 96 h. The absorption bands at 3442 cm⁻¹ and 1650 cm⁻¹ were due to O-H stretching and bending vibrations, respectively. The broad band at around 983 cm⁻¹ was assigned to the asymmetric stretching vibration of T-O-T (T = Si, Al), while that appearing at around 722 cm⁻¹ was due to symmetric stretching of T-O-T. The band at around 560 cm⁻¹ was attributed to Al-O vibration. The sharp absorption band at around 455 cm⁻¹, characteristic of bending vibration of O-T-O, confirmed the single four-membered ring (S4R) of the sodalite unit[17].

DTA and TG analyses of the sample prepared hydrothermally at 100 °C for (a) 24 h, (b) 48 h, (c) 72 h and (d) 96 h are shown in Fig. S1 (Supplementary data). The DTA curve of the sample shows a broad
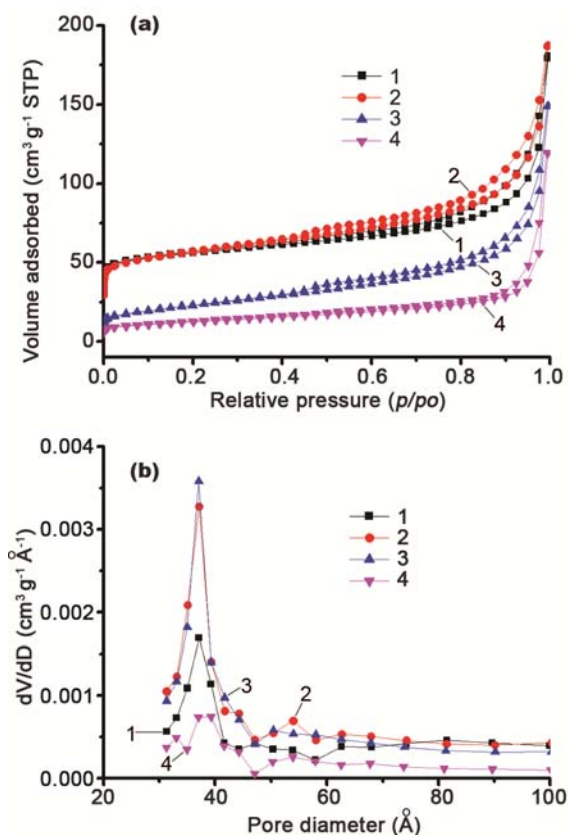

Fig. 3 — (a) Nitrogen adsorption and desorption isotherms and (b) pore size distributions of hydroxy sodalite synthesized from coal fly ash at 100 °C for (1) 24 h, (2) 48 h, (3) 72 h and (4) 96 h reaction time.

endothermic peak at around 122 °C, 113 °C, 101 °C and 95 °C for the reaction time of 24 h, 48 h, 72 h and 96 h, respectively. The TG analysis shows a total weight loss of about 11.7%, 14.7%, 13.8% and 26.6% up to 800 °C for the reaction time of 24 h, 48 h, 72 h and 96 h, respectively. The endothermic peak and the weight loss are attributed to the removal of adsorbed water in the sample.

Figure 3(a) shows the N_2 adsorption and desorption isotherms of hydroxy sodalite synthesized at 100 °C for 24 h, 48 h, 72 h and 96 h. The uptake of nitrogen increases steeply above the relative pressure of ~0.8, showing an IUPAC type IV isotherm in which the hysteresis loops are due to the formation of textural mesoporosity originated from the intergrowth of the crystals[18,19]. The mesopores generated during the formation of zeolite crystals have a slit-like shape reflecting H3 type hysteresis loops of the isotherms. The BET surface area values were found to be 193, 197, 82 and 44 m² g⁻¹ for the samples obtained for the reaction time of 24 h, 48 h, 72 h and 96 h, respectively
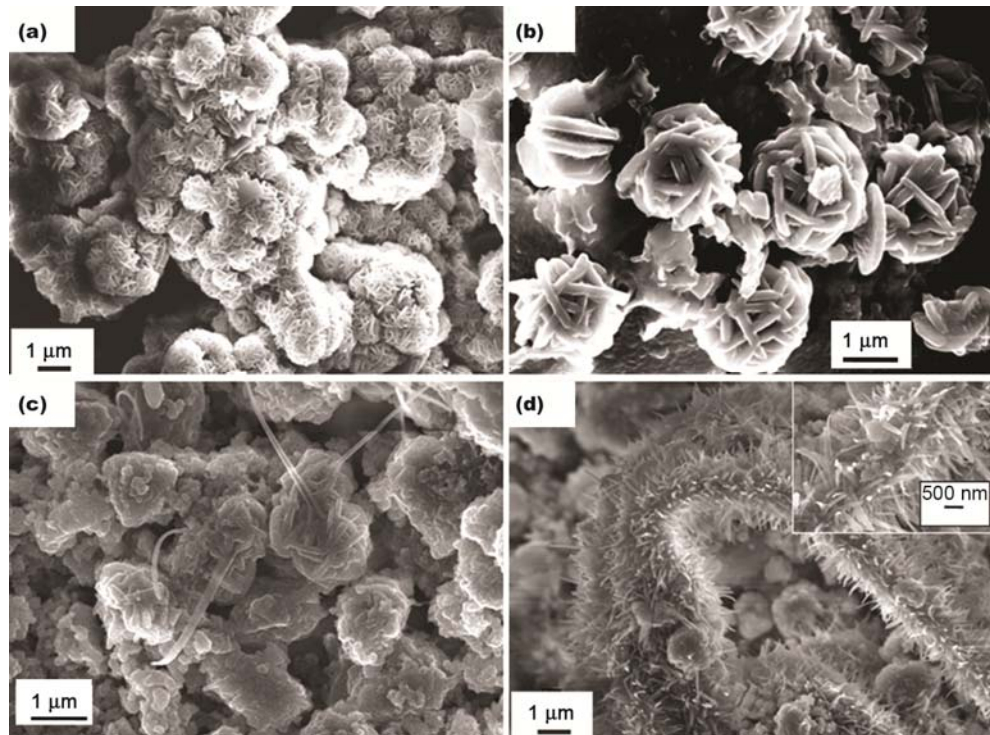
Fig. 4 — FESEM images of hydroxy sodalite synthesized from coal fly ash at 100 °C for (a) 24 h, (b) 48 h, (c) 72 h and (d) 96 h reaction time.

Table 1 — Textural properties of hydroxy sodalite particles obtained from coal fly as at 100 °C and 24-96 h

React. time at 100 °C (h)	S_{BET} $(m^2g^{-1})^a$	$V_{p\text{-Total}}$ $(cm^3g^{-1})^b$	D_p $(nm)^c$
24	193	0.28	3.7
48	197	0.29	3.7
72	82	0.23	3.7
96	44	0.18	3.9

(Table 1). Interestingly, with increase in crystallization time, the BET surface area decreased. The BJH pore size distribution curves of the corresponding samples (Fig. 4b) derived from the desorption data of the isotherm shows a prominent peak at around 37 Å (3.7 nm), indicating the generation of mesopores in the synthesized hydroxy sodalite particles.

Figure 4 shows the FESEM images of the hydroxy sodalite particle obtained hydrothermally at 100 °C for 24 h, 48 h, 72 h and 96 h. It reveals thread-ball-like particles of hydroxy sodalite of diameter of 1-2 μm for the reaction time of 24-72 h. A close inspection of the morphology shows that the nanoplate-like particles assembled together to form thread-ball-like particles. Interestingly, with increase in reaction time up to 96 h, rod-like particles with the diameter of 100-200 nm protruded from the surface of thread-ball like hydroxy
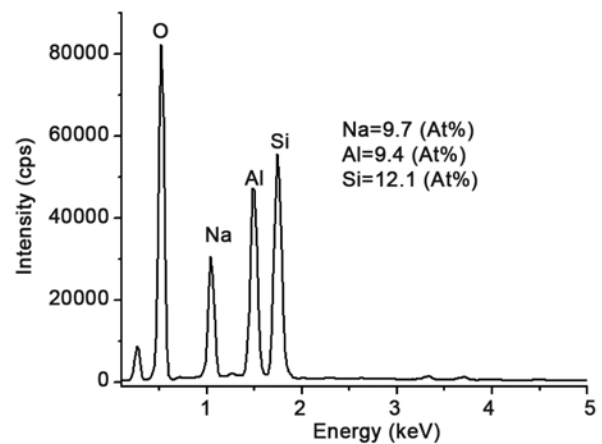

Fig. 5 — EDAX of hydroxy sodalite synthesized from coal fly ash at 100 °C for 96 h.

sodalite particles. The assembly of such particles looked like urchin shaped morphology. Elemental analysis of the product studied by EDX indicates the Si/Al and Na/Al ratios of 1.28 and 1.03, respectively (Fig. 5), which is close to the stoichiometric composition of hydroxy sodalite[10].

In this study, we report the synthesis of urchin-shaped hydroxy sodalite particles by direct extraction of coal fly ash in the presence of alkali without

using any surfactants and emulsion technique. The most abundant of industrial waste material (coal fly ash)**,** which is environmentally hazardous**,** can be exploited to yield a value added product like hydroxy sodalite in an economic and environmentally friendly process.

Supplementary data

Supplementary data associated with this article, viz, Fig. S1, is available in the electronic form at http://www.niscair.res.in /jinfo/ijca/IJCA_56A(04)394-398 SupplData.pdf.

Acknowledgement

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