Custard apple-shaped NaX zeolite with a large surface area derived from rice husk ash by a single-step template-free process

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ABSTRACT
Custard apple-shaped NaX zeolite with a large surface area was synthesized from rice husk ash without use of a templating agent via a single-step autoclave process at 90 °C/6h. The crystallinity of the particles was confirmed by XRD. An FTIR study shows the characteristic bands at 560 cm\(^{-1}\) for a double 6-membered ring (D6R), while a Raman shift at around 500 cm\(^{-1}\) indicates the bending mode of 4-membered ring fragments of NaX zeolite. The total BET surface area of the product was found to be 703 m\(^2\)g\(^{-1}\) comprising a micropore surface area of 623 m\(^2\)g\(^{-1}\) and a mesopore surface area of 80 m\(^2\)g\(^{-1}\). A hierarchical porous structure with micropores in the range of 0.72–1.76 nm and mesopores centred at 3.5 nm was obtained. FESEM and TEM images of NaX zeolite show a custard apple-like morphology (1–2 μm) of secondary particles which was formed by self-assembly of nanometer-sized (50–100 nm) primary particles. A proposed formation mechanism was illustrated.

1. Introduction
In recent years, research interest has focussed on utilizing waste materials for the production of valuable products via an environmentally friendly process. Rice husk ash (RHA) is one such waste product in the agriculture sector. It is usually dumped as land-fill material causing environmental pollution in the neighbouring areas. Due to its high pozzolonic properties, RHA is used in the cement industry to enhance the durability of concrete. The silica content of RHA is more than 90 wt%. By extracting SiO\(_2\) from RHA, silica and silica-based products such as SiC, Si\(_3\)N\(_4\), SiCl\(_4\) and zeolite can be produced [1].

Zeolite comprises crystalline microporous aluminosilicate with SiO\(_4\)\(^4-\) and AlO\(_4\)\(^3-\) tetrahedra linked by an oxygen bridge. Due to the presence of a uniform microporous structure, an ion-exchange capability, high thermochemical stability and molecular sieving properties, zeolite has industrial importance as a heterogeneous catalyst, adsorbent and ion-exchange product. Among the various zeolites, zeolite X is in the FAU (faujasite) family with its larger pore diameters (7.4 Å). Its framework structure is a truncated octahedral β cage connected tetrahedrally via a D6R (double-six ring) with eight cavities accessible by a 3D 12-ring pore structure. Due to its solid basicity and polar character, zeolite X is used as a catalyst, adsorbent and membrane material [2–4]. There are many reports of the synthesis of zeolite X (NaX zeolite) [5–7]. Mesoporous NaX zeolite was prepared using polydiallyldimethylammoniumchloride (PDADMAC) as an organic template [8].
Tetramethylammonium hydroxide was used as an organic template for the preparation of NaX zeolite [9]. Zhang et al. synthesized NaX zeolite at room temperature with up to 40 days aging [10]. Microporous zeolite having zeolitic pores is required as a shape- or size-selective catalytic or separation process. It hinders the diffusion and kinetic efficiency of a reaction process, however, for molecules larger than zeolitic pores [11]. Generation of mesopores within zeolitic micropores, i.e. the hierarchical porosity of zeolite, facilitates the molecular diffusion process. For generating mesopores within zeolite crystals, mesoporogens such as surfactants [12] and hard templates [13] are used. Considering the economic aspect, desilication and dealumination processes [14] are followed to create mesopores within the zeolite framework structure.

Rice husk ash (RHA), the agro-waste material, is used as a silica source for the preparation of NaA [15], LTL [16], ZSM-5 [17], NaX zeolites [18], NaY zeolites [19], zeolite beta [20], SUZ-4 [21], hydroxy sodalite [22], etc. Using waste materials such as RHA is important from an environmental, economic and industrial point of view. Extraction of silica from RHA is a tedious process, however, in light of which involves many processing steps towards the preparation of NaX zeolite. The importance of rice husk ash, in the present study, single-step template-free processing of rice husk ash-derivated zeolite X (NaX) was prepared with a hierarchical microstructure (nano/micro) and pores (micro/mesopores) having the maximum surface area, and reported for the first time to the best of our knowledge.

2. Experimental

Rice husk ash containing 96.5% SiO$_2$ was used as the silica source, and sodium hydroxide (Merck India, purity > 97%) and sodium aluninate (Sigma Aldrich, 45%Na$_2$O + 55%Al$_2$O$_3$) were utilized as the sources of Na$_2$O and Na$_2$O/Al$_2$O$_3$, respectively. For the preparation of NaX zeolite, 7.00 g of RHA was added to a NaOH solution (10.50 g NaOH in 50 mL DI H$_2$O) in a Teflon-lined autoclave, followed by stirring at 80–90°C for 2 h under closed conditions. 4.41 g of sodium aluninate in 20 mL H$_2$O was added to the above dispersion, and stirring was continued for another 15 min. The molar ratio of the component was 6.8Na$_2$O: 1Al$_2$O$_3$: 4.65SiO$_2$: 164H$_2$O. The above dispersion was treated at 90°C for 6 h under static hydrothermal conditions. The synthesized product was collected by washing with water and centrifugation several times to reach a supernatant pH of 7–8, followed by drying at 70°C/5 h.

The synthesized NaX zeolite was analyzed by DTA/TG (Netzsch STA 449C, Germany), XRD (Philips X’Pert Pro XRD, PW 3050/60), FTIR (Spectrum II, Perkin Elmer), Raman spectrometer (RENISHAW spectrometer at 514 nm radiation from an argon laser at room temperature), nitrogen adsorption-desorption measurements (Quantachrome, ASIQ MP), FESEM (Zeiss, SupraTM 35VP, Oberkochen, Germany) and TEM (Tecnai G2 30ST, FEI).

3. Results and discussion

Figure 1(a) shows the DTA/TG of the synthesized NaX zeolite. A broad endothermic peak at around 137 °C in the DTA curve indicates the removal of adsorbed water, which is reflected by a maximum weight loss of 15.7% up to 300 °C in the TG curve. XRD analysis of the as-prepared powder is shown in Figure 1(b). The formation of NaX zeolite is confirmed with the appearance of peaks at 2 theta (degree) values of around 6, 10, 11.7, 15.4, 18.4, 20.1, 22.5, 23.3, 26.6, 29.2, 30.3, 30.9, 32, 33.6, 37.4 and 40.8, which correspond to the (hkl) values of (111), (220), (311), (331), (511), (440), (620), (533), (642), (733), (822), (157), (840), (664), (1022) and (−880), respectively (JCPDF File No. 39–218). Figure 1(c) shows the FTIR spectra of NaX zeolite. The characteristic absorption bands of NaX zeolite were obtained at around 459, 560, 667, 748 and 985 cm$^{-1}$ [23–25]. The band at 459 cm$^{-1}$ is assigned to Si-O-Al bending vibrations while the band at 560 cm$^{-1}$ represents the D6R of FAU-type zeolite [24]. The absorption bands at 667 and 748 cm$^{-1}$ are attributed to Si-O-Al-O 54R symmetric bending and symmetric stretching vibrations, respectively [25]. The antisymmetric stretching vibration of Si-O and Al-O is observed at 985 cm$^{-1}$. The band at 985 cm$^{-1}$ is also due to the silanol group [26]. Figure 1(d) shows the Raman spectra of NaX zeolite. A strong Raman shift at around 500 cm$^{-1}$ indicates the bending mode of 4-membered ring fragments, while the less intense peaks at around 275 and 370 cm$^{-1}$ are due to the bending mode of the double six-membered ring (D6R) structure of zeolite X [27].

Figure 2(a) shows the $N_2$ adsorption-desorption isotherm of zeolite X. It indicates the type IV isotherm signifying mesoporosity of the crystals [28–30]. The isotherm also indicates the initial steep micropore filling at $p/p_0 < 0.02$ followed by H4-type narrow hysteresis loops at a relative pressure of around 0.45–0.85. This indicates slit-like mesopores [31] generated via intercrystal NaX zeolite packing. At a higher relative pressure (0.85), a sudden rise in isotherms is attributed to the formation of macropores by the larger aggregated NaX particles. The total BET surface area of the product was found to be 703 m$^2$·g$^{-1}$—comprising a micropore surface area of 623 m$^2$·g$^{-1}$ and a mesopore surface area of 80 m$^2$·g$^{-1}$. The percentages of microporosity and mesoporosity are 88.6% and 11.4%, respectively. The pore volume and BJH pore size of NaX zeolite were 0.41 cm$^3$·g$^{-1}$ and 3.5 nm, respectively. Figure. 2(b and c) represent the pore size distributions curve obtained from the BJH.
Figure 1. (a) DTA/TG, (b) XRD, (c) FTIR and (d) Raman analysis of NaX zeolite.

Figure 2. (a) $N_2$ adsorption-desorption isotherm and pore size distributions by (b) BJH and (c) a NLDFT model of NaX zeolite.
A mesopore size of around 3.5 nm was calculated from the BJH pore size distributions, while the NLDFT model rendered micropore size distribution in the range of 0.72–1.76 nm. The pore sizes centred at 0.72 and 1.41 nm are comparable to the free aperture (0.74 nm) and cavity (1.3 nm) dimensions of unit cell NaX zeolite [32]. The pores centred at 1.7 nm could, however, be due to intercrystalline micropores of zeolite X crystals.

Figure 3(a,b) shows low and high magnification FESEM images of NaX zeolite. It is apparent that small nanoparticles (50–100 nm) aggregate together to form custard apple (Annona reticulate)-like NaX particles 1–2 μm in size. A TEM image also shows the aggregation of nanosized (50–100 nm) NaX particles (Figure 4(a)), which are clearly visible in the higher magnification image (Figure 4(b)). The crystallite size calculated from Scherrer’s equation is found to be 27 nm. It should be noted that the primary nanoparticles are assembled to form micron-sized secondary particles with a custard apple-shaped morphology. Thus, a hierarchical microstructure is formed in NaX zeolite. The intra- and/or intercrystalline micropores and intercrystalline mesopores are revealed by a higher magnification TEM image (Figure 4(b)). HRTEM (Figure 4(c)) shows a lattice fringe of 1.44 nm crystalline NaX, which is assigned to the (111) planes of the cubic FAU-type structure. A SAED pattern (Figure 4(d)) of zeolite X shows diffraction rings corresponding to the characteristic lattice planes of (220), (331), (511), (440), (620) and (533) of NaX zeolite. Figure 4(e) shows an EDX analysis of synthesized NaX particles indicating the presence of Si, Al, Na and O with their atomic percentages of 15.21, 11.71, 13.49 and 59.57, respectively. The Si/Al and Na/Al ratios are found to be 1.29 and 1.15, respectively, which are

Figure 3. FESEM images of NaX zeolite: (a) low magnification and (b) high magnification.

Figure 4. (a,b) TEM image, (c) HRTEM image, (d) SAED pattern and (e) EDX analysis of NaX zeolite.
comparable to the stoichiometric composition of typical NaX zeolite \([\text{Na}_86(\text{AlO}_2)_{86}(\text{SiO}_2)_{106})_{2.64} \text{H}_2\text{O}].\)

The tentative formation mechanism of zeolite X crystals from RHA is illustrated in Figure 5. It is worth noting that RHA contains about 96% SiO\(_2\) which undergoes dissolution as a soluble silicate species in the presence of strong NaOH. As the reaction proceeds, RHA particles are surrounded by Na\(^+\), OH\(^-\) and Al(OH)\(_4^-\) ions resulting from dissolution of silicate species from RHA. Under autogenic pressure under alkaline conditions at 90 °C both aluminate and silicate species render SiO\(_4^-\) and AlO\(_4^-\) tetrahedron through bridging with Na\(^+\) ions. Thus, monomeric silicate/aluminate species in the liquid phase turned into the amorphous aluminosilicate solid phase composed of 4-membered rings, which are connected to each other via double six-membered ring (D6R) followed by nucleation of NaX zeolite crystals. This was confirmed by FTIR and Raman spectroscopy. A microstructural study illustrated that the nanometer-sized (50–100 nm) primary particles self-assembled to form micron-sized secondary particles with a custard apple-like morphology (1–2 μm). Textural analysis showed a maximum surface area of 703 m\(^2\)g\(^{-1}\) of zeolite X particles comprising micropores (0.72–1.76 nm) and mesopores (3.5 nm). This hierarchical porous NaX zeolite with a large surface area synthesized from agro-waste material (RHA) by a single-step process meets the demand from industrial sector for various applications in catalytic, adsorption and membrane separation.

**4. Conclusion**

Custard apple-shaped NaX zeolite with a hierarchical microstructure and porosity was synthesized from rice husk ash without the use of any templating agent. During hydrothermal synthesis at 90 °C/6 h, monomeric silicate species in the liquid phase extracted from RHA turned into an amorphous aluminosilicate solid phase composed of 4-membered rings connected to each other via a double six-membered ring (D6R) followed by nucleation of NaX zeolite X crystals. This was confirmed by FTIR and Raman spectroscopy. A microstructural study illustrated that the nanometer-sized (50–100 nm) primary particles self-assembled to form micron-sized secondary particles with a custard apple-like morphology (1–2 μm). Textural analysis showed a maximum surface area of 703 m\(^2\)g\(^{-1}\) of zeolite X particles comprising micropores (0.72–1.76 nm) and mesopores (3.5 nm). This hierarchical porous NaX zeolite with a large surface area synthesized from agro-waste material (RHA) by a single-step process meets the demand from industrial sector for various applications in catalytic, adsorption and membrane separation.

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**Disclosure statement**

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