Synthesis and characterization of NaX and Cu-exchanged NaX zeolites from silica obtained from rice husk ash

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Sodium X zeolite and a number of other zeolites such as PC, HS and analcime were synthesized using rice-husk ash as a source of silica. Also, a number of NaCuX zeolites were prepared by ion-exchange method with copper contents from 2.8 to 10.5 wt%. The products were characterized using X-ray diffraction analysis. The morphological characteristics of the prepared zeolites were also studied. The NaX zeolite exhibits typical octahedral form whereas analcime and zeolite PC have trapezohedral and spheroid forms, respectively. Differential thermal patterns of NaCuX zeolites revealed the presence of an initial sharp and intense endotherm for dehydration around 190-220°C followed by an exotherm around 830-860°C representing structural change and dissociation, which were confirmed by X-ray diffraction analysis.

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Zeolites find wide applications in diverse areas, starting from catalysis in bulk and fine chemicals production to gas purification and waste treatment. These materials are usually synthesized from pure chemicals1-3. As such, the costs of the synthesized zeolites are high enough to draw attention for economic applications. Efforts have been made to synthesize zeolite materials from low cost raw materials such as fly ash. NaX zeolite, with its most open structure (50% void volume and 7.4 Å dehydrated free aperture), has extensive industrial applications as a catalyst for a variety of reactions. Present work is concerned with the detailed synthesis and characterization of NaX zeolite from silica obtained from rice husk ash.

Rice husk is available in plenty and at a low cost in agricultural countries like Bangladesh, Burma, China, India, Japan and Sri Lanka. The husk on burning yields a porous, cellular and light grey colored ash, which contains amorphous silica up to 90 wt%. This silica, extracted from rice husk ash by sodium hydroxide, has been used for NaX zeolite synthesis. In the process of crystallizing NaX with different compositions of the reaction mixture, temperature and time as the variables, zeolites PC, HS and analcime have been obtained in several experimental runs. These species also find extensive industrial use. In the present work, the morphological characteristics of different zeolites obtained at various stages of zeolitization have been studied. In addition, NaCuX zeolite has been synthesized by replacing part of the sodium of synthesized NaX zeolite with copper and analyzed for morphology and thermal characteristics. Cu-exchanged zeolites find extensive use in heterogeneous catalysis such as in NOx decomposition, NOx reduction with ammonia or with hydrocarbons, ammonoxidation of toluene to benzonitrile, in the production of aniline from chlorobenzene and ammonia, in the cyclopropanation of olefins by ethyl diazoacetate. Gas phase catalytic oxidation of benzyl alcohol has also been carried out over Cu-NaX with added alkali metals.

Experimental

Materials

In the present work, rice husk ash, sodium hydroxide, aluminum hydroxide and silica gel were used as the starting materials for the initial mix for the synthesis of NaX and other zeolites. Pellets of sodium hydroxide (Supplied by ARC Industries, Kanpur, India) were used in the present study. Aluminum hydroxide in the form of fine powder was obtained from APEX Chemicals, Mumbai, India. Silica gel of 98.59% purity (BDH) was ground in a ball mill to ~200 mesh size. Rice husk, obtained from a rice mill in Kanpur, India was burned in a muffle furnace at
1000°C for 10 h, and the carbon-free ash obtained was ground in a ball mill to 0.074 mm particle size. The X-ray diffraction pattern of the ash indicated that the silica was in the form of α-cristobolite. The chemical composition of the ash is presented in Table 1. Pure NaX (13X) zeolite from Linde (U.S.A.) was used for comparison with the prepared zeolite.

Procedure

The silica solution was first prepared by treating the rice husk ash with 2.5 molar aqueous NaOH solution at 80°C for 5 h with continuous shaking. The solution was then filtered under vacuum to separate it from the insolubles. Fine silica gel was added to this solution, if additional amount of silica was desired.

The sodium aluminate solution was prepared by adding aqueous NaOH solution to Al(OH)₃ powder and the solution was heated to boiling. The sodium silicate and aluminate solutions were mixed slowly with continuous shaking to get the sodium aluminosilicate gel of desired composition. This reaction mixture was then charged into the autoclave for hydrothermal reaction and it was raised to the desired temperature. Liquid samples containing fine solids were taken at regular intervals of time, while the reaction proceeded. These samples were filtered under vacuum and the solid samples were dried in an oven at 120°C for 12 h.

In the synthesis, the temperature of the reaction was varied from 95 to 120°C and the reaction time from 2 to 12 h. In the starting gel, the Na₂O/Al₂O₃ molar ratio was varied from 3 to 10 with the SiO₂/Al₂O₃ molar ratio ranging from 2 to 7. The water content of the gel was varied from 90 to 98 mol%. A standard high pressure reactor (Parr, Series 4500) of one litre capacity was used for the synthesis. Quantitative estimation of NaX zeolite in the end product of each run was made by comparing the X-ray diffraction pattern of the product with that of the pure NaX zeolite (Linde). The associated zeolites formed during synthesis were found to be analcime, P₉, and hydroxysodalite (HS).

For the preparation of NaCuX zeolite, known amount of NaX zeolite was mixed with cupric acetate solutions of varying concentrations and stirred for 10 h at a temperature of 30°C. After equilibrium, the exchanged zeolites were filtered, repeatedly washed with distilled water and dried. The degree of exchange was determined from the concentrations of the sodium ions in the filtrate with the help of a flame photometer. The absence of free cupric acetate in the Cu-exchanged zeolite was confirmed by X-ray diffraction.

NaX and other prepared zeolites were characterized for morphology, surface properties and thermal properties using various techniques. X-ray diffraction analyses were carried out on a GE unit fitted with an XRD-6 diffractometer using Ni-filtered copper Kα radiation. Scanning is done in the range of 5-50° (2θ) at a scanning speed of 3°/min and a chart speed of 30 mm/min.

The scanning electron microscopic (SEM) studies were performed mainly to study the structure, nature and crystal of the synthesized zeolites. The SEM instrument (ISI, 60) for the present study was operated at 30 kV/SE and 50° inclination.

The infra-red (IR) spectra for the pure NaX and the NaCuX zeolites were recorded using a Perkin-Elmer 521 IR Spectrometer. The spectra were obtained in the range of 400 to 4000 cm⁻¹, which covers the frequency ranges for the framework structure and water association.

Results and Discussion

NaX Zeolite

NaX zeolite was prepared with two different initial batch compositions, namely 5.2Na₂O.Al₂O₃, 4.0SiO₂.208H₂O and 5.6Na₂O.Al₂O₃, 5.0SiO₂, 286H₂O. The temperature for synthesis was 95°C and the batch time was 6 h. Fig. 1 shows the X-ray diffraction pattern of synthesized NaX zeolites and also that of commercial one (Linde, USA). It is evident from the XRD patterns that the synthesized NaX zeolites are comparable to the commercial NaX. The "d" spacings for the synthesized NaX are in conformity with the reported values⁸.

PC Zeolite

The zeolite PC was synthesized with an initial batch composition of 4.4Na₂O.Al₂O₃.5.5SiO₂.396H₂O and at a temperature of 100°C with a batch time of 6 h. The XRD pattern of the zeolite is shown in Fig. 2.
The "d" spacings for the synthesized zeolite compare well with the reported values\(^1\).

**Hydroxysodalite (HS)**
The typical formula for hydroxysodalite is \( \text{Na}_6[(\text{AlO}_2)\alpha(\text{SiO}_2)\beta].8\text{H}_2\text{O} \). Hydroxysodalite was prepared with an initial batch composition of \(4.0\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.4.0\text{SiO}_2.120\text{H}_2\text{O} \). The temperature of synthesis was 120°C and the batch time was 4 h. The "d" spacings of the synthesized HS are comparable with that obtained by Barrer and White\(^17\).

**Analcime**
This is the most common and extensively occurring species. The typical formula of analcime is \( \text{Na}_6[(\text{AlO}_2)\alpha(\text{SiO}_2)\beta].16\text{H}_2\text{O} \). The initial batch composition for analcime synthesis was \(4.4\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.5.5\text{SiO}_2.396\text{H}_2\text{O} \), processed at 100°C for 8 h. The XRD pattern of synthesized analcime is given in Fig. 2.

**Morphology**
Scanning electron micrograms of all the prepared zeolites were taken to determine their crystal structures. The NaX species has a framework with a truncated octahedra linked tetrahedrally in an arrangement.
similar to the carbon in diamond. It has a cubic symmetry and occurs in typical octahedral crystals as shown in Fig. 3a.

Zeolite Pₐ occurs as a polycrystalline spheroid. Single crystals have also been reported. In the present work, the spheroid particles of this species have been observed to be much smaller in grain size compared to NaX octahedral grain (Fig. 3b).

Hydroxysodalite (HS) has a cubic symmetry and is built up of single 6-fold tetrahedra. The scanning electron microgram has revealed equigranular form with cubic symmetry (Fig. 3c).

Analcime has cubic symmetry and exhibits two crystal forms, namely trapezohedral and cuboctahedral. In the present investigation, analcime has been observed to be present as subhedral crystals (Fig. 3d).

Copper exchanged NaX zeolite (NaCuX)

From the prepared NaX zeolite (from silica obtained from rice husk ash), NaCuX zeolites were prepared by ion exchange method with cupric acetate solutions containing 2.79, 2.98, 4.26, 5.20 and 10.69% by weight copper. Corresponding weight percentages of sodium replacement (by copper) were 25.6, 27.3, 39.1, 47.6 and 98.1, respectively. These NaCuX zeolites were characterized by X-ray diffraction and infra-red techniques. The XRD patterns are shown in Fig. 4. The absence of cupric acetate in the
NaCuX species was confirmed by comparing the diffraction patterns of NaX and NaCuX zeolites. The lattice parameters for the NaX and copper substituted samples were estimated from the ‘d’ spacings (see Table 2). The data revealed a linear contraction of the unit cell with increase in the percentage of copper in NaCuX zeolite.

Effect of increasing copper content is also evident from the infra-red spectra of NaCuX zeolites. The mid-infra-red region (1250-350 cm\(^{-1}\)) of the spectra is informative in characterizing the framework of zeolites under consideration. The first group of frequencies of the strongest vibrations (1250-950 cm\(^{-1}\)) can be assigned to internal tetrahedron vibrations. The occurrence of the strongest band around 985 cm\(^{-1}\) for the NaX zeolite indicates high silica and low alumina in its framework structure (Fig. 5). With increase in copper content, this band was observed to shift to a lower frequency side. A similar shift of the stretching modes involving mainly the tetrahedral atoms was also noticed in the region of 820-650 cm\(^{-1}\) (Fig. 6). The shift of the band towards lower frequency side with increase in copper content can be explained on the basis of Hook’s law,\(^\text{18}\) which is stated as:

\[
\bar{\nu} = \frac{1}{2C} \left[ \frac{f}{(M_X - M_Y)} \right]^{1/2} \left[ \frac{(M_X + M_Y)}{(M_X - M_Y)} \right]
\]

where, \(\bar{\nu}\) is the vibrational frequency (cm\(^{-1}\)), \(C\) is the velocity of light (cm/s), \(f\) is the force constant of the band in dynes/cm, \(M_X\) and \(M_Y\) are the mass (g) of atoms X and Y, \((M_X - M_Y)/(M_X + M_Y)\) is the reduced mass, respectively. During the process of ion ex-

<table>
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<tr>
<th>Zeolite</th>
<th>% Cu replacing Na</th>
<th>hkl (111)</th>
<th>Contraction (Å)</th>
<th>hkl (533)</th>
<th>Contraction (Å)</th>
<th>hkl (822)</th>
<th>Contraction (Å)</th>
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<td>0.0</td>
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<td>0.04</td>
<td>24.83</td>
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<td>24.70</td>
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<td>24.66</td>
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change, with the increase in the percentage of copper, the reduced mass increases leading to a decrease in the vibrational frequency.

Thermal studies
The dehydration and decomposition processes for zeolites were studied using differential thermal analysis (DTA). In general, the differential thermal analysis pattern for a zeolite species exhibits endothermic changes in the low temperature region due to dehydration followed by exothermic event in the high temperature region, corresponding to the conversion of zeolite to another amorphous or crystalline phase. Each of zeolite species has its own characteristic thermal behaviour. The differential thermal and thermogravimetric data were obtained with a MOM derivatograph. The heating rate was 10°C/min. Around 500-800 mg of sample was used in each case. As the weight of the sample taken was known, it was possible to estimate quantitatively the heat energies for the endothermic and exothermic peaks by calibrating the peak areas with that of a standard material, whose heat of reaction was known.

The details of the differential thermal data are presented in Table 3. In the differential thermal patterns for all the NaCuX samples, an initial endotherm at 190-220°C followed by an exotherm at 840-860°C was observed as in the case of NaX (see Figs 7a and 7b). The significant difference between the copper exchanged and the pure NaX species is that while in the case of the pure NaX species, no change was noticed in the temperature range of 500-700°C, between the dehydration and exothermic events in the DTA patterns; NaCuX species appear to undergo significant change in this region as evidenced from two broad endothermic peaks. X-ray diffraction data revealed structural collapse in NaCuX zeolites when

![Fig. 7a—DTA/TGA thermograms of NaX zeolite](image)

![Fig. 7b—DTA/TGA thermograms of NaCuX zeolite with 39.1% Cu replacing Na](image)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>% Cu replacing Na</th>
<th>Total weight loss (%)</th>
<th>Endotherm</th>
<th>Exotherm</th>
<th>Heat energy (kcal/g)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Range (°C)</td>
<td>Peak (°C)</td>
<td>Weight loss (%)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Endotherm</td>
<td>Exotherm</td>
<td>Endotherm</td>
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<td>NaX</td>
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<td>200</td>
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<td>35-400</td>
<td>200</td>
<td>14.00</td>
</tr>
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</table>
heated at temperatures >200°C (see Fig. 8). Recrystallization of a new phase appears to take place at higher temperatures (750-900°C).

While the weight loss suffered by pure NaX zeolite was around 19%, the same for NaCuX zeolite was found to vary from 14% to 15%, depending on the percent of copper in place of sodium. The weight loss corresponding to the exothermic change in all the cases was observed to be negligible (Table 3).

The heat energy involved in the dehydration process appears to decrease with an increase in percent of copper in the zeolite lattice up to about 28% of copper replacing sodium in NaX zeolite (see Table 3). Beyond this amount, with increase of copper in the lattice, the energy tends to increase for the dehydration process. However, for the dissociation and recrystallization of a new phase as evidenced in Fig. 8, the heat energy involved in the exotherm registered a continuous increase with the replacement of sodium by copper in the NaX matrix.

To understand the endothermic and exothermic peaks in the range 70-375°C and 820-960°C, respectively, X-ray diffraction patterns were obtained for NaCuX samples, with 39.1% copper replacing sodium, heat treated at 200, 550, 750, 850 and 900°C for 18 h. It can be observed from Fig. 8 that the structural collapse takes place earlier to 500°C as evidenced from the collapse of characteristics reflections. New product starts developing from 500°C onwards, which improves in its quantity up to 900°C.

Conclusions
A number of zeolites such as NaX, P₃, analcime and hydroxydsodalite were synthesized using silica obtained from rice husk ash and characterized using various standard techniques. A series of NaCuX zeolites were also prepared by exchanging Na of the synthesized NaX with copper and a detailed thermal analysis of the copper exchanged NaX zeolites was performed. The weight loss suffered by pure NaX zeolite was found to be around 19%; the same for NaCuX zeolite was found to vary from 14 to 15%, depending on the percent of copper in place of sodium. The weight loss corresponding to the exothermic change in all the cases was negligible, though there is a strong evidence for the production of new species at higher temperature conditions.

References
2 Milton R M, U. S. Pat. 2 882 244, 1959.
(1971) 380.