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THERMAL CHARACTERISTICS OF SYNTHETIC SODIUM ZEOLITES PREPARED WITH SILICA FROM RICE-HUSK ASH

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The differential thermal analysis and thermogravimetric data on the synthetic sodium zeolite species NaX, P_c, HS, Z–21 and analcime, prepared with silica from rice-husk ash, are presented. The DTA curves revealed the presence of an initial endotherm for dehydration, followed by an exotherm at around 800 to 850°, representing the structural change and dissociation of all these species, except in the case of zeolite Z–21. For the latter, the initial endotherm was followed by an endotherm in the 900° region. The structural changes inferred on the basis of the DTA curves were confirmed by X-ray diffraction analysis.

Zeolite NaX has been synthesized for the first time with rice-husk ash as the silica source, and it has been characterized for use as a molecular sieve in the separation of miscible organic fluids. Hitherto, this species has been synthesized from pure chemicals [1–3] and also using other silicate minerals [4]. Rice-husk is available in plenty in rice-producing countries such as India, Sri Lanka, Burma, Thailand, Bangladesh and China. On burning, the husk yields an ash of porous cellular silica of about 99% purity.

A typical oxide formula of zeolite NaX is $Na_2O \cdot Al_2O_3 \cdot 2.5SiO_2 \cdot 6H_2O$. With a high SiO_2/Al_2O_3 molar ratio, this zeolite has dehydrated pore apertures of 740 pm. Zeolite X has extensive industrial applications as a catalyst and as a molecular sieve [5–12]. In studies of the field of crystallization of NaX, with composition, temperature and time as the variables, zeolites P_c, HS, Z–21 and analcime have been prepared in several experimental runs. These species also find extensive industrial use [13].

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The thermal study of these zeolites is of significance as it concerns their use in industry. The species synthesized by the authors have been characterized by means of X-ray diffraction analysis. The differential thermal and thermogravimetric patterns for these zeolites are discussed, and the thermal energies involved in the dehydration and the dissociation events for each of these members are given in the present paper. The compositional changes in NaX during dissociation have been established by a systematic X-ray diffraction study.

Experimental

The experimental procedure for the synthesis of NaX and other associated zeolites is quite similar to the procedure for mordenite synthesis [14]. In the present study, rice-husk ash, sodium hydroxide, aluminium hydroxide and silica gel were used as the starting materials for the initial mix for the synthesis of NaX and other associated zeolites. Rice-husk ash was obtained from a rice mill in Kanpur. The autoclave used in the synthesis was a standard high-pressure reactor (Parr, Series 4500) of one litre capacity, designed to withstand a gauge pressure of 6895 Pa and a temperature of 350°.

The differential thermal and thermogravimetric data were obtained with a MOM derivatograph. The heating rate was 10 deg/min.

For estimation of the thermal energies involved in the dehydration and dissociation of the zeolites, K_2SO_4 was used as a standard reference material. The estimated weight losses were obtained from the TG patterns of these zeolite species.

X-ray diffraction analyses were carried out on a G. E. unit fitted with an XRD–6 diffractometer, using Ni-filtered copper radiation. Scanning was done in the range of 5–50° (2θ) at a scanning speed of 3°/min with a chart speed of 30 mm/min.

Results and discussion

Zeolite NaX

The differential thermal pattern of zeolite NaX (Fig. 1) exhibits a broad endotherm between 40 and 500°, with its peak at around 220°, corresponding to dehydration. The weight loss in this region is around 19.3%. The structure remains essentially the same up to the commencement of the exotherm, as confirmed from the presence of reflections for zeolite NaX in its X-ray diffraction pattern at 750°

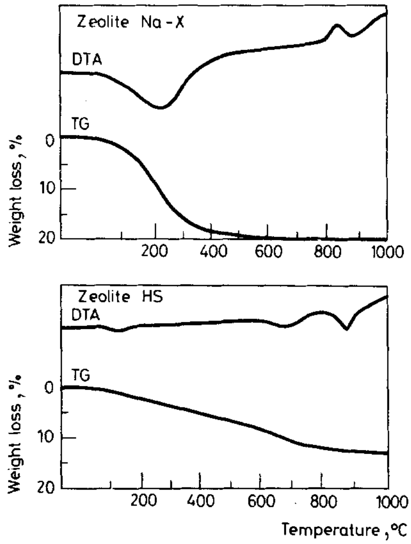

Fig. 1 DTA and TG curves for zeolite NaX and HS

(Fig. 2). The exotherm in the temperature range 780–880°, with its peak at around 830°, represents the dissociation of zeolite and the formation of a new phase.

The X-ray diffraction data (Fig. 2) on the sample at 850° reveal the formation of nepheline and α-carnegieite, as evidenced from the development of reflections at 418, 380, 324, 318, 302, 291, 257, 247, 239, 234, 230, 215, 205, 195 and 187 pm for

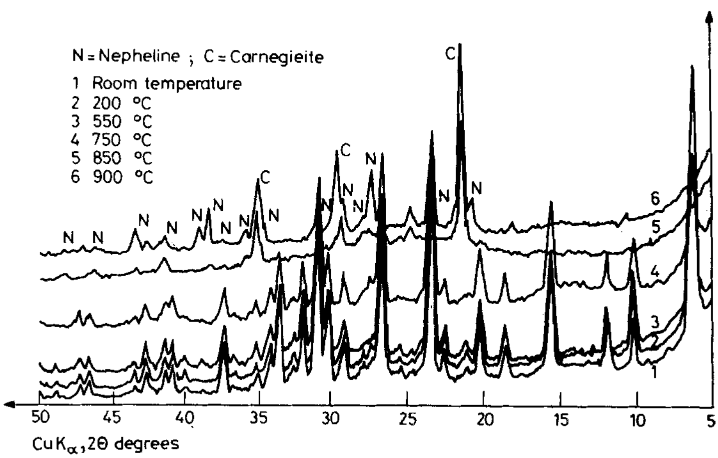

Fig. 2 X-ray diffraction patterns for zeolite NaX heated to different temperatures for 18 hours

nepheline, and at 416, 255 and 302 pm for α-carnegieite. These two products increase in amount with the increase of temperature, as observed from the increased intensities of their respective reflections in the sample at 900° (Fig. 2).

Zeolite P_c

The differential thermal pattern (Fig. 3) indicates an initial endotherm between 80 and 280°. This corresponds to dehydration. Between 300 and 650°, there is no change, as evidenced from a nearly horizontal baseline. From 650° onwards, a drastic upward trend of the baseline signifies structural change in the sample, as confirmed by its X-ray diffraction pattern. The weight loss of 16% estimated for the endothermic region from the TG pattern (Fig. 3) is in agreement with the literature data [15, 16].

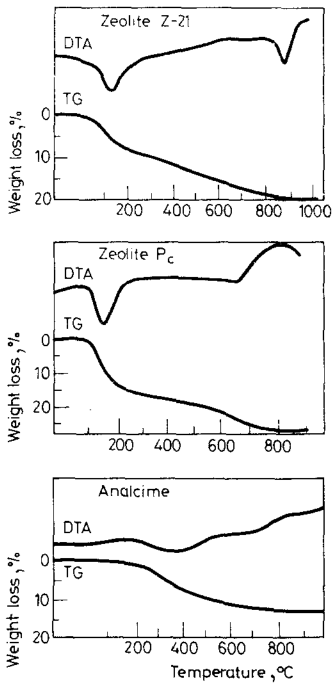

Fig. 3 DTA and TG curves for zeolites Z-21, P_c and analcime

Zeolite HS

The differential thermal pattern (Fig. 1) reveals the presence of a shallow endotherm between 60 and 200°, corresponding to dehydration. The baseline thereafter remains unaffected up to around 600°, beyond which an endothermic dip in the baseline is noticed prior to the onset of a broad exotherm at 690°, with its peak at around 800°. The exothermic event is complete at 900°. This corresponds to structural change in the sample. The upward trend of the baseline from 900° onwards indicates the formation of a new phase.

The thermogravimetric data indicate continuous weight loss from the start of the first endotherm. The total weight loss up to 1000° is 12.3%, of which the exothermic event accounts for 3.0%.

Zeolite Z–21

The differential thermal pattern (Fig. 3) reveals an intense endothermic reaction between 40° and 240°, with its peak at around 175°, beyond which a gradual increase in the baseline slope is evidenced. The baseline exhibits a minor endotherm at 750°, followed by an intense and sharp endotherm between 800 and 950°, with its peak at around 900°.

The total weight loss estimated from the TG curve (Fig. 3) is around 20.75% of which the initial endotherm accounts for 9.37%. A change in the slope is indicated in the curve at the end of the first endotherm, and the sample continues to suffer weight loss up to 1000°.

Analcime

The differential thermal and thermogravimetric patterns for analcime are given in Fig. 3. The DTA pattern exhibits a broad endotherm commencing from 180° and continuing up to 600°, with its peak at around 360°, corresponding to dehydration, followed by an exotherm between 780 and 950°, representing structural change. The

Table 1 Thermal data on synthetic sodium zeolites

Species	Endotherm			Exotherm			Total weight loss % up to 1000°
	peak, °C	weight loss, %	heat energy, kCal/g	peak, °C	weight loss, %	heat energy kCal/g	
NaX	220	19.3	0.21	830	negligible	0.02	19.9
P_c	140	16.0	0.15	800	2.67	—	26.0 (up to 900°)
HS	120	8.0	0.014	800	3.0	0.05	12.33
Z-21	175	9.37	0.084	—	—	—	20.75
	900	3.0	0.064	—			
Analcime	360	10.67	0.1	850	0.3	0.02	13.03

thermogravimetric curve indicates a total weight loss of 13% between room temperature and 1000°. Of this, the weight loss pertaining to the endotherm is around 10.67%. Beyond this endotherm, there is a change in the slope of the weight loss curve. A further weight loss of 2% is recorded in the temperature region between the completion of the endotherm and the onset of the exothermic reaction. The exothermic event involves minimal weight loss (about 0.3%). It has been reported in the literature that analcime contains around 9.1% water and does not change its structure up to 700° [17,18].

The thermal data on all these synthetic sodium zeolites are presented in Table 1.

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Zusammenfassung — Differentialthermoanalytische und thermogravimetrische Daten von den synthetischen, unter Verwendung von Reisschalenasche als Siliciumdioxidquelle hergestellten Na-Zeolithen NaX, P_c, HS, Z-21 und Analcim werden angegeben. Die DTA-Kurven zeigen anfangs einen der Dehydratisierung zuzuschreibenden endothermen Peak, dem bei 800–850° ein exothermer folgt, der auf den Zusammenbruch der Zeolithstruktur zurückzuführen ist. Nur im Falle von Z–21 tritt dieser exotherme Peak erst bei 900° auf. Die mittels DTA festgestellten strukturellen Veränderungen wurden röntgendiffraktometrisch verifiziert.

Резюме — Представлены данные ТГ и ДТА для синтетических цеолитов типа NaX, P_c, HS, Z–21 и анальцима, полученного с кремнезема золы рисовой шелухи. ДТА-кривые показали наличие начальной эндотермы дегидратации с последующим экзотермическим пиком между 800–850°, указывающим на структурное изменение и диссоциацию всех типов цеолита, за исключением Z–21. В случае этого цеолита начальная эндотерма сопровождается последующей в области 900°. Структурные изменения, установленные на основе ДТА-кривых, подтверждены фазовым анализом.