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Sintering behaviour of calcium exchanged low silica zeolites synthesized from kaolin

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Abstract

The novel route for the synthesis of aluminosilicate ceramics through zeolite precursors is found to have certain advantages over the traditional methods using oxides, kaolinite etc. and the non-conventional use of sol–gel precursors. The published work in this area consists of sintering the ion exchanged low silica zeolites prepared from commercially available zeolites. Generally, zeolites are manufactured by crystallisation of sodium aluminosilicate gel prepared from different aluminium and silica sources. The present paper deals with the ion exchange and sintering of calcium exchanged zeolites A and X synthesised from a locally available china clay. Kaolinite is a combined source of silica and alumina and the zeolites prepared from it are always contaminated with trace amounts of Fe, Ti, Ca, Mg etc. which are originally present in the naturally occurring clay as ancillary minerals. A systematic study has been done on the calcium exchange of kaolin based zeolites A and X, sintering of these modified zeolites at various temperatures and measurement of properties of the sintered products. The effect of rate of heating on the properties was also investigated. It has been found that the zeolite structure is not lost during ion exchange and remains somewhat the same on sintering up to 750°C. Further heating results in the crystallisation of anorthite resulting in an anorthite–glass composite material. A firing rate of 3°C/min resulted in a material with large volume expansion, high porosity and water absorption and low density. Reducing the rate of heating to 1°C/min, a normal sintering behaviour was observed to give products with high shrinkage and density and good hermeticity. However, the strength of the products was found to be quite low. For a comparative study, the two zeolites were synthesised from sodium aluminate and sodium silicate and the ion exchange and sintering were carried out in a similar way. The preliminary results showed that there are some differences in the sintering behaviour indicating the possible influence of the origin of the zeolites. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; B. Electron microscopy; B. X-ray methods; D. Clays; D. Silicate; Zeolites

1. Introduction

Zeolites are crystalline aluminosilicates with uniform pores, channels and cavities. The unique properties of low silica zeolites (zeolites NaA and NaX with SiO_2/Al_2O_3 ratios ~2 and ~3 respectively) such as ion exchange capacity, sorption and catalytic activity, make them ideal for various industrial applications [1]. A number of metal ions can be exchanged with the sodium ions of the zeolites and these modified zeolites can act as precursors for a variety of aluminosilicate ceramics [2–13]. Some advantages have been reported for this novel route of ceramic preparation compared to the traditional methods of mixing of oxides and non conventional use of sol gel precursors followed by sintering.

Zeolites are generally synthesised from sodium aluminosilicate gel prepared from various silica and alumina sources. Kaolinite has been reported as an ideal, combined source for silica and alumina for the synthesis of "low silica zeolites" as early as 1964 [1]. The zeolites from kaolinites are always contaminated with trace amounts of Fe, Ti, Ca, Mg etc. which are originally present as ancillary minerals in the naturally occurring kaolin. Even though processing of the raw clay improves the quality of the clay to some extent, traces of these impurities still remain in the zeolite either in the structure or as associated ions. There is a possibility that the ion exchange and sintering behaviour of these zeolites and the properties of the sintered products may get influenced by these impurities.

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Choudhary et al. studied the synthesis of ceramics from zeolites for the first time in 1989 where monolithic anorthite, anorthite-cordierite or cordierite based ceramics were prepared from Ca, Ca-Mg and Mg forms of zeolites A, X and Y [2]. Taga et al. reports the preparation of anorthite ceramic bodies from zeolite CaA and CaX [8]. Synthesis of leucite pollucite and spodumene based ceramics were carried out by Bedard et al. from zeolites B, W and ZK 19 [5–7]. Recently, synthesis of pollucite and celsian ceramics are reported by Pareira and Hoghoogi respectively [10,11]. All these work has been carried out using zeolites synthesised by the Gel Route i.e. different silica and alumina sources.

The present paper deals with a systematic study on the calcium ion exchange of zeolites A and X synthesised from kaolin, sintering of these modified zeolites at various temperatures and measurement of properties of the sintered products. The effect of rate of heating on the properties was also investigated.

2. Experimental

2.1. Synthesis of zeolites

The best coating grade kaolin (BCK) supplied by M/s English Indian Clays Ltd., Thiruvananthapuram, India was used as the raw material for the synthesis of zeolites A and X. The clay was calcined in a muffle furnace to get metakaolin which on hydrothermal reaction with aqueous alkali gave zeolite A [14]. Calculated amount of sodium silicate was added to the reaction mixture before subjecting to the hydrothermal reaction [15] to synthesise zeolite X.

2.2. Ion exchange of the zeolites

The sodium zeolites were exchanged with calcium ions by conventional method. Nearly 10 g of the zeolite was added to 100 ml of 10% calcium nitrate solution and stirred for 8 h. Then the slurry was kept for about 16 h, centrifuged, the supernatant liquid was decanted and the solids were again treated with a fresh solution of calcium nitrate in a similar manner. This experiment was repeated five times to ensure that maximum ion exchange has taken place. The ion exchanged zeolites A and X thus prepared, were filtered, washed thoroughly and dried. The zeolites and their ion exchanged products were analysed for their chemical composition including the estimation of sodium and calcium to confirm the maximum exchange. The zeolites were also characterised by XRD and DTA methods.

2.3. Sintering

The ion exchanged zeolites were pressed into thin (1.5 mm thickness) and thick (20 mm thickness) pellets of 10 mm diameter under a pressure of 125 MPa and heated in a programmable furnace at temperatures 750, 850, 950, 1050 and 1150°C at a rate of 3°C/min with a soaking time of 3 h. Samples were also fired at a rate of 1°C/min at selected temperatures 950 and 1050°C giving the same soaking time.

2.4. Characterisation

The zeolites A and X, the calcium exchanged forms and the sintered products were characterised by various methods including chemical, X-ray Diffraction (XRD) and thermal analysis. Particle size distribution analysis and brightness of the zeolites and kaolin have also been determined. The characterisation of the sintered products include measurement of water absorption, shrinkage, true density, porosity and compressive strength. The morphology of selected samples were examined under the scanning electron microscope.

(i) Chemical analysis: standard wet chemical analysis along with instrumental methods were adopted [16]. SiO_2 was estimated gravimetrically, Al_2O_3, CaO and MgO by complexometry and Fe_2O_3 and TiO_2 by colorimetry. Na_2O was found out by flame photometry.

(ii) X-ray diffraction analysis: powder XRD patterns were recorded on a Philips PW 1710 X-ray Diffractometer with Ni filtered CuK_α radiation.

(iii) Thermal analysis: differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were carried out on a Shimadzu thermal analyser at a heating rate of 40°C/min.

(iv) Water absorption: standard methods were followed for the determination of water absorption [17].

(v) Shrinkage: the shrinkage/ expansion was measured in a thermo mechanical analyser (TMA) 50 MHz, at a heating rate of 10°C/min from 30 to 1000°C. The dimensional changes during firing were also calculated by measuring the diameter of the pellets before and after firing.

(vi) Density: a helium auto pycnometer (Micromeritics 1320) was used for determining the true density of the samples and the apparent density was measured using Archimedes' principle.

(vii) Porosity: porosity was determined from the following equation, % Porosity = (saturated weight–dry weight)/(saturated weight–suspended weight) [18].

(viii) Compressive strength: ASTM procedure was followed for the measurement of compressive strength and INSTRON 1195 was used for the same [19].

(ix) Particle size distribution analysis: Sedigraph 5100 model was used for determining the particle size distribution analysis of the kaolin and the zeolites.

(x) Morphology: a scanning electron microscope, Jeol JSM 5600 LV was used for the morphological study of the samples.

3. Results and discussion

3.1. Kaolin and the zeolites

The properties of the kaolin and the zeolites A and X are given in Table 1. The chemical analysis shows that most of the impurity metal ions in the clay are retained in the zeolites also. The Si/Al ratios of the kaolin as well as the zeolite A are almost the same whereas zeolite X has a higher ratio. The brightness (which is mainly influenced by the iron impurities) of the zeolites was found to be much lower compared to that of the kaolin.

The kaolin based zeolites are expected to have certain fundamental differences from those prepared by the conventional gel route. Even the processed kaolin contains trace impurity minerals of iron, titanium, calcium, magnesium etc. which are mostly retained in the zeolites, sometimes in different chemical forms. These elements may have some influence on the zeolite properties such as brightness, hardness, catalytic activity, electrical properties etc. When the zeolites A and X are to be used in the detergent industry, brightness is one of the most important parameters. The brightness of the zeolites under study were found to have much lower values than the gel-route product. This is because, during the hydrothermal reaction or zeolitisation, the iron present in the metakaolin dissociates and gives a coloured coating on the zeolite surface. The lower brightness of zeolite X compared to A can be attributed to the longer synthesis time for the former and hence possible formation of a thicker coating of iron hydroxide on the zeolite particles [20].

The particle size distribution analysis shows that the ultrafine kaolin particles (< 2 μm) during metakaolinisation undergo aggregation which on hydrothermal reaction give zeolite A with a narrow size distribution (2–10 μm). The zeolite X particles were found to have a wider size range. The X-ray diffraction analysis of the zeolites indicates their high phase purity as given by Fig. 1a and c.

Particle size of the gel route product is highly uniform whereas in the case of kaolin based zeolites, it is mostly dependent on the particle size of the metakaolin and also the synthesis conditions such as alkali/water ratio, stirring speed etc. During the present investigation, the zeolite A was prepared under stirring condition and hence has a narrow size distribution. The zeolite X was synthesised by ageing for 24 h at room temperature and heating in an air oven for 15 h and a broad size distribution is observed. The uniformity in particle size is reported to be more favourable for sintering and ceramic formation [21]. The excess silica may be playing a dominant role in the sintering behaviour.

Table 1
Properties of kaolin and kaolin based zeolites

Property (%)	Kaolin	Zeolite A	Zeolite X
SiO_2	45.90	28.68	34.01
Al_2O_3	38.90	24.92	23.46
Fe_2O_3	0.56	0.48	0.53
TiO_2	0.64	0.73	0.78
Na_2O	0.08	12.61	12.03
Loss on ignition	13.80	22.29	21.57
Si/Al	1.00	0.98	1.23
ISO brightness %	85.48	78.19	74.91
Mineralogical analysis	Kaolinite, quartz and mica	Zeolite A	Zeolite X
Particle size distribution, μm			
>45	0.8	0.98	32.14
<45>10	2.5	1.24	14.43
<10>2	16.7	06.54	50.90
<2	80.0	1.24	2.55

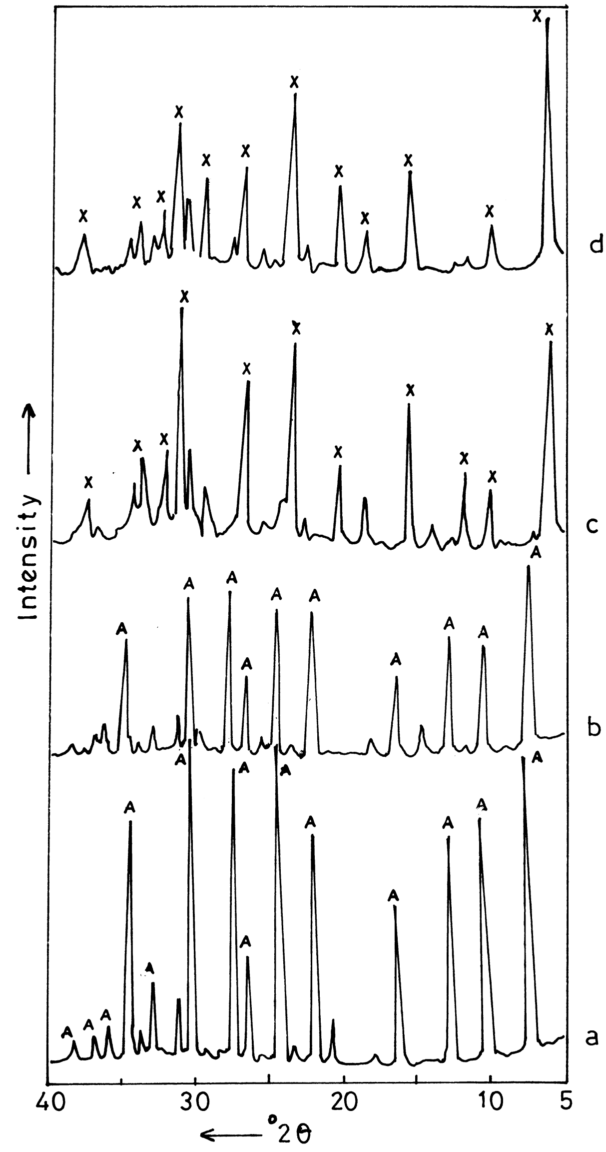


Fig. 1. XRD patterns of the zeolites and there Ion exchanged products. (a) Zeolite A; (b) Ca Zeolite A; (c) Zeolite X and (d) Ca Zeolite X. A — Zeolite A; X — Zeolite X.

3.2. Ion exchanged zeolites

The X-ray diffractograms of the zeolites and their calcium exchanged forms are almost identical indicating that no structural change has taken place during the ion exchange (Fig. 1). This is because the replacement of sodium ions by calcium is taking place at the atomic level. The chemical assay of the calcium exchanged forms are given in Table 2. More exchange has taken place in the case of zeolite A. Other chemical constituents in the ion exchanged zeolites do not differ much from the original zeolites.

The TGA of the Ca exchanged zeolites indicates almost the same loss in weight compared to that of the sodium forms. The DTA patterns of the zeolites are found to be almost similar (Fig. 2), but the temperatures of exotherms and endotherms shift towards higher temperatures for CaX. Two exotherms at 870–910°C and 980–990°C and one endotherm at 100–180°C are clearly observed for both the zeolites. Very small exotherms are also found at 370–390°C and ~700°C for both the zeolites. In general, the endotherms and exotherms are found to be sharper for zeolite CaA. The weight loss of the Ca zeolites during heating can be attributed to the loss of water. The DTA gives information regarding the temperature of dehydroxylation, structural breakdown/amorphisation and formation of new phases. The endotherms at 100–180°C correspond to the loss of water [22]. The small exotherms at 870–910°C in both the zeolites can be due to the breakdown of the zeolite structure and some sintering due to the glass formation. The exotherms at ~983°C (for CaA) and at ~1022°C (for CaX) can be attributed to the crystallisation of new phases. All these changes are observed to take place at lower temperatures for CaA compared to CaX. This can be attributed to the higher silica content in CaX.

Table 2
Chemical analysis of Ca exchanged zeolites

Constituents	CaA	CaX
SiO_2	30.66	34.29
Al_2O_3	24.43	23.24
Fe_2O_3	0.36	0.45
TiO_2	0.71	0.72
Na_2O	3.12	1.08
Si/Al	1.07	1.25
LOI	22.9	~22
CaO/MgO	11.59	8.64

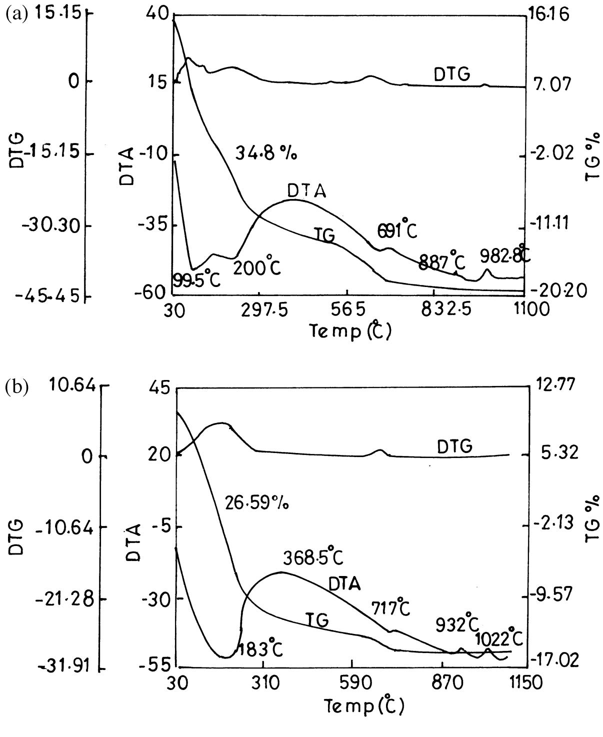


Fig. 2. DTA curves of ion exchanged zeolites. (a) Ca Zeolite A and (b) Ca Zeolite X.

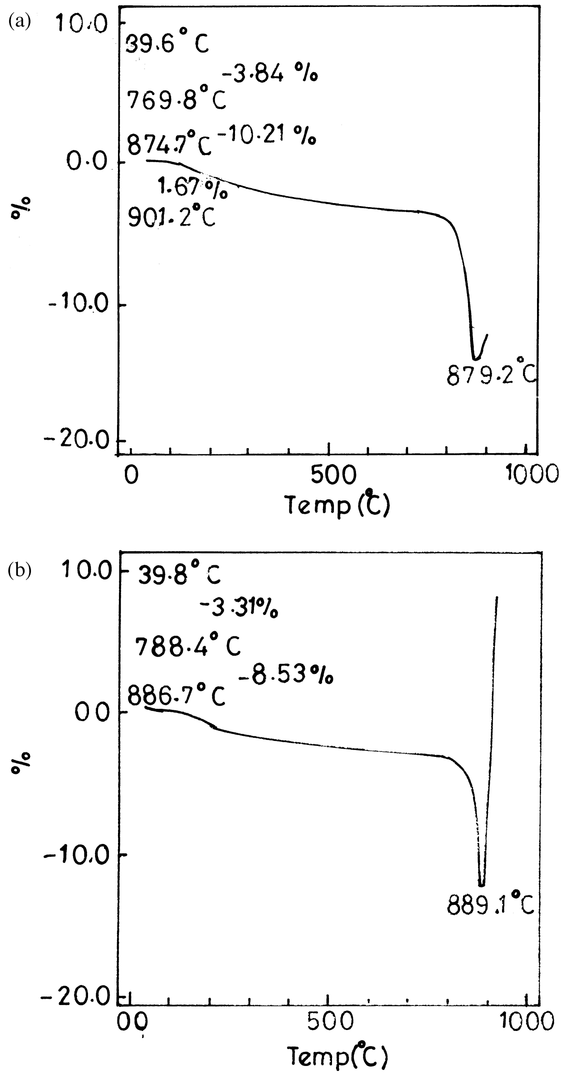


Fig. 3. TMA curves of ion exchanged zeolites (a) Ca Zeolite A and (b) Ca Zeolite X.

Shrinkage and water absorption of the products as well as their electron micrographs support this fact.

The TMA curves of both the Ca exchanged zeolites are quite similar in nature. Gradual shrinkage is indicated during heating and a sudden increase is observed at 850–860°C, CaX again having a higher temperature. After that both the zeolites show a sharp expansion (Fig. 3).

3.3. Sintering of the ion exchanged zeolites

3.3.1. At heating rate 3°C/min

The products obtained by heating the Ca zeolites at various temperatures were characterised by different methods. Figs. 4 and 5 give the XRD patterns of the sintered products from the zeolites CaA and CaX respectively. The structure of both the zeolites remain intact up to 750°C and the products at 850°C are totally amorphous for CaX and a small peak of anorthite is shown by CaA. At 950°C, anorthite starts crystallising with other forms of calcium aluminosilicates and silica (β-quartz). As the temperature increases, the % of anorthite increases and the % of other phases decrease. In the case of zeolite CaA, maximum crystallinity is observed for the product fired at 1150°C whereas for CaX, the product prepared at 950 and 1050°C are giving maximum phase pure anorthite. However, some amount of amorphous phase appears to be present in all the products.

The CaA and CaX zeolite pellets fired at 750°C do not show any change in their size. At 850°C, CaA is found to show a shrinkage of ~28% and CaX shows a lower value of ~19%. An expansion of 15 and 12% is observed for the samples CaA and CaX respectively when fired at 950°C. Firing at a higher temperature 1050°C results in a higher expansion for CaA and less for CaX. Further heating to 1150° does not cause any more change in both the zeolites. However, no uniformity was observed in the shapes of the pellets (Fig. 10) and hence accurate measurements of expansion could not be made. Table 3 gives the values of the change in dimensions of the samples.

The water absorption and apparent density of the fired products are separately plotted against the temperature of firing as given in Fig. 6a and b for CaA and CaX respectively. Both the zeolites fired at 750°C show high water absorption. Heating at 850°C makes the CaA almost hermetic whereas the CaX remains unchanged. At 950°C, both the zeolites show high values, that for

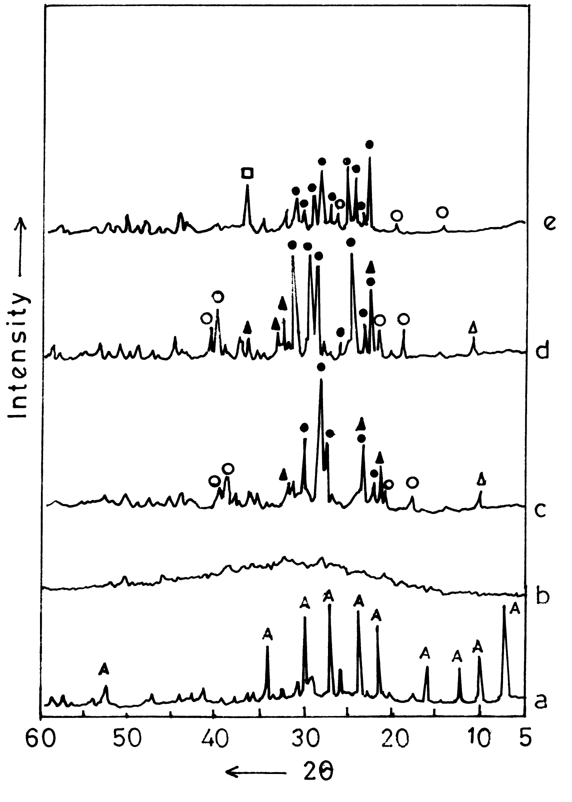


Fig. 4. XRD patterns of CaA fired at different temperatures. (a) 750; (b) 850; (c) 950; (d) 1050 and (e) 1150°C. A — Zeolite A; o — SiO_2 (β-quartz); ● — Anorthite; Δ — $Al_{1.4}Si_{0.3}O_{2.7}$; ▲ — Ca $Al_2Si_2O_8$; □ — $CaAl_2SiO_6$.

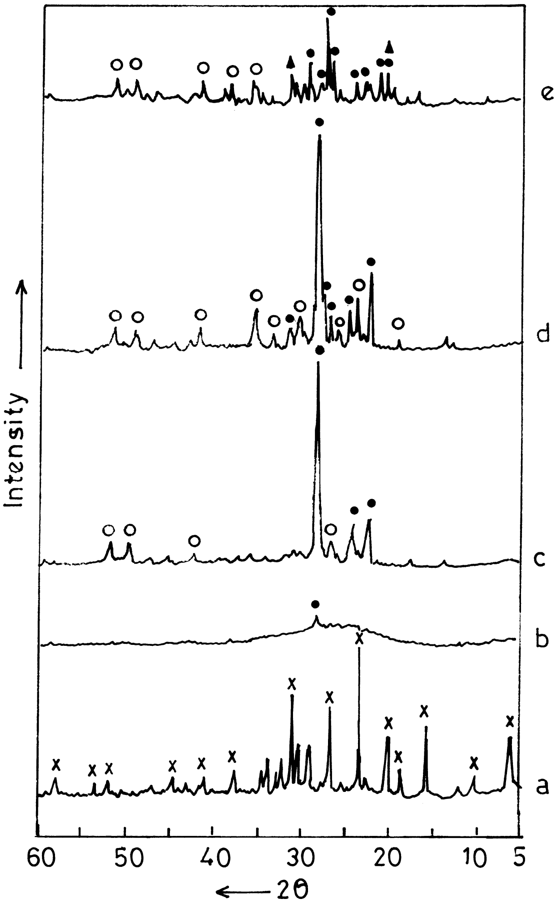


Fig. 5. XRD patterns of CaX fired at different temperatures. (a) 750; (b) 850; (c) 950; (d) 1050 and (e) 1150°C. X — Zeolite X; o — SiO_2 (β-quartz); ● — Anorthite; ▲ — Ca $Al_2Si_2O_8$.

Table 3
Expansion/shrinkage of Ca zeolites

Temperature °C	CaA % shrinkage/expansion	CaX % shrinkage/expansion
750	0	0
850	28.04	18.96
950	−15.1	−11.9
1050	−23.4	−8.5
1150	−21.9	−7.6

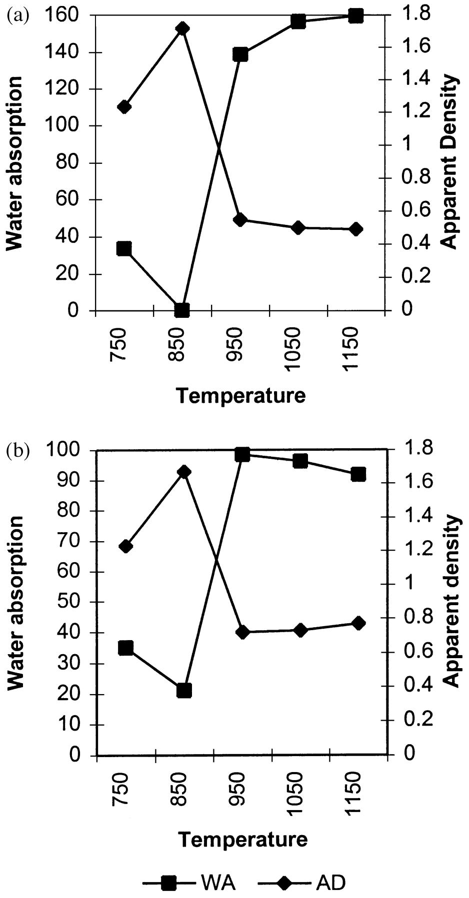


Fig. 6. Changes in % water absorption and apparent density of Ca zeolites. (a) CaA and (b) CaX. WA — % water absorption; AD — apparent density.

CaA being much higher than that for CaX. Further increase in temperature does not seem to influence the water absorption values. The apparent densities of the samples closely agree with the water absorption, the higher the water absorption the lower is the density. It is interesting to note that the samples fired at and above 950°C result in highly porous materials with very low density so that the samples float in water.

The compressive strength of the sintered products are given in Table 4. In general, the strength of all the samples is quite low. The CaX fired at 950°C is found to have the maximum strength followed by CaX fired at 1050°C. However, the values for the CaX fired at 950, 1050 and 1150°C are almost close to each other unlike those of the CaA products.

Electron microscopic studies were conducted to examine the morphology of the fractured surfaces of selected samples fired at 750, 850, 950 and 1050°C and Figs. 7 and 8 give the photographs of products from A and X respectively. Zeolite A particles are reported to have bevelled cubic structure and zeolite X has typical octahedral geometry [1]. Multiple crystal growth is observed in both the zeolites. The calcium exchange and heating at 750°C for 3 h appear to have little influence on the shape of the zeolite particles as shown by Figs. 7a and 8a. The porous nature of the material is clearly shown in the pictures. Heating at 850°C for 3 h results in the loss of particle shape in both the zeolites. Initiation of sintering by viscous flow of the material is indicated in CaA at 850°C whereas CaX fired at 850°C remains unchanged.

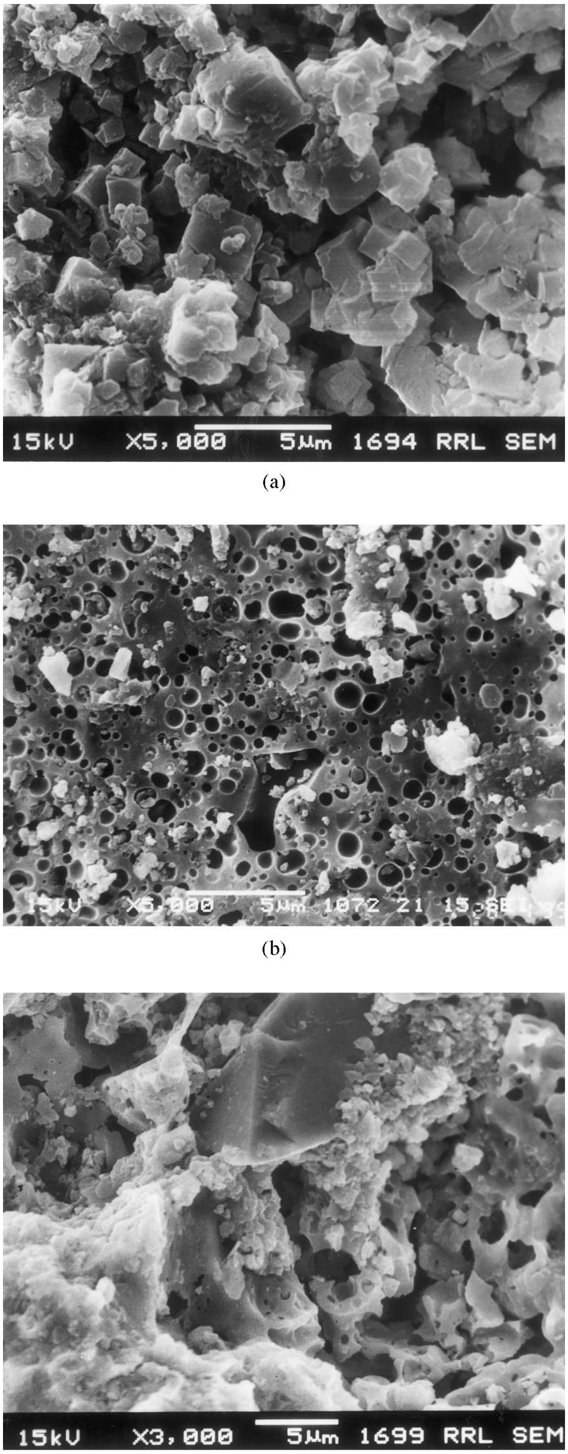
3.3.2. At heating rate 1°C/min

The calcium exchanged zeolites are found to behave differently when the samples are fired at a lower rate. The XRD patterns of CaA zeolite fired at 950°C under the different rates of heating (1 and 3°C) are almost identical indicating the crystallisation of anorthite (Fig. 9). However, the CaX zeolites fired at the same rates seem to have certain differences. Fig. 9 shows the XRD pattern of CaA and CaX fired at 950 and 1050°C at the rate of 1°C/min.

It is interesting to note that during firing at the lower rate, no expansion was observed at any temperature unlike in the higher rate experiments. In fact, the behaviour was normal like any other sintering in ceramic

Table 4
Properties of Ca zeolites at various temperatures

	CaA			CaX		
Properties	950	1050	1150	950	1050	1150
Compressive strength (MPa)	6.87	13.35	7.39	17.49	17.45	16.89
True density	2.37	1.92	2.24	2.34	2.12	2.32
% Porosity	75.4	77.58	77.73	70.48	69.69	70.73

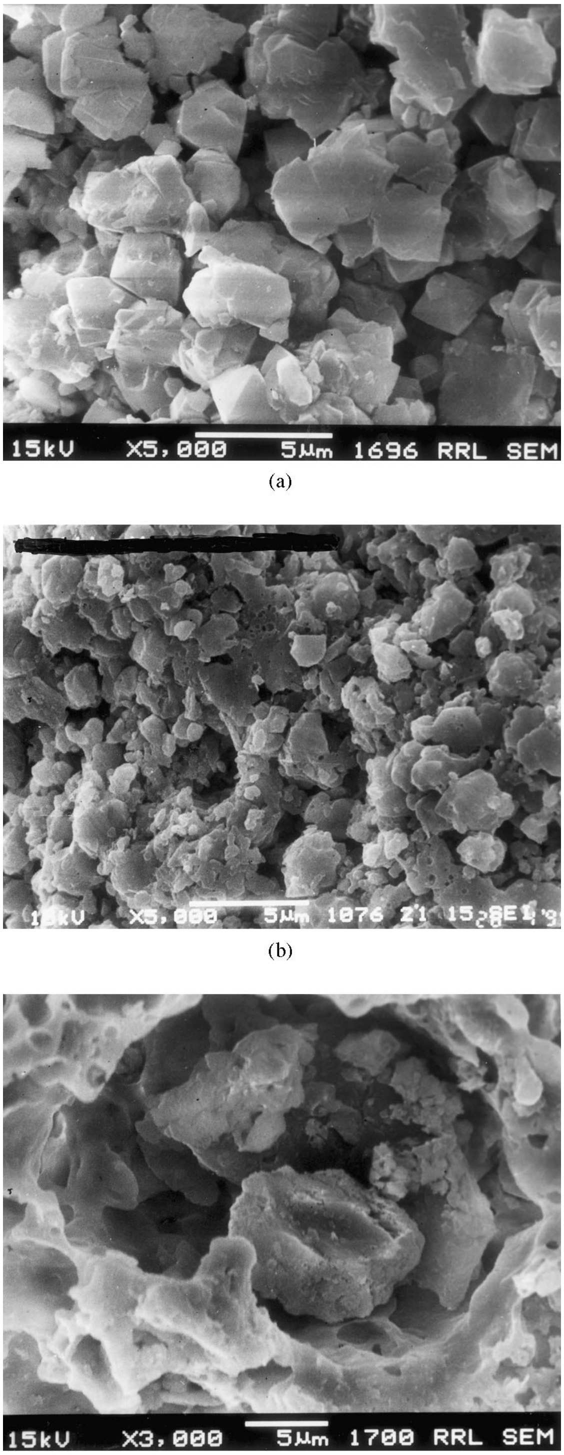


(a)

(b)

(c)

Fig. 7. SEM of CaA at different temperatures. (a) 750; (b) 850 and (c) 950°C.



(a)

(b)

(c)

Fig. 8. SEM of CaX at different temperatures. (a) 750; (b) 850 and (c) 950°C.

processes. A high shrinkage was observed for samples fired at both 950 and 1050°C attaining almost zero water absorption and high density (Table 5).

The scanning electron micrographs clearly show that the glassy formation is taking place with a much lower number of pores compared to the corresponding products fired at the higher rate. The crystalline particles are clearly seen embedded on to the glassy phase. Fig. 11 represents the SEM pictures of the zeolites CaA and CaX fired at 950°C at a rate of 1°C/min.

The sintering studies of the calcium exchanged zeolites indicate that the phase formations in the calcination

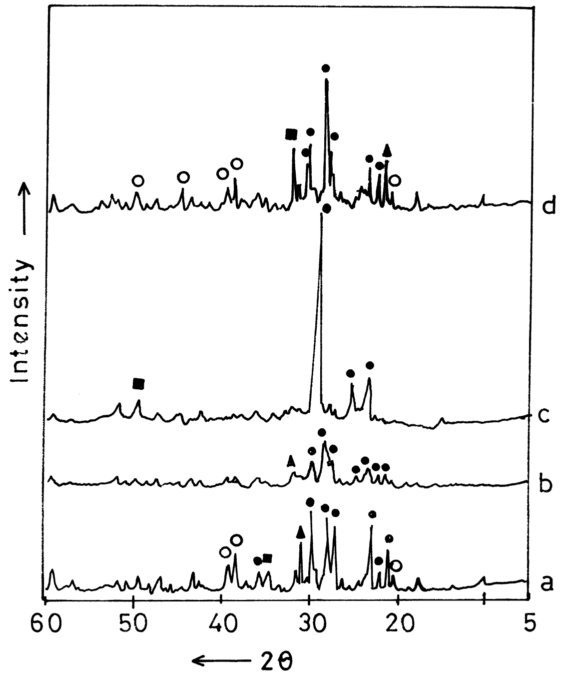


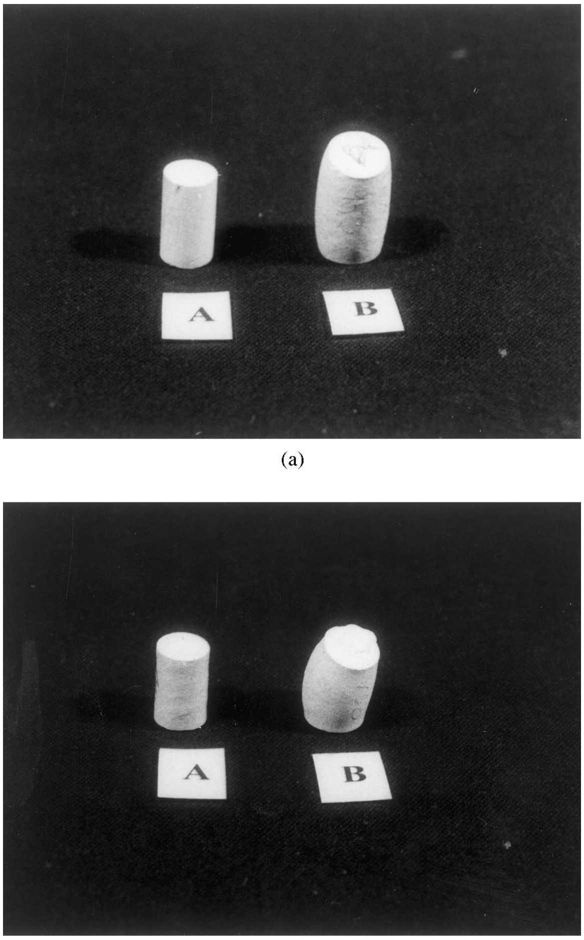
Fig. 9. XRD patterns of CaA and CaX fired at different temperatures at a heating rate of 1°C/min. (a) 950 and (b) 1050°C. A — Zeolite A; X — Zeolite X; o — SiO_2 (β-quartz); ● — Anorthite; ▲ — Ca $Al_2Si_2O_8$; ■ — $CaAl_2Si_2O_7$.

process are quite complex and some amount of amorphous material remains in all the fired products. Heating at 750°C for 3 h does not bring out any change for the zeolites. But both the zeolites at 850°C give XRD patterns corresponding to amorphous nature indicating the breakdown of the zeolite structure. Initiation of sintering at 850°C is indicated by the sudden shrinkage in the TMA curves of the zeolites at ~860°C. Densification of the material is a result of the viscous flow as shown by the electron microscopic study. The shrinkage is higher for CaA and the product is hermetic whereas CaX is porous and has good water absorption. The exotherms at 910°C for CaA and 990°C for CaX indicate the formation of new phases. The higher silica content in the zeolite X appears to influence the sintering behaviour and the properties of the products. XRD patterns show that anorthite is the major crystalline phase in all the samples along with the formation of some silica (quartz) in varying percentages depending upon the firing temperature and type of zeolite. Different types of anorthite such as ordered, disordered and sodian appear to form.

It is observed that a sharp volume expansion occurs in the samples fired at and above 950°C. The high porosity created during the process results in a large water absorption and very low density. Even at 1150°C, no change is observed. The crystalline phases formed during sintering remain anorthite and silica.

When the rate of firing is changed to 1°C/min, a normal ceramic sintering pattern is observed. At 950°C, the product is sintered well with almost zero water absorption and considerable shrinkage. The XRD study shows that the phases formed in both the zeolites are similar to those formed at a higher rate of heating.

The products fired at 1050°C also show properties similar to the 950°C samples. However, anorthite with low crystallinity is formed at the lower rate of firing whereas a more crystalline product is formed for the other (Fig. 9) The volume expansion observed at the high firing rates can be attributed to the formation of more β-quartz



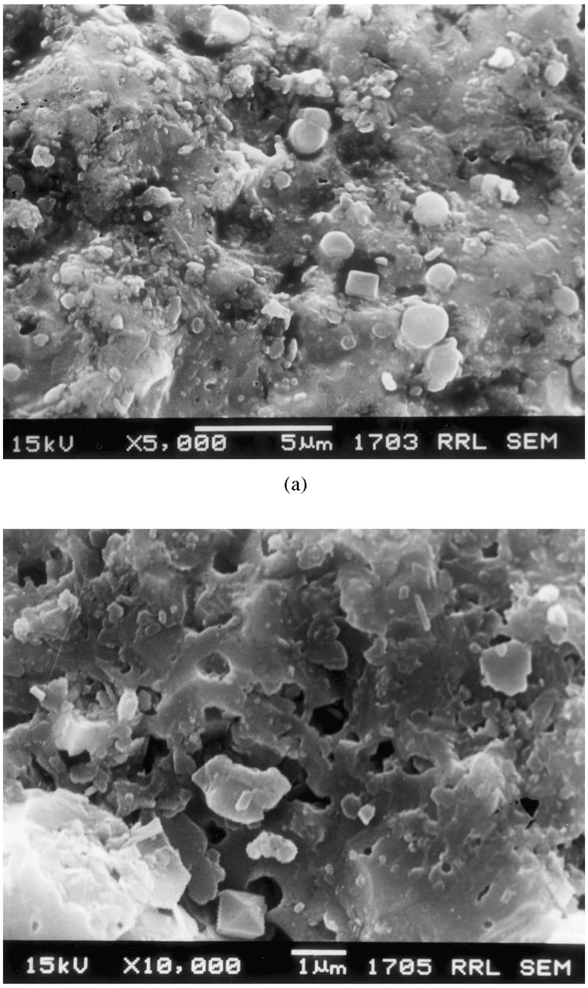
(a)

(b)

Fig. 10. Photographs of CaZeolites before firing and after firing at 1050°C at a heating rate of 3°C/min. (a) CaA and (b) CaX. A — before firing; B — after firing.

Table 5
Properties of CaA and CaX fired at 1°C/min

	CaA		CaX	
Property	950°C	1050°C	950°C	1050°C
% Water absorption	0.04	0	0.66	0
% Shrinkage	27.6	28	23.6	24.2
Apparent density	2.50	2.69	2.23	2.49
True density	2.19	1.68	1.84	1.73



(a)

(b)

Fig. 11. SEM of CaA and CaX fired at 950°C at a heating rate of 1°C/min. (a) CaA and (b) CaX.

phase. This can be further confirmed by the fact that the formation of this phase is much less in the case of the slow fired samples. The presence of titanium and iron may also be contributing to this behviour [25,26]. The higher percentages of silica in the zeolite CaX may be contributing to the formation of a higher quantity of β-quartz [23].

Anorthite is conventionally prepared by sintering a mixture of Ca $(OH)_2$ and kaolin at high temperatures i.e. >1400°C. Low temperature fabrication of anorthite ceramics has been recently reported by Y. Kobayashi an E. Kato at ~1000°C by using the same raw materials but of much finer particle size [24]. Taga et al. prepared anorthite sintered body from Ca zeolites A and X (gel route product) with SiO_2/Al_2O_3 ratio <3. They claim that when a calcium zeolite is directly sintered, a contraction in volume is observed. The rate of heating mentioned is 5°C/min. The product was found to have a density near to the theoretical value of anorthite and linear shrinkage of ~30% and flexural strength 157 MPa. We have observed that the Ca zeolites synthesised from kaolin with an SiO_2/Al_2O_3 ratio 2–2.5 when fired at a rate of 3°C/min show volume expansion at and above 950°C. The compressive strength of the products was found to be quite low. However, a lower rate of 1°C/min gave a normal ceramic firing i.e. shrinkage at 850°C and product density 2.3, 2.7 and the strength also appears to be better. However, the origin of the zeolites may be playing an important role in the sintering properties of zeolites.

4. Conclusions

(i) The zeolites A and X synthesised from kaolin contain most of the impurity elements originally present in the clay.

(ii) These zeolites on exchange with Ca ions give products with very low sodium content. The structure of the zeolites is not lost during ion exchange. The Ca exchanged zeolites on heating lose their crystallinity/structure above 750°C. Further heating results in the crystallisation of anorthite and formation of an anorthite–glass composite material.

(iii). Rate of heating has been found to influence the sintering behaviour of the Ca zeolites. Firing the samples at the rate of 3°C/min resulted in large expansion of the material with high porosity, water absorption and low density. Reducing the rate to 1°C/min, no expansion was observed and normal sintering pattern was followed to give products with high shrinkage and very low water absorption and high density.

(iv) The mechanical strength of the fired samples is quite low.

(v) The origin of the zeolites seems to have some influence on the sintering properties of zeolites.

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