



Incorporation of Zeolites Na-A and Na-X from Condensed and Calcite Coal Fly Ash

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ABSTRACT

The major components of CFA are silicon dioxide (SiO_2) and Aluminium trioxide (Al_2O_3), which are the essential reagents in the synthesis of zeolites. Synthetic zeolites obtained by reprocessing of CFA have huge potential as a cost-effective, environmentally-friendly solution that can improve the efficiency of these materials as efficient heterogeneous catalysts, mainly as solid acids, as adsorbents, as molecular sieves in gas separation and purification and in purification of contaminated waste water. The low price and the additional ecological benefit of the production of zeolites from wastes increased their popularity and inspired growing interest among zeolite.

This paper presents zeolite synthesis from Coal fly ash (CFA). The Coal fly ash was activated by using NaOH solution prior to fusing process with a weight ratio of 1:2, 1:3 and mixing with distilled water at a weight ratio of 1:5. Thereafter, the addition of alumina with a concentration of 0.75 %, 1.82 %, 2.19 %, and 3.2 % was performed. The effects of heating and ultrasound radiation on the characteristic of zeolite products were investigated. SEM images demonstrated that the presence of ultrasound wave resulted in crystals structure morphology as also supported by XRD characterization.

Keywords : CFA, Ultrasonic treatment, IR, SEM, XRD, Na-A and Na-X Zeolites

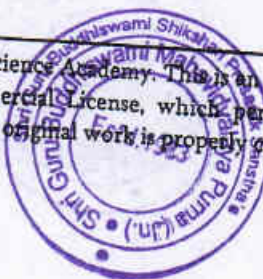
I. INTRODUCTION

Coal fly ash (CFA) is the major residue from coal and biomass combustion and is mainly composed of fine-grained particles of SiO_2 and Al_2O_3 . In 2015, more than 1 billion tons of CFA was produced worldwide¹. The amount of CFA produced grows continuously, making the disposal and handling of CFA an important issue that strongly impacts various aspects of our daily life, especially the environment. Therefore, it is important to develop techniques for the utilization of CFA and several have been proposed in this category. CFA has been used for soil remediation^{2,3} embankments or building as adsorbent for waste and contaminant handling, gas separation and capture and mineral recovery as catalyst or catalyst support etc. Furthermore, it is of more

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economic significance to develop eco-friendly techniques that convert CFA to value-added products. CFA utilization as raw material for production of cement and glass has also been reported.

Most of zeolites are periodic framework compounds of aluminium silicates formed by interconnected SiO_4 and AlO_4 tetrahedrons. CFA is mainly composed of particles of SiO_2 and Al_2O_3 at micrometer dimension with a weight percentage up to 85 and can principally be used as the precursor of Si and Al for zeolite synthesis. However, SiO_2 and Al_2O_3 are in the form of their most stable minerals in CFA, such as mullite and quartz. They must be chemically converted to reactive precursors by reactions with concentrated NaOH solution or calcination with solid NaOH or KOH at high temperature and the process is not energy efficient^{4,5}. Following the first synthesis of zeolite with CFA by Holler & Wrisching, the reported procedures for zeolite synthesis are all through hydrothermal crystallization using raw or NaOH or KOH calcinated CFA. Alternative energy sources, such as ultrasonic and microwave radiation, are proposed for the hydrothermal synthesis to lower the cost for zeolite synthesis with CFA^{6,7,8}, though they are less meaningful for industrial mass production. Apart from these, it would be more interesting to replace the expensive NaOH and KOH used for the calcination and activation with low-cost alkalis, such as Na_2CO_3 . However, due to the low alkalinity of Na_2CO_3 and the sluggish reactions at interface, higher calcination temperature will be required unless the process is intensified with other procedures⁹⁻¹². As the size of Al_2O_3 and SiO_2 particles is of micrometer dimension, their reactions will, in principle, be greatly promoted by close contacts with Na_2CO_3 or NaOH. In this work, we used tablet compression to intensify the calcination of CFA with Na_2CO_3 . We also showed phase-pure Na-A can be synthesized with calcinated CFA in low alkalinity solution under low temperature, while phase-pure Na-X can be synthesized in the same way but with the introduction of silica sol^{13,14}. The effects of varying $\text{Na}_2\text{CO}_3/\text{CFA}$ ratio and reaction temperature were also investigated and the optimum conditions for the synthesis of Na-A and Na-X were determined

2. Experimental

2.1. Material and methods

CFA was obtained from Hydrothermal Power Station Chandrapur Maharashtra. Chemical composition of the CFA sample was analysed with X-ray fluorescence (XRF) and the results are summarized in table 1. The X-ray diffraction (XRD) was used to determine the crystalline phase in CFA and the morphology was determined with a scanning electron microscope (SEM). As shown in figure 1, CFA sample is mainly composed of microspheres of quartz and mullite. The measured Si/Al molar ratio of 1.67 in the sample is suitable for the synthesis of Na-A zeolite. As the synthesis of Na-X zeolite requires higher Si/Al molar ratio, silica sol was introduced as additional Si source and sodium hydroxide was also added.

2.2. Synthesis of zeolite Na-A and zeolite Na-X

Synthesis of Na-A zeolite was done by a two-step process. First, a tablet compression machine was used to treat the mechanically mixed CFA and Na_2CO_3 . The resulting mixture was calcinated at 800°C for 3 h and then cooled to room temperature. According to the XRD patterns of the CFA sample before and after calcination (figure 1), the mullite and quartz phases in CFA disappear and are converted into sodium

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aluminum silicate (NaAlSiO_4) and sodium silicate (Na_2SiO_3) after calcination at 800°C . It is hard to get phase-pure zeolite Na-A through the hydrothermal process if the mixture of CFA and

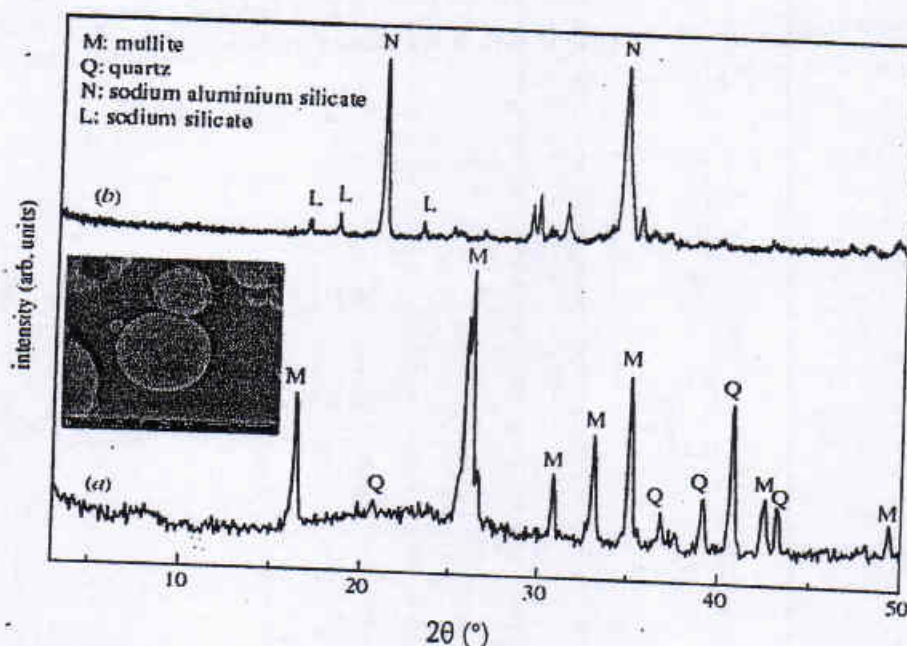


Figure 1. (a) XRD patterns of the raw CFA sample (b). The SEM image of raw CFA

Table 1. The chemical composition of coal fly ash.

component	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	P_2O_5	SO_3	ZrO_2	SrO	MgO
content(%)	45.48	44.86	2.73	2.69	2.19	0.45	0.35	0.30	0.25	0.22

Na_2CO_3 has not been tablet-compressed. The calcinated mixture was mixed with different quantity of deionizer water at room temperature for 1 h under magnetic stirring, and then further heated to different temperatures and subjected to hydrothermal crystallization for a period of time. After that, the reaction mixtures were annealed to room temperature, filtered, washed with demonized water and then the solid residues were dried at 90°C for 20 h before further measurement and characterization. The addition of silica sol and sodium hydroxide to the mixture before stirring is needed to get phase-pure zeolite Na-X.

3. Hydrothermal synthesis of zeolite Na-A from coal fly ash

The impacts of $\text{Na}_2\text{CO}_3/\text{CFA}$ mass ratio and crystallization temperature on the crystallinity of the resulting zeolite synthesized from calcinated CFA powder were investigated. Controlled experiments were carried out, with $\text{Na}_2\text{CO}_3/\text{CFA}$ mass ratio of 0.5, 0.7, 0.9, 1.2, 1.5, calcinated at 800°C for 2 h and hydrothermally treated

at 100°C for 6 h, to investigate the influence of alkalinity on the formation of zeolite. Figure 2 shows the XRD patterns of products obtained at different Na₂CO₃/CFA mass ratios. According to the XRD pattern of calcinated Na₂CO₃/CFA mixture (figure 1), the product is mainly unconverted NaAlSiO₄ formed during calcination with the lowest Na₂CO₃/CFA mass ratio of 0.8. The XRD patterns of the samples obtained after crystallization at different temperatures for 8 h are shown in figure-3. The characteristic XRD peaks of Na-A zeolite appear even after crystallization at

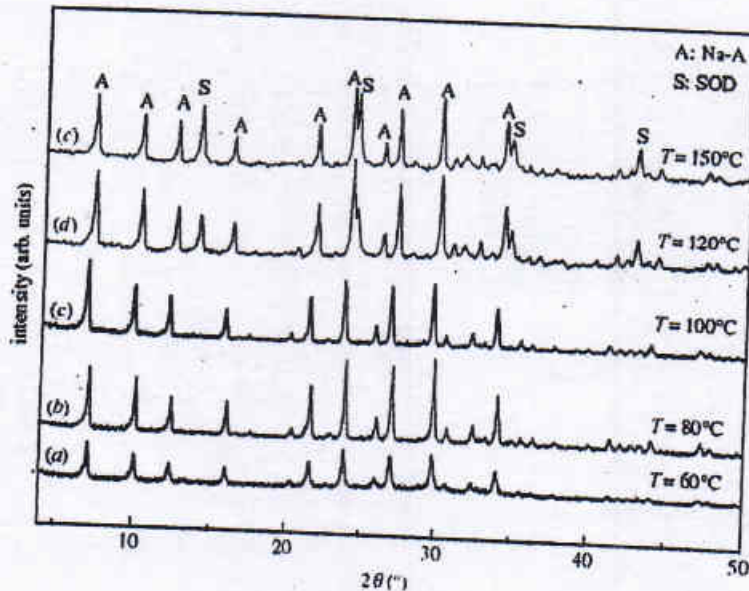


Figure 3. The crystallization temperature on the structure of the products (Na-A)

60°C. However, these peaks are broad and short, showing the low crystalline and purity of the product (figure 3a). The XRD peaks are narrowed and sharp from 60°C to 100°C (figure 3a-c), showing that in this temperature range, rising temperature would promote the crystallization of Na-A and there is a positive correlation between the crystalline of the zeolite product and the crystallization temperature. According to the XRD pattern, phase-pure Na-A can be obtained from 60°C to 100°C. As zeolite Na-A is thermodynamically less stable than sodalite (SOD) in the current reaction mixture, we noted the SOD phase from 120°C to 150°C (figure 3c-e). This is because higher temperature will promote the conversion of metastable zeolite into a more thermodynamically stable phase [30]. Thus, to obtain pure-phase Na-A zeolite from CFA and to lower the energy consumption for the synthesis, the crystallization temperature should be controlled in the range 80-100°C.

3.1. Hydrothermal synthesis of zeolite Na-X from coal fly ash

As aforementioned, the Si/Al ratio in the CFA sample used eventually satisfied the requirement for the synthesis of Na-A zeolite. It would be more interesting if other zeolites of industrial significance can be synthesized by altering the Si/Al ratio. We then investigated the potential synthesis of Na-X from the same CFA sample by changing the composition of calcinated Na₂CO₃/CFA mixture with silica sol and using NaOH to keep the Na/Si ratio to satisfy the requirements for Na-X crystallization. In the controlled experiments,

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silica sol and NaOH were added to the calcinated $\text{Na}_2\text{CO}_3/\text{CFA}$ mixture to keep the $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ constant as 2.2 and 40, respectively.

The characteristic XRD peaks of zeolite Na-A disappear and new peaks associated with zeolite Na-X appear when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio reaches 3 (figure 4b). With the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, the peaks of Na-X get intensified and sharpened and those of Na-A disappear completely (figure 4c-e). This is in excellent agreement with previous reports [30]. These findings prove that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is a key parameter to obtain phase-pure zeolite Na-X.

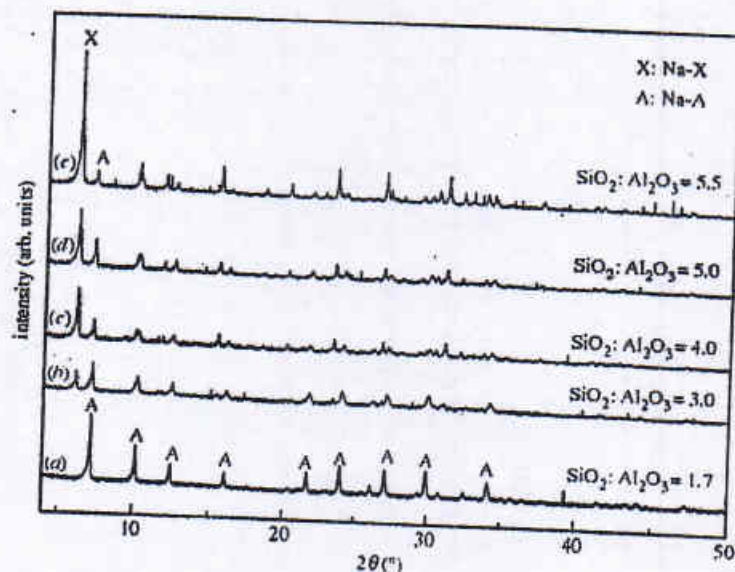


Figure 4. The impact of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio on the structure of the hydrothermal reaction products at 100°C for 8 h

In controlled experiments, the $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were kept constant as 2.2 and 40, respectively. The crystallization temperature was 100°C and the duration for crystallization was 8 h. The XRD patterns of the products after hydrothermal crystallization are shown in figure 5. When only tablet-compressed calcinated CFA was used as reactant (fig 5a), there are only quartz and mullite in the product, showing that Na_2CO_3 is required to convert quartz and mullite into precursors for zeolites. When the $\text{Na}_2\text{CO}_3/\text{CFA}$ ratio is increased to 1, phase-pure Na-X zeolite was obtained, as indicated by the sharp characteristic XRD peaks of Na-X in figure 5b. When the $\text{Na}_2\text{CO}_3/\text{CFA}$ ratio is increased further, the characteristic peaks of Na-A appear on the XRD patterns of the products (figure 5c,d). This shows that a mixture of Na-A and Na-X will be obtained at $\text{Na}_2\text{CO}_3/\text{CFA}$ ratio larger than 1. According to the chemical composition of the CFA (table 1) and the mentioned experiments, we concluded that phase-pure zeolite Na-A can be synthesized with CFA at reactant molar ratio, hydrothermal reaction temperature and reaction time of $1.3\text{Na}_2\text{O} : 0.6\text{Al}_2\text{O}_3 : 1\text{SiO}_2 : 38\text{H}_2\text{O}$ at 80°C for 6 h, respectively, while phase-pure zeolite Na-X can be synthesized at $2.2\text{Na}_2\text{O} : 0.2\text{Al}_2\text{O}_3 : 1\text{SiO}_2 : 88\text{H}_2\text{O}$ at 100°C for 8 h, respectively. With these set-ups, the yields of Na-A and Na-X are approximately 68% and approximately 62%, respectively. The relatively low yield of Na-X is due to the introduction of silica sol to get phase-pure Na-X.

3.2. Characterization of zeolite Na-A and Na-X

We then characterized the chemical composition of synthesized Na-A and Na-X samples with XRF. The result of XRF on Na-A sample indicates that it contains 44.64% SiO₂, 37.29% Al₂O₃, 18.22% Na₂O, 3.80% CaO, 3.36% Fe₂O₃, 3.06% TiO₂, 0.55% MgO and 0.41% K₂O and the corresponding Si/Al molar ratio is

1.48 and is typical for commercial Na-A, while that for the Na-X sample is 5.12. The high Si/Al molar ratio of Na-X is due to the introduction of silica sol to get phase-pure Na-X. FT-IR spectroscopy was used to confirm the structure of synthesized Na-A and Na-X samples.

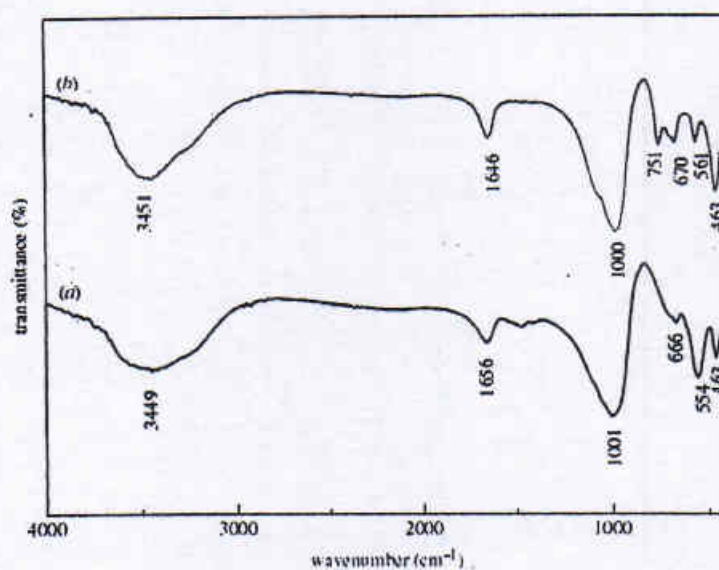


Figure 6. FT-IR spectra of Na-A (a) and Na-X (b) zeolites synthesized from calcinated CFA.

The band at 463 cm⁻¹ was ascribed to the internal vibration of T-O bending. Moreover, the bands observed at 1656 and 3449 cm⁻¹ correspond to the presence of H₂O and hydroxyls, respectively. The observed FT-IR bands of Na-A samples are in good agreement with those reported in previous works, which further proves the successful synthesis of Na-A from CFA [30,31]. We also examined the FT-IR spectrum of the synthesized zeolite Na-X sample. As shown in figure 6b, Na-X zeolite has FT-IR bands at wave numbers of 459, 561, 669, 747, 982, 1646 and 3451 cm⁻¹. A broad band at 3451 cm⁻¹ and the sharp peak at 1646 cm⁻¹ can be assigned to the structural hydroxyl groups and bending mode of physically adsorbed water, respectively. The peak at 561 cm⁻¹ can be attributed to the vibration of distorted double five-member ring in the high silica framework.

4. Conclusion

We showed that tablet compression can enhance the contact with Na₂CO₃ for the activation of CFA through calcination for the synthesis of zeolites Na-A and Na-X under mild conditions. We optimized the control variables for zeolite synthesis and showed that phase-pure zeolite Na-A can be synthesized with CTA at

reactant molar ratio, hydrothermal reaction temperature and reaction time of $1.3\text{Na}_2\text{O} : 0.6\text{Al}_2\text{O}_3 : 1\text{SiO}_2 : 38\text{H}_2\text{O}$ at 80°C for 6 h, respectively, while phase-pure zeolite Na-X can be synthesized at $2.2\text{Na}_2\text{O} : 0.2\text{Al}_2\text{O}_3 : 1\text{SiO}_2 : 88\text{H}_2\text{O}$ at 100°C for 8 h, respectively.

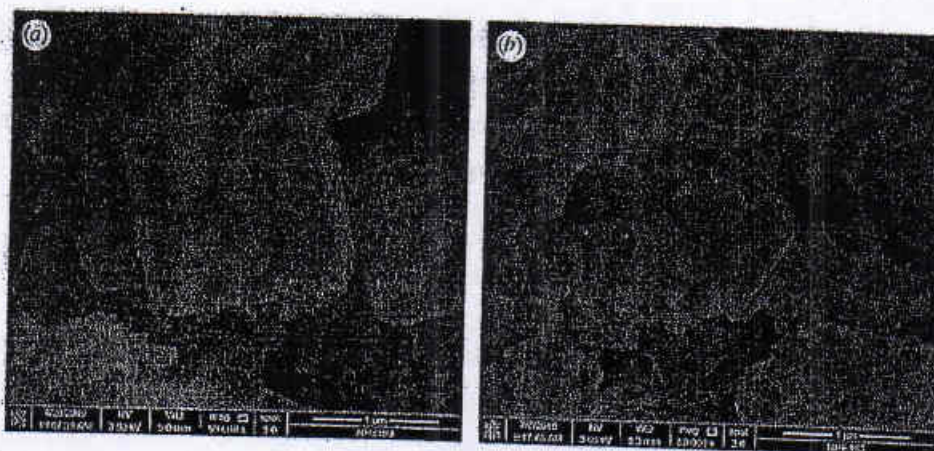


Figure 8. SEM images of synthesized Na-A (a) and Na-X(b) zeolites obtained from calcinated CFA.

Further SEM, BET, FT-IR characterization confirmed that the Na-A and Na-X synthesized under optimized conditions would exhibit properties the same as phase-pure Na-A and Na-X. In this sense, the zeolites synthesized can principally be used as adsorbents for gas separation, wastewater treatment and soil remediation, as heterogeneous Lewis/Bronsted acid catalysts for the conversion of chemicals, as support materials for stabilization and dispersion of catalytic reaction centers, as cation-exchange materials for resource recovery and in other industrial applications where Na-A and Na-X play a role. Furthermore, the developed protocols for the synthesis of Na-A and Na-X from CFA are simple and cost- and energy effective, so they can be adapted for mass production of zeolites in chemical plants. Related works are now being carried out in our laboratory.

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