Selective preparation of zeolite X and A from flyash and its use as catalyst for biodiesel production

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HIGHLIGHTS

- Flyash was utilized for zeolites preparation for transesterification.
- Single phase and highly crystalline zeolite was obtained at flyash/NaOH ratio of 1:1.2.
- Si/Al ratio of 2 resulted in the formation of zeolite X.
- At 5 wt% of catalyst loading conversion was 84.6%.
- The biodiesel obtained has a calorific value of 37.5 MJ/Kg.

ARTICLE INFO

ABSTRACT

This work discusses the utilization of flyash for synthesis of heterogeneous catalyst for transesterification. Different types of zeolites were synthesized from alkali fusion followed by hydrothermal treatment of coal flyash as source material. The synthesis conditions were optimized to obtain highly crystalline zeolite based on degree of crystallinity and cation exchange capacity (CEC). The effect of CEC, acid treatment, Si/Al ratio and calcination temperature (800, 900 and 1000 °C) on zeolite formation was also studied. Pure, single phase and highly crystalline zeolite was obtained at flyash/NaOH ratio (1:1.2), fusion temperature (550 °C), fusion time (1 h), hydrothermal temperature (110 °C) and hydrothermal time (12 h). The synthesized zeolite was ion-exchanged with potassium and was used as catalyst for transesterification of mustard oil to obtain a maximum conversion of 84.6% with 5 wt% catalyst concentration, 12:1 methanol to oil molar ratio, reaction time of 7 h at 65 °C. The catalyst was reused for 3 times with marginal reduction in activity.

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1. Introduction

Heterogeneous alkaline transesterification of triglycerides has emerged as an alternative to the conventional homogeneous system due to its high selectivity, easier separation and fewer disposal problems. The growing environmental concerns and stringent legislations made the scientific community to develop catalysts that could enable its use in large scale industrial applications and help in subsiding pollution. Zeolites, aluminosilicate members of the family of microporous materials are basic solids and can act as supports for alkali metals and metal oxides [1]. The basicity of these materials can further be improved by occlusion of alkali metal oxide clusters by impregnated alkali metal salts [2,3]. Zeolites occur naturally (analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite) and can be synthesized commercially in large scale by hydrothermal process (zeolites A, X, Y and ZSM-5) [4–7]. The principle raw materials used for the synthesis of these zeolites are silica and alumina.The preparations of zeolites from these chemical sources are expensive. Therefore, the possibility of the use of cheaper raw materials like clay minerals [8], oil shale ash [9], kaolinite [10], municipal solid wastes [11–15] and coal ashes [12–20] as starting materials for the synthesis of zeolite was successfully investigated.

Zeolite Y and X was synthesized from rice husk with alkali metal loading and was used as catalyst for transesterification of jatropha oil. Biodiesel yield of 73.4% and 95.2% was obtained at 65 °C in 3 h with methanol to oil molar ratio of 16:1 using 14 wt% K loaded zeolite Y and 16 wt% Na loaded zeolite X, respectively [21,22]. Leclercq et al. [23] performed the transesterification of rapeseed oil using cesium-exchanged Na-X, mixed magnesium–aluminum oxides, magnesium oxide, and barium hydroxide for different methanol to oil ratios. Maximum conversion of 76% was obtained
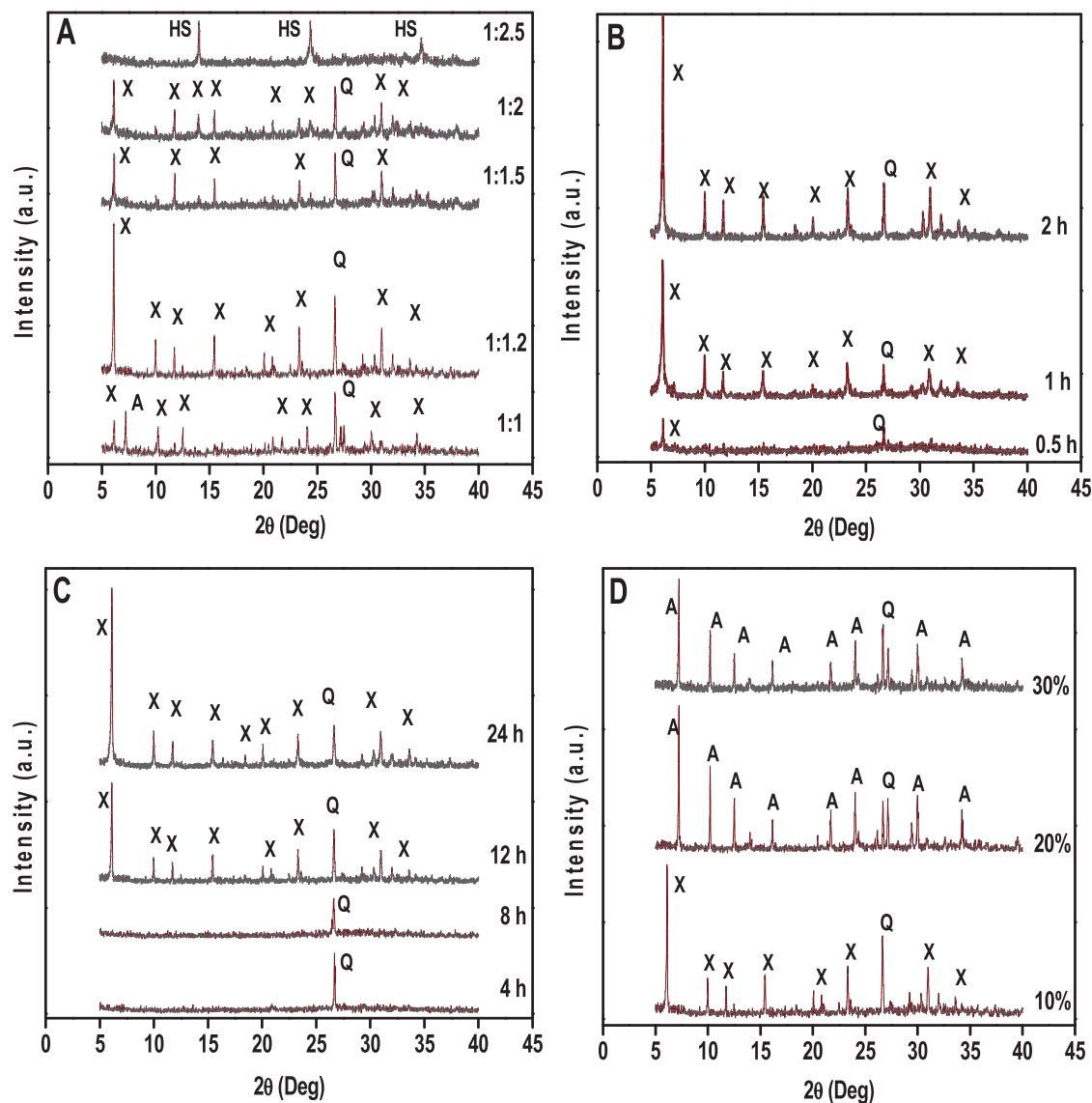
Fig. 1. XRD patterns showing the effect of (A) flyash/NaOH ratio, (B) fusion time, (C) crystallization time and (D) sodium aluminate addition on zeolite formation. Quartz (Q); Zeolite X (X); Zeolite A (A).

for Cs exchanged Na-X zeolite with methanol to oil molar ratio of 275 for 22 h of reaction and 20 wt% catalyst concentrations. The transesterification of palm oil to methyl ester was done in a packed-bed reactor using KOH/Na-Y as catalyst. It was found that KOH/Na-Y created strong basic sites, and the agglomeration was greatly increased by increasing the potassium content. The highest yield of 92.18 % was obtained for the 15 wt% K/Na-Y at reaction temperature of 60 °C for 7 h [24].

Kusuma et al. [25] studied the transesterification of palm oil using KOH modified natural zeolite at different concentrations (25, 50, 75 and 100 g/L) at zeolite to KOH solution weight ratio of 1:4. The maximum yield of biodiesel was obtained (95.09%) at 3 wt% catalyst loading. Use of microwave irradiation for the synthesis of Na-Y, KL and Na/ZSM-5 zeolites with different CaO loading was investigated by Wu et al. [26]. A high quality biodiesel with yield of 83.53% was obtained when flyash based zeolite was used at the following reaction conditions: methanol:oil ratio of 6:1, catalyst amount of 3% (w/w) of oil and reaction temperature of 65 °C after 8 h [27].

Use of coal flyash for zeolite synthesis could not only add value addition to waste but also helps in development of better technologies to promote its utilization. Comprehensive studies regarding the optimum parameters for zeolite synthesis, effect of flyash calcination temperatures, acid treatment, and variation of Si/Al ratio on type of zeolite product formed and the effect of these parameters on CEC and crystallinity of zeolitic materials has not been reported. Studies on the use of zeolite synthesized from flyash and its use on the transesterification by mustard oil has not been accounted yet. In this study, alkali fusion prior to hydrothermal treatment was used when compared to conventional hydrothermal synthesis. This is because of the fact that larger amounts of aluminosilicates can be dissolved using this method that helps in enhancing hydrothermal conditions for zeolite synthesis. The catalytic activity of the synthesized zeolites was measured by using the transesterification of mustard oil.

The main objective of the present study is the selective production of zeolite X and A from flyash. The effect of synthesis condition like NaOH/flyash ratio, temperatures (fusion, calcination and hydrothermal), time (fusion and crystallization) and addition of aluminum source on the formation of final product was studied. Further, effect of acid treatment of flyash on zeolites formation was also studied. The synthesized zeolite was characterized for its physico-chemical properties by XRD, XRF, FESEM, BET, FTIR and
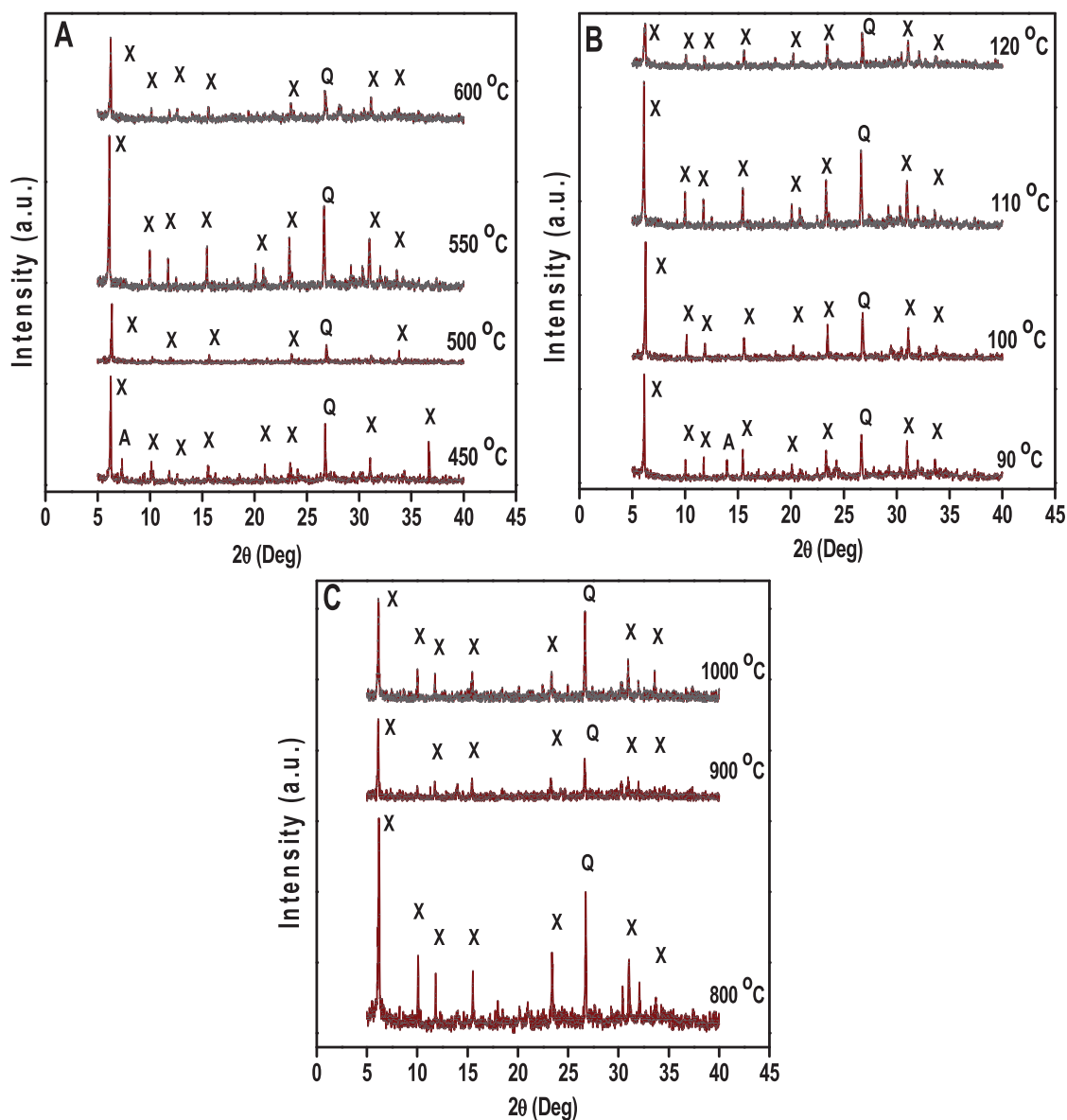
Fig. 2. XRD patterns showing the effect of temperature (A) fusion, (B) crystallization, and (C) flyash calcination on zeolite formation. Quartz (Q); Zeolite X (X); Zeolite A (A).

CEC. Zeolite X thus obtained was ion-exchanged with potassium source and was used as a catalyst for biodiesel production.

2. Experimental

2.1. Materials

The coal flyash used in this study was collected from M/s SARACA laboratories limited, Andhra Pradesh, India. Hydrochloric acid (10%), sodium hydroxide (98%) and sodium aluminate (99.99%), sodium acetate, ammonium acetate and isopropyl alcohol obtained from Sigma–Aldrich Pvt. Ltd. were used in zeolite synthesis and its characterization.

2.2. Zeolite synthesis and ion-exchange process

Zeolite was synthesized from flyash by alkaline fusion prior to hydrothermal treatment. The unburnt carbon along with other volatile materials present in flyash were removed by calcination at 900 ($\pm$10)°C for 2 h. Flyash sample was further treated with

hydrochloric acid (10%) at 80°C for 1 h to increase its activity in zeolite formation. A homogenous fusion mixture of flyash and NaOH was prepared by proper grinding and mixing in NaOH/flyash ratio of 1:1–1:2.5. The sample was heated in temperature range of 450–600°C for about 1–2 h to study the effect of NaOH/flyash ratio, fusion temperature and time on the extent of zeolite formation. The resultant fused mass was cooled, milled and mixed thoroughly in de-ionized water in the ratio of 1:10 (flyash to water) with simultaneous addition of sodium aluminate (10–30 wt%) to control the Si/Al ratio and to study its effect on zeolite formation. The slurry was then subjected to aging for 12–16 h, allowed to crystallize between 90°C and 120°C for about 24 h to study the effect of hydrothermal temperature and time on zeolitization. The solid crystalline product was recovered by filtration and washed thoroughly until the filtrate pH was around 10 and dried at 110°C. The effect of calcination temperatures (800–1000°C) and acid treatment of flyash on zeolite formation was also studied. The synthesized zeolite was modified by an ion exchange process using potassium acetate as a precursor. The dried zeolite was dispersed in 1.0 M solution of potassium acetate with powder to the solution ratio of 1:10 and
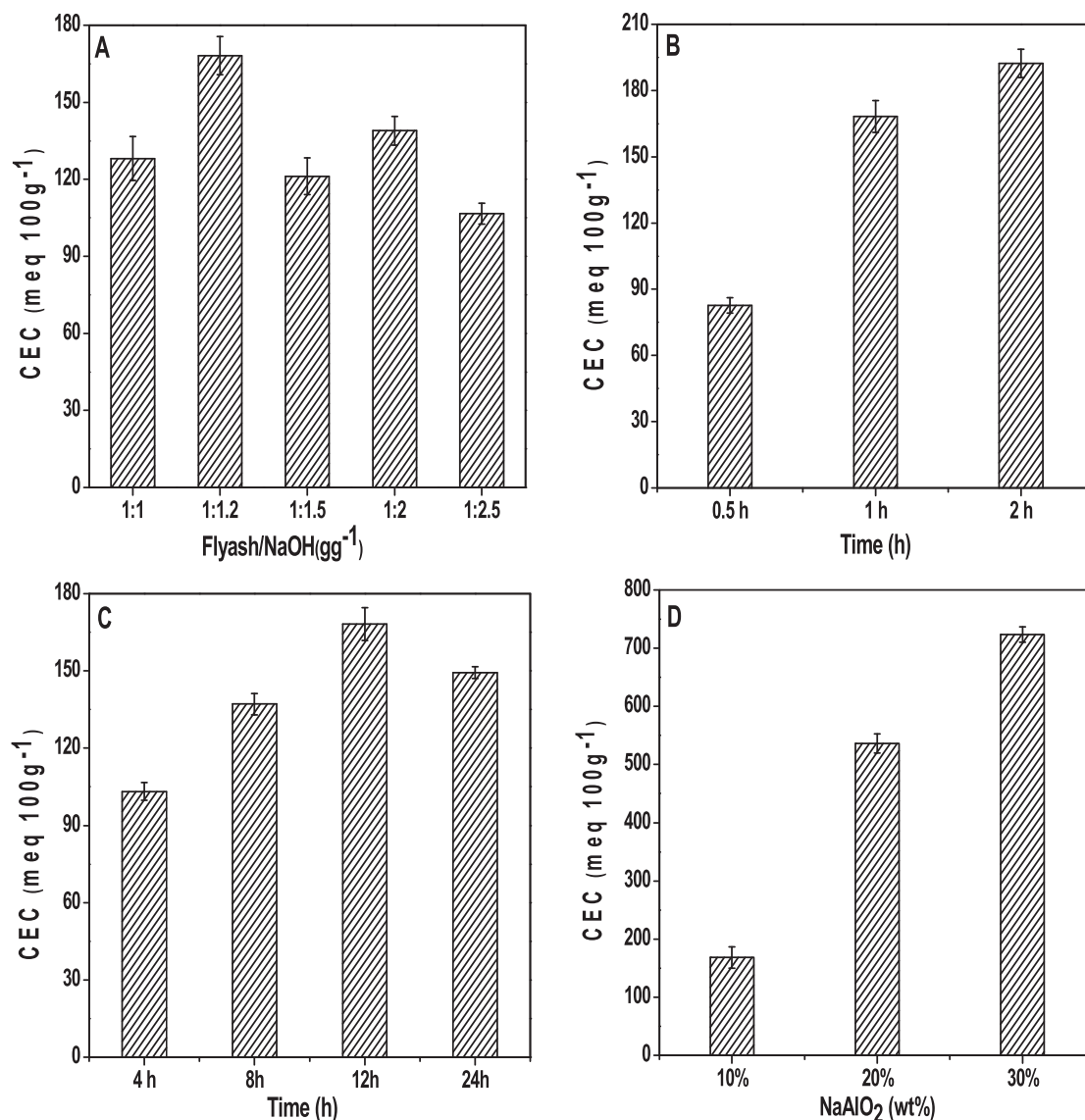
Fig. 3. Effect of (A) flyash/NaOH ratio, (B) fusion time, (C) crystallization time, and (D) NaAlO$_2$ addition on CEC.

heated at 60 °C for 24 h. The mixture was repeatedly washed with distilled water, dried in air at 110 °C and then calcined at 500 °C for 2 h to obtain the ion exchanged zeolite.

2.3. Catalytic activity

To study the catalytic activity, transesterification of refined mustard oil was carried out in a 500 ml three neck round bottom flask equipped with reflux condenser which was heated using oil bath provided with a PID temperature controller. A fixed quantity of refined mustard oil and prepared catalyst was mixed with methanol (alcohol/oil) at molar ratio of 6:1–18:1 and was stirred at 65 °C for 10 h. After carrying out the reaction, the mixture was cooled to room temperature, centrifuged at about 6000 rpm for 10 min. Ester was separated from catalyst, glycerol and unreacted methanol using a rotary evaporator. The final product was allowed to settle overnight to produce two phases: bio-diesel at the upper layer and glycerol at the bottom layer. The biodiesel yield (% FAME) was calculated from the ratio of the integrations of the ^{1}H NMR signals of the methoxy protons (—CH$_3$O—) in the methyl ester at chemical shifts of 3.68 ppm (singlet peak) and methylene protons

(—CH$_2$—) of all triglycerides at chemical shifts of 2.30 ppm (triplet peak), according to the following Eq. (1):

$$\% \, FAME = \left[\frac{2A_{CH3}}{3A_{CH2}} \right] \times 100 \tag{1}$$

where A_{CH3} is the integration value of the methoxy protons and A_{CH2} is the integration value of the methylene protons [28]. The factors 3 and 2 derive from the number of attached protons at the methoxy and methylene carbons, respectively.

2.4. Methods

Thermogravimetric analysis (TGA) of zeolite was done using Netzsch STA449F3A00 with argon as carrier gas at a constant flow rate of 45 ml/min from 25 to 1200 °C at heating rate of 10 °C/min. Presence of various characteristic functional groups were collected in the range of 400–4000 cm^{-1} using SIMADZU CORP Fourier transform infrared spectroscopy (FTIR). The surface morphology of flyash was examined using Sigma/Zeiss FESEM. The metal concentration in the material was determined by using PerkinElmer A Analyst 200 Atomic adsorption spectroscopy (AAS). The
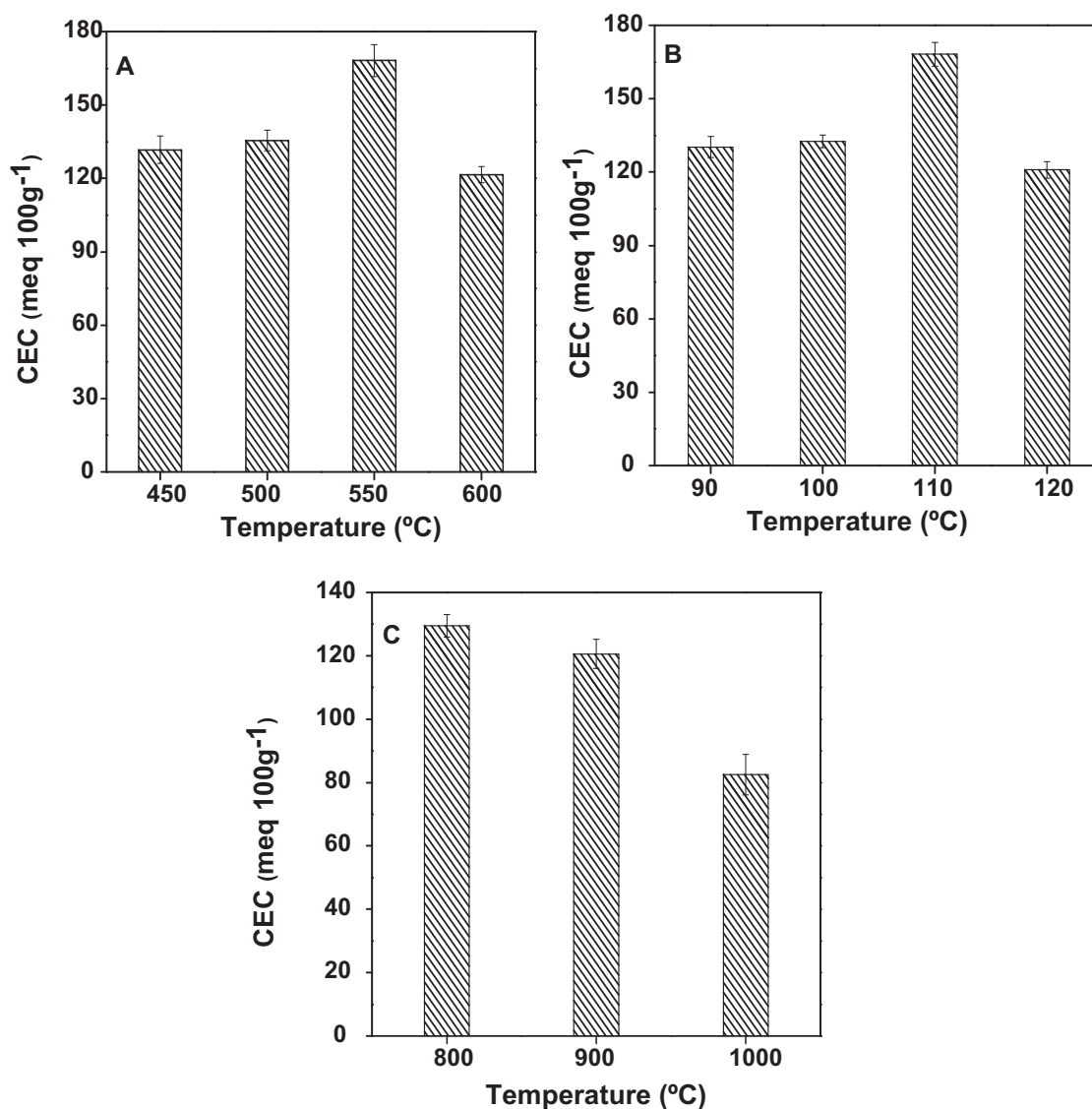
Fig. 4. Effect of CEC on (A) fusion, (B) crystallization, and (C) flyash calcination temperatures on zeolite formation.

overall crystalline phases of samples were determined by Bruker D Advance X-ray diffraction (XRD) system using a Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) between 10 and 45° of 2θ. Percentage crystallinity was calculated from Topaz software. The surface area of the synthesized catalyst was measured by using Beckman Coulter SA-3100. ^{1}H NMR analyses were acquired at 25 °C on a Varian DRX-600 using DMSO D6 as the solvent and trimethylsiloxysilane (TMS) as the internal standard. X-ray fluorescence (XRF) analysis was performed for flyash and the synthesized catalyst for elemental composition using Philips PW 2404 wavelength dispersive spectrometer fitted with Rh tube. The TPR (temperature-programmed reduction) profiles of the samples were determined using Micromeritics-2720. A bed of quartz wool was made and then required amount of catalyst (35 mg) was taken and outgassed at 150 °C for 1 h. Then the reduction of catalyst was done in a flow of 10% H_2/Ar in 30 ml up to 850 °C to determine the reduction temperatures. The cation exchange capacity (CEC) of the materials was determined by ammonium acetate method described elsewhere [29]. Various fuel properties were determined using standard methods. The acid value was determined as per ASTM D664-89. Viscosity was measured at 40 °C using Rehostress RS 1 rheometer from Thermo Electron as per ASTM D 445. Calorific value

of biodiesel was measured by using bomb calorimeter as per ASTM D 240-92.

3. Results and discussion

3.1. Zeolite synthesis and its parametric study

Numerous experiments were performed using different flyash/NaOH ratio, hydrothermal, fusion and flyash calcination temperatures, fusion and crystallization time to determine the optimal conditions for the synthesis of pure zeolites based on degree of crystallinity and CEC of the synthesized product. The Si/Al ratio was strictly controlled by the addition of sodium aluminate (10–30%) for avoiding the formation of other zeolitic phase or mixture of them. The effect of variables are discussed in the subsequent sections.

3.1.1. Effect of flyash/NaOH ratio

The XRD pattern of original flyash mainly represents the presence of crystalline quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Besides some crystalline phases (quartz, mullite, hematite etc), ash is primarily composed of amorphous material. The phases in flyash were quartz (SiO_2) with major peaks at 20.86 and 26.65 degrees 2θ (d
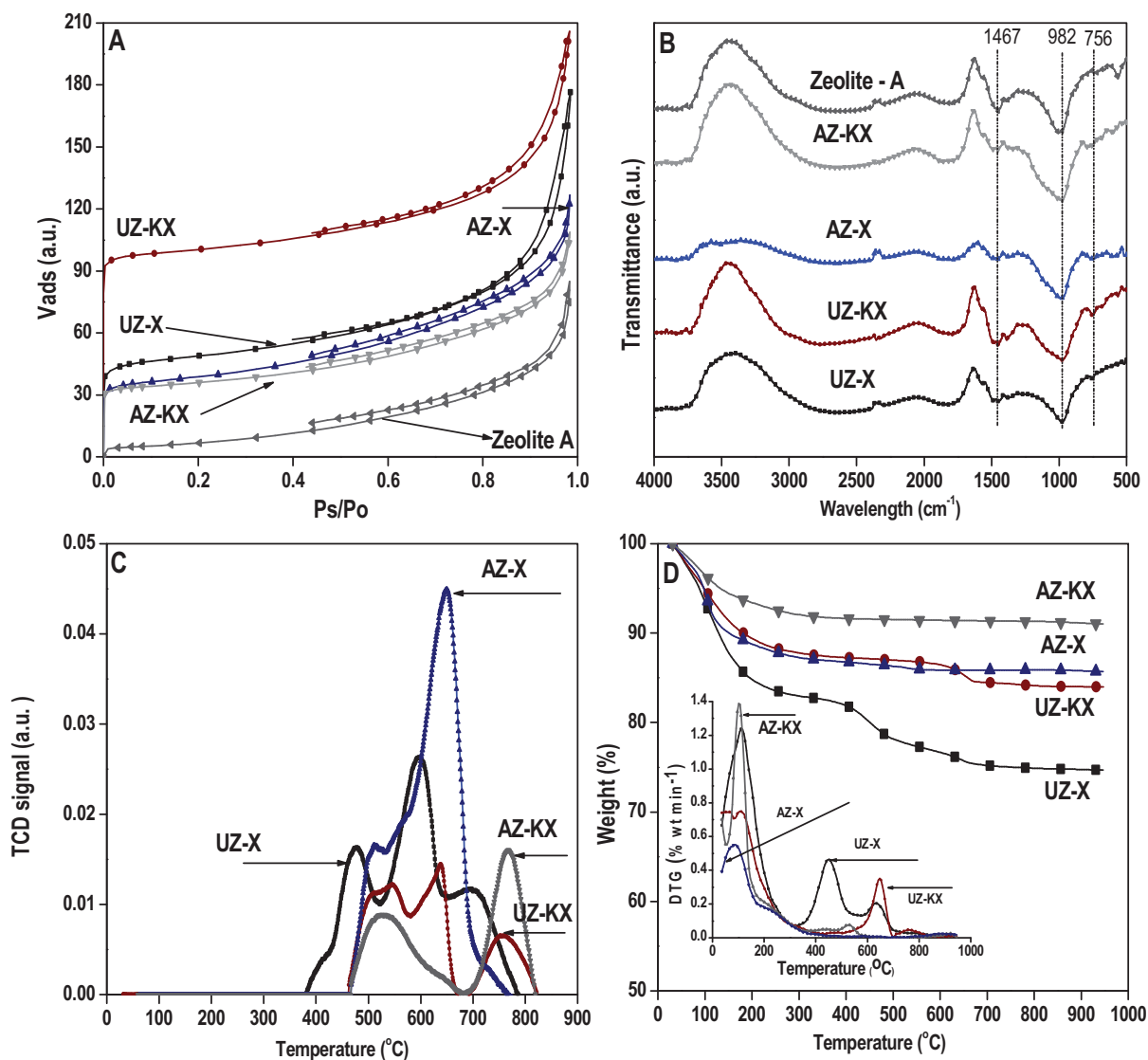
Fig. 5. (A) Nitrogen adsorption–desorption isotherms, (B) FTIR spectra, (C) TPR, (D)TGA and DTG curves of UZ-X, UZ-KX, AZ-X, AZ-KX and zeolite A.

spacing d_{hkl} of 4.2745 and 3.3508 Å). Less intense peaks were also identified as mullite at 16.42 and 40.82 degrees 2θ (d spacing d_{hkl} of 5.399 and 2.208 Å) and hematite [16,17]. The hump at 18–35 degree 2θ represents the presence of amorphous glassy phase in flyash.

Zeolite formation in terms of crystallinity and CEC was examined as a function of NaOH concentration. The sodium hydroxide added to flyash not only works as an activator, but also adjusts the sodium content in the starting material. The glass phase on the surface of flyash particles easily dissolves into the alkaline source. Sodium ions are known to stabilize the sub-building units (specially six member ring) of zeolite frameworks and usually are required for zeolite synthesis under hydrothermal conditions. Insufficient concentration of alkali might lead to minimal extraction of alumino-silicates from flyash which adversely affects the crystallization process [12].

The effect of flyash/NaOH (1:1–1:2.5) ratio on zeolite formation was studied and XRD patterns were shown in Fig. 1(A). At flyash/NaOH ratio of 1, mixture of zeolite X and A was formed. The crystallinity increased with the increase in flyash/NaOH ratio upto 1:1.5. The same was slightly decreased at the ratio of 1:2 with the formation of single phase zeolite X and then decreased rapidly due to the formation of hydroxysodalite (HS) at ratio of

1:2.5. The change in the type of zeolite product could be due to increase in supersaturation with increase in NaOH concentration [30]. According to Ostwald's rule of successive transformation, the higher the supersaturation, better the condition to nucleate metastable phases, such as zeolite X, which later recrystallizes and is replaced by highly stable zeolite HS [31]. Thus the optimum value of flyash/NaOH ratio was found to be 1:1.2.

3.1.2. Effect of time

The effect of fusion and crystallization time on the formation of resultant zeolites was shown in Fig. 1(B) and (C), respectively. Homogeneous fusion mixture of flyash and NaOH was heated at 550 °C for 0.5, 1 and 2 h to study its effect on zeolitization. It was observed that fusion time of 30 min shows no peaks. However, after 1 h zeolite X peaks appears, with a maximum crystallinity occurring after 2 h. From the above it is clear that a fusion time of 1 h is required for the formation of zeolite X.

It can be seen from the XRD pattern (Fig. 1(C)) that the minimum time required for the complete formation of zeolite is 12 h. No product was obtained at crystallization time of 4 and 8 h. A slight decrease in degree of crystallinity of the zeolite was observed with increase in time of crystallization.
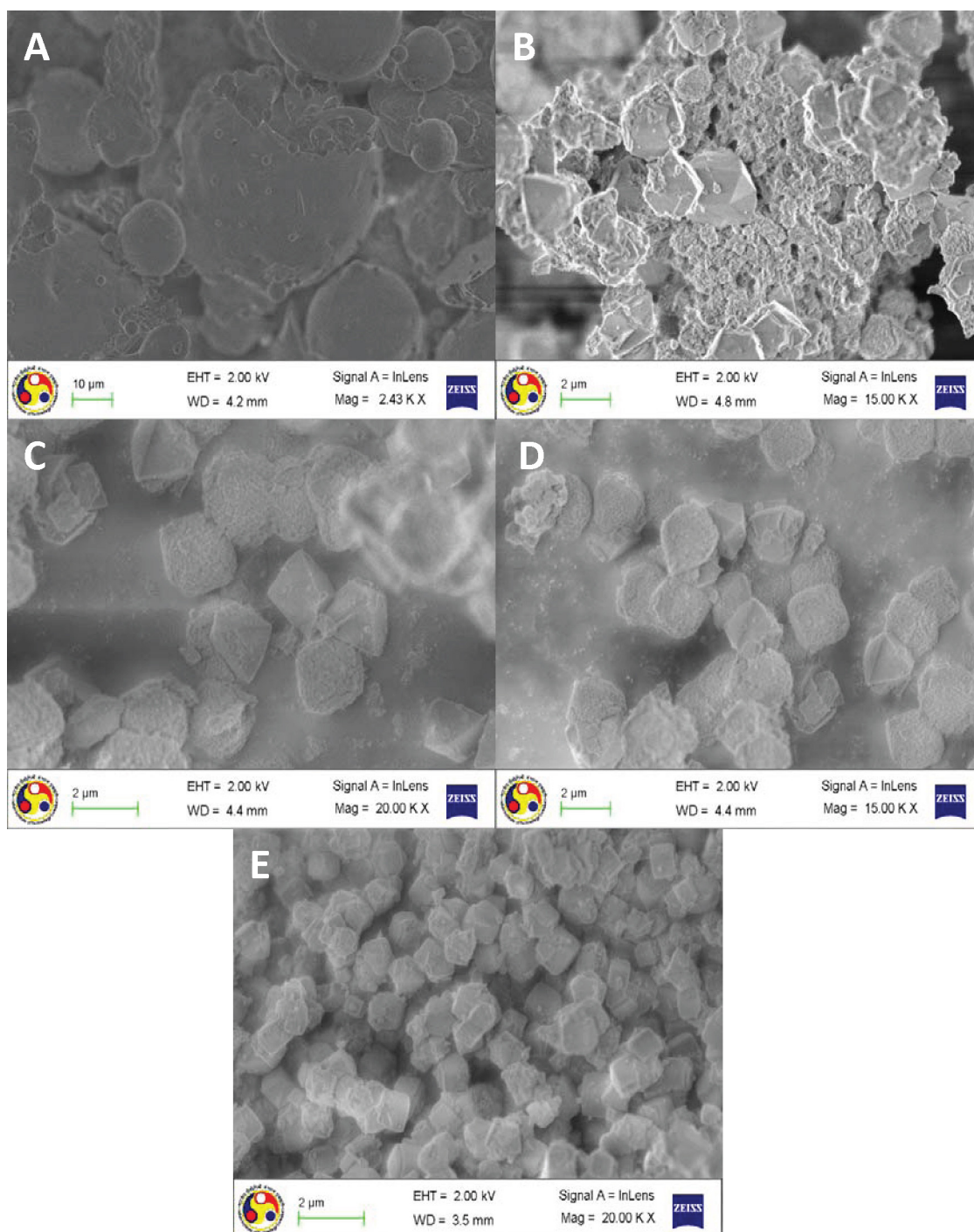
Fig. 6. Surface morphology of (A) flyash, (B) UZ -X, (C) AZ-X, (D) AZ-KX and (E) zeolite A.

3.1.3. Effect of sodium aluminate

The effect of Si/Al ratio, by the addition of sodium aluminate (10–30 wt%) on the type of zeolite formation was studied and Fig. 1(D) shows the XRD patterns. Addition of 10% of sodium aluminate resulted in the formation of highly crystalline zeolite X with Si/Al ratio of 1.94. With further increase in amount from 20 to 30%, zeolite A (LTA) was formed with Si/Al ratio of 1.67 and 1.48, respectively. For the flyash used in the present study, it is clear that at Si/Al ratio <1.8 would result in the formation of zeolite A and Si/Al ratio > 1.8 would result in the formation of zeolite X.

3.1.4. Effect of temperature

The effect of fusion, crystallization and flyash calcination temperatures for a mixture of flyash/NaOH of 1:1.2 on zeolite formation was studied and the XRD patterns are shown in Fig. 2(A)–(C), respectively. It can be seen from the XRD plot (Fig. 2(A)) that the fusion temperatures of 450 °C did not result in the formation of single phase zeolite. The minimum fusion temperature required for the complete formation of single phase zeolite is 500 °C. However, maximum crystallinity of zeolite was obtained at fusion temperature of 550 °C. Further increase in temperature to 600 °C did not affect the crystallinity of the material.
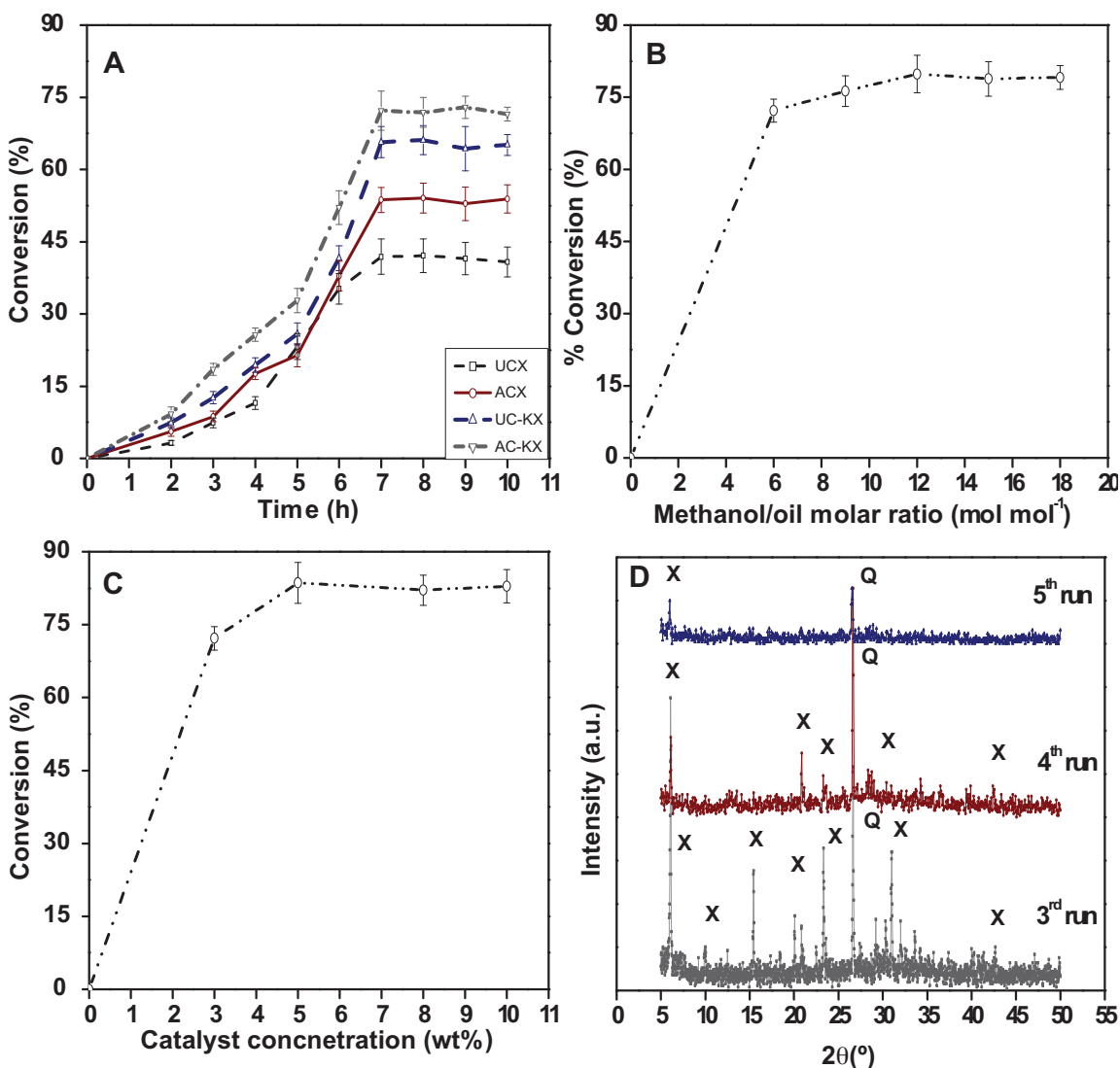
Fig. 7. Effect of (A) time, (B) methanol: oil molar ratio, (C) catalyst concentration on biodiesel conversion and (D) XRD spectra for catalyst reusability studies.

From the Fig. 2(B) it can be observed that 90 °C temperature resulted the formation of mixture of zeolite X and A during hydrothermal process. Highly crystalline single phase zeolite X was formed as the temperature was increased from 100 to 120 °C. The minimum temperature required for the complete crystallization of zeolite was 110 °C. Above this temperature no significant change in the crystallinity of the product was observed. The formation of zeolite A along with zeolite X was explained by Catalfamo et al. [32]. At the initial stages of zeolite formation, rate of dissolution of alumina is faster than that of silica and with increase in temperature, dissolution of silica increases. At 90 °C, Si/Al ratio is low enough to promote the formation of zeolite A and it can be assumed that at higher temperatures dissolution of silicon increase. Change in Si/Al ratio favors the formation of zeolite X. Most of the literatures indicated that fusion temperature above 500 °C favors the formation of single phase zeolite. On the contrary Rungsuk et al. [29] reported that fusion temperature at 450 °C resulted in the formation of zeolite X.

The flyash used in the present study was calcined at 800 °C, 900 °C and 1000 °C to study the effect of calcination temperature on zeolite formation (Fig. 2(C)). From the figure it is clear that single phase zeolite X was formed at above calcination temperatures. Calcination of flyash at 800 °C resulted in the formation of highly

crystalline zeolite X. It may be envisaged that the optimum value of temperature for fusion, crystallization and calcination are 550 °C, 110 °C and 800 °C, respectively.

3.2. Characterization of modified flyash and synthesized zeolite X and A

3.2.1. Cation exchange capacity (CEC)

The effect of flyash to NaOH ratio, fusion and crystallization time and NaAlO$_2$ addition on CEC values of the synthesized zeolite was presented in Fig. 3(A–D), respectively. From Fig. 3(A) it is clear that with increase in NaOH concentration in flyash, CEC value increased and was maximum (168.2 meq/100 g) at flyash to NaOH ratio of 1:1.2. This was due to the increase of degree of zeolitization with higher NaOH content in the reaction. With further increase in NaOH concentration, CEC values decreased and the product transformed from zeolite X to hydroxysodalite (HS) which was in agreement with the literature [11,29]. With increase in fusion time from 0.5 to 2 h, CEC value was also increased from 82.6 to 192.3 meq/100 g as shown in Fig. 3(B). The effect of crystallization time on CEC is represented in Fig. 3(C). CEC values were found to be increasing with reaction time and reached a maximum value at 12 h and decreased thereafter. With an addition of sodium aluminate from 10 to 30%,

Table 1
Chemical composition of flyash, acid treated flyash, UZ-X, CZ-X, AZ-X and zeolite A.

Component	Flyash			Zeolite		
	Raw	Acid treated	UZ-X	CZ-X	AZ-X	Zeolite-A
CaO	7.93	1.57	3.52	4.49	0.36	3.49
Fe_2O_3	5.89	2.41	5.02	3.51	2.21	5.71
K_2O	1.39	0.82	0.69	0.75	1.29	0.65
MnO	0.05	0.04	0.04	0.05	0.03	0.04
P_2O_5	0.27	0.17	0.05	0.07	0.09	0.04
SO_3	0.53	0.01	0.02	0.01	0.01	0.02
SrO	0.06	0.02	0.08	0.08	0.07	0.08
TiO_2	1.35	1.1	1.05	1.21	1.25	1.07
Al_2O_3	23.21	22.88	18.64	22.64	21.74	23.09
MgO	1.53	0.10	0.40	0.59	0.55	0.19
SiO_2	56.61	62.94	36.12	44.34	47.63	38.55
Na_2O	0.28	0.58	32.48	18.21	18.48	26.12
SiO_2/Al_2O_4	2.44	2.75	1.94	1.96	2.19	1.67

CEC values increased from 168.2 to 723.4 meq/100 g (Fig. 3(D)). It may also be seen that the CEC value was initially increased and then decreased with increase in fusion and hydrothermal temperatures. The CEC value was maximum at fusion and hydrothermal temperatures of 550 °C and 110 °C, respectively (Fig. 4(A and B)). Zeolite X (CZ-X) was synthesized from flyash calcined at different temperatures (800–1000 °C) and its effect on CEC was shown in Fig. 4(C). It was found that with increase in calcination temperatures, CEC value decreases.

The CEC value of the synthesized uncalcined zeolite X with Si/Al ratio of 1.94 was found to be 168.2 meq/100 g. The CEC value increased to 276.5 meq/100 g when uncalcined zeolite X was ion-exchanged with potassium. At Si/Al ratio of 2.19, acid treated zeolite Xhad a CEC of 352.7 meq/100 g and the corresponding ion-exchanged zeolite had CEC of 380.6 meq/100 g. Zeolite A at Si/Al of 1.67 had the highest CEC of 536.3 meq/100 g. Zeolite A is known to be an excellent cation exchanger owing to the higher proportion of aluminum in its framework which dictates the highest CEC.

The chemical composition of flyash, modified flyash and product was analyzed by XRF analysis and the results are tabulated in Table 1. From the above it is clear that flyash used in this study accounts for more than 60–80% of the glass phase ($SiO_2 + Al_2O_3 + Fe_2O_3$) and can be classified as class F (according to the ASTM standard C618). The average SiO_2/Al_2O_3 weight ratio of the flyash and acid treated flyash used in this study was found to be 2.44–2.75, respectively. Upon acid treatment, the calcium oxide content decreased from 7.93 wt% in the raw flyash to 1.57 wt% causing an increased portion of all other oxides, especially SiO_2. The decreased CaO content in the HCl treated flyash was due to the neutralization between HCl and CaO causing dissolution of CaO [33]. The acid treatment helped to dealuminate the flyash and remove iron to a certain extent, thereby increasing the activity, thermal stability and acidity of the zeolite, all aiming for better catalytic applications [34].

The formation of a particular zeolite species depends on the Si/Al ratio in the raw material. Change of this ratio may result in a change of the final structure obtained and may also lead to the crystallization of unwanted phases [35]. The synthesized uncalcined, calcined, acid treated zeolite X and A had Si/Al ratio of 1.94, 1.96, 2.19 and 1.67, respectively. It was observed that lower Si/Al ratios favors formation of zeolite A and Si/Al ratio of 2 results in the formation of zeolite X. Zeolite synthesized from acid treated flyash had lower CaO content.

3.2.2. Surface area and pore analysis by nitrogen adsorption measurements

The BET surface area of flyash, UZ-X, AZ-X and zeolite A was determined to be 1.7, 164.9, 167.4 and 24.1 m^2/g with total pore

volume of 0.03, 0.24, 0.25, and 0.11 cc/g, respectively. Zeolite X obtained from coal flyash has much higher specific surface area than zeolite A and flyash. The surface area of ion-exchanged UZ-KX and AZ-KX were found to be 323.7 and 334.7 m^2g^{-1} with total pore volume 0.29, 0.312 ccg^{-1} and shown in Fig. 5(A). According to IUPAC classification all the samples showed type II isotherm. In the case of isotherm of zeolite A and zeolite X (type II isotherms), it can be observed that adsorption increases more at relatively low pressure than in original flyash sample. This proves that samples contain certain number of micropores in relation to original flyash. Hysteresis loops for zeolites can be classified similarly to flyash as H3, which indicates uniform size slit pores in parallel plates.

3.2.3. Structural analysis of the synthesized zeolites

The IR spectra of uncalcined zeolite X (UZ-X), uncalcined zeolite KX (UZ-KX), acid treated zeolite X (AZ-X), acid treated zeolite K-X (AZ-KX) and zeolite A was illustrated in Fig. 5(B). The characteristic IR vibration band at 1467 cm^{-1} represents asymmetric stretching of Si/Al—O. The main asymmetric stretching of Si—O—Si was at 982 cm^{-1}. Symmetric stretching of Si—O—Si occurs at 756 and 675 cm^{-1}. The band at 560 cm^{-1} is associated with the double 6 rings that connect the sodalite cages.

3.2.4. TPR studies of zeolite

The reduction profiles of UZ-X, UZ-KX, AZ-X and AZ-KX zeolite was given in Fig. 5(C). From the figure it is clear that the reduction of uncalcined X zeolite started at a temperature of 378 °C. A clear shift in the value to about 467 °C was observed for ion-exchanged uncalcined KX zeolite. Acid treated X and KX zeolite had almost the same reduction temperature of uncalcined KX zeolite. Shift in the temperatures at 680–50 °C was observed when acid treated zeolite X was ion-exchanged with KX.

3.2.5. TGA analysis

The thermal stability of the synthesized zeolite was determined through weight loss at 950 °C and shown in Fig. 5(D) for TGA and DTG curves. A weight loss of 26%, 17%, 15% and 9% was observed for UZ-X, UZ-KX, AZ-X and AZ-KX zeolites, respectively. Initial weight loss was due to the removal of physisorbed and occluded water within 95–110 °C. A major decomposition of material was observed at 453 °C with partial weight loss at 636 °C for UZ-X. Ion exchange of zeolite resulted in shift of temperature of this major degradation to 647 °C. A partial weight loss was observed at 531 °C after which the degradation curve becomes almost flat for acid treated zeolite. No further weight loss was observed with increase in temperature indicating complete destruction of crystalline lattice of zeolite [15].

3.2.6. Morphological analysis

The surface morphology of flyash is shown in Fig. 6(A). Flyash particles are primarily spherical in shape with a relatively smooth surface texture and a wide particle size range. In some cases smaller particles are attached to the surface of larger particles, serving as substrates. The spherical particles are either solid or hollow (Cenospheres). The FESEM images of UZ-X (B), AZ-X (C) and AZ-KX(D) revealed the typical octahedral crystals of zeolite X. The structure of ion-exchanged zeolite remained same and similar kind of observation was reported by Babajide et al. [27]. The FESEM image of the surface of the synthesized zeolites revealed a clear transformation of the spherical particles of the flyash (A) into cubic crystalline structures which is a characteristic of zeolite A (E). However, these cubes had smooth edges and were covered with unconverted amorphous materials.

Table 2
Comparison of % yield of methyl ester with some reported zeolite based catalysts.

Author	Raw material	Oil	Time (h)	Temperature (°C)	Catalyst con. (wt%)	Meth/oil molar ratio (wt%/wt%)	Conversion (%)
Present study	Flyash zeolite - X	Mustard oil	7	65	5	12:1	84.6
Singh and Patel [38]	12-Tungstophosphoric acid (TPA) supported MCM-48	Jatropa oil	16	65	6	8:1	93
Sanchez et al. [39]	K, Ca, Na, Li, Ba - γAl_2O_3	Soybean oil	4	60	6	7.28:1	90
Suppes et al. [3]	Na-X, ETS-10 zeolite and metal catalysts	Soybean oil	24	120, 150	0.03g	6:1	90
Feyzi and Khajavi [40]	Strontium nano catalysts supported on the ZSM-5	Sunflower oil	4	60	3	9:1	87.7
Shu et al. [41]	La/zeolite beta	Soybean oil	4	60	0.011 (mass ratio)	14.5:1	48.9
Intarapong et al. [24]	KOH/Na-Y zeolite	Palm oil	7	60	15		92.1
SathyaSelvabala et al. [42]	Phosphoric acid modified β-zeolite	Calophyllum inophyllum oil (Tamanu)	1	60	1	9:1	93

3.3. Catalytic activity in transesterification process

The catalysts UZ-X, UZ-KX, AZ-X and AZ-KX were selected for transesterification of mustard oil because of their high surface area when compared to zeolite A. Samples were collected after 1 h interval using catalyst load of 3 wt%, methanol/oil molar ratio of 6:1 and reaction temperature of 65 °C with all experiments done in triplicate. The order of conversion after 7 h of reaction was AZ-KX (72.2%) < UZ-KX (65.7%) < AZ-X (53.7%) < UZ-X (41.9%). Interestingly, acid treated ion-exchanged zeolite showed more conversion compared to other zeolites (Fig. 7(A)). This could be due to the increase in base strength of ion-exchanged zeolite when modified with materials containing more electropositive nature (K^+) from parent zeolites [27,36].

Based on conversion, zeolite AZ-KX was considered further to optimize methanol/oil molar ratio keeping other reaction conditions constant. As per stoichiometry, 3 moles of methanol is required for every mole of oil but commonly excess methanol is used inorder to shift reaction equilibrium towards biodiesel formation. From Fig. 7(B) it is clear that when methanol/oil molar ratio was increased from 6:1 to 18:1, a maximum conversion of 79.8% was obtained at methanol/oil molar ratio of 12:1, beyond which addition of methanol did not show any significant increase in conversion. The presence of excess methanol helps in dissolution of glycerol which would constrain the reaction of methanol in oil aswell increasing the difficulty in separating biodiesel [26]. A methanol/oil molar ratio of 12:1 was found to be optimum for the present study.

The effect of catalyst concentration (3, 5, 7 and 10 wt%) on conversions of biodiesel was shown in Fig. 7(C). From the figure it is clear that with increase in catalyst concentration (5 wt%), biodiesel conversion increased to 84.6% and remained almost same with further increase in catalyst concentration which could be due to mixing (mass transfer) resistance concerning solid catalyst, oil and product. At low catalyst concentrations, deficient amounts of catalyst might have resulted in lower conversions [37]. The yields were in agreement with the literature explained in Table 2. The biodiesel obtained was tested for their physical properties. The acid value was found to be 0.07 mg KOH/g with viscosity of 6.8 cP and calorific value of 37.5 MJ/Kg. These values were in agreement with standard biodiesel with acid value 0.08 mg KOH/g, viscosity and calorific value in the range of 1.9–6 cP and 38–43 MJ/Kg, respectively.

3.4. Catalyst reusability studies

The spent catalyst was separated from the reaction mixture by centrifugation, washed with methanol and filtered to remove impurities (if any). It was then calcined at 300 °C for two hour and was used for next run. In reusability studies, transesterification was carried out at optimum conditions (reaction time: 7 h, catalyst loading: 5 wt% and methanol/oil molar ratio: 12:1). For the first 3 runs, a small decrease in conversions 82.8%, 80.4% and 78.1%, respectively, was observed. The blockage of active sites by adsorption of intermediates and products could be the possible reason. With further use of catalyst for 4th and 5th runs resulted in the significant deactivation of the catalyst that can be confirmed from XRD patterns Fig. 7(D). In spite of its heterogeneity, the above catalyst can be reused upto three times with a marginal decrease in its activity for transesterification.

4. Conclusion

In this work, single phase and highly crystalline zeolites X and A were synthesized from Indian flyash and condition was optimized (flyash/NaOH ratio 1:1.2; fusion and crystallization time of 1 and 12 h; fusion, crystallization and calcination temperatures of 550 °C, 110 °C and 800 °C, respectively. The CEC value of the synthesized UZ-X (168.2 meq/100 g) and AZ-X (352.7 meq/100 g) increased to UZ-KX (276.5 meq/100 g) and AZ-KX(380.6 meq/100 g), respectively, when ion-exchanged with potassium. Zeolite A had the highest CEC of 536.3 meq/100 g. Si/Al ratio of 2 results in the formation of zeolite X andlower Si/Al ratios favoring formation of zeolite A. The catalytic activity of synthesized zeolite (AZ-KX) was studied for transesterification of mustard oil and maximum conversion of 84.6% was obtained at 5 wt% catalyst loading, 12:1 methanol to oil molar ratio, reaction time of 7 h at 65 °C. The biodiesel obtained has a calorific value of 37.5 MJ/Kg. Finally, it can be concluded that the use of flyash might be a good alternative for synthesizing heterogeneous catalyst for transesterification.

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