

Synthesis and characterization of Na-Y zeolite from coal fly ash and its effectiveness in removal of dye from aqueous solution by wet peroxide oxidation

Arun Kumar Kondru¹, Pradeep Kumar², Tjoon Tow Teng³, Shri Chand¹, Kailas L. Wasewar^{4*}

¹Department of Chemical Engineering, Indian Institute of Technology, Roorkee-247667, India

²Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi – 221005 India

³Environmental Technology Division, School of Industrial Technology, University Science of Malaysia, 11800 Minden, Penang, Malaysia

⁴Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT) Nagpur - 440011, Maharashtra, India

*To whom correspondences should be addressed

E-mail: k_wasewar@rediffmail.com

Received June 8, 2011. Revised manuscript received August 16, 2011, Accepted August 18, 2011

Abstract

Na-Y zeolite was synthesized from coal fly ash by alkali fusion followed by hydrothermal treatment. Characterization of synthesized Y zeolite was done using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and BET surface area. The effect of various factors on the formation of zeolite, such as, fusion temperature, heating rate, ageing time, crystallization time and treatment with acids etc. were studied and the conditions optimized. The maximum surface area of the synthesized zeolite was 160 m²/g at 550°C fusion temperature, 10 h aging time (at room temperature), crystallization at 100°C for 17 h. In another set of experiments the fly ash was pretreated with hydrochloric acid. Formation of Na-P zeolite took place along with Na-Y and the effect of synthesis parameters on the formation of Na-P zeolite, mullite and quartz were discussed. Heating rates of 1 and 3°C/min and fusion temperature of 750°C gave the maximum Na-P zeolite formation. Na-Y zeolite after ion exchange with Fe was tested as a catalyst towards its effectiveness for degradation of Congo red from an aqueous solution.

Keywords: Coal Fly Ash, Na-P Zeolite, Hydrothermal Treatment, Color Removal, Cod Removal

1. Introduction

Coal-based thermal power installations in India contribute about 65% of the total installed capacity for electricity generation as per the report by Bhattacharjee and Kandpal and Central Pollution Control Board [1]. Indian coal has very high ash content. The ash content of coal used by thermal power plants in India varies between 25 and 45%. As the electricity requirement is more, about 461 million tonnes of coal is necessary to meet the requirement. The fly ash generation in 2001 was 80 million tonnes, during 2006-07 it was 116 million tones and expected to reach more than 140 million tonnes by 2012. As a consequence, a huge amount of fly ash is generated in thermal power plants, causing several disposal-related problems.

Fly ash has other sources like rice husk, municipal incinerator, ferro-aluminous, and oil shale. But fly ash from thermal power plants makes a huge impact compared to other sources. Among several methods for utilization of fly ash,

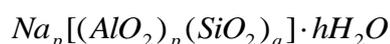
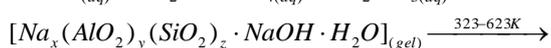
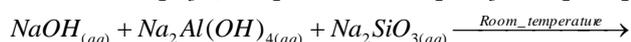
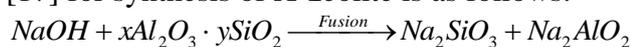
conversion of fly ash to zeolites is one of the approaches, which has wide applications in catalysis, ion exchange, as molecular sieves and adsorbents [2].

Major composition of fly ash is alumina and silica. Apart from these many oxides are also present. Due to the presence of alumina and silica in excess amounts and constant compositions irrespective of source prompted many research works on synthesis of zeolites from fly ash [3-7]. Among them Holler and Wirsching [3] are the first to synthesize zeolites from fly ash by hydrothermal method. Later others synthesized zeolites using various methods.

Although all the methods of synthesis are based on hydrothermal alkaline conversion of fly ash, they are classified into four methods. Classic alkaline conversion methods attempted combination of different ratios of activation agents/ fly ash with temperature, pressure, and reaction time to synthesize various zeolites [8]. Shigemoto et al. [6,9] and Berggaut and Singer [10] introduced an additional fusion stage

before hydrothermal treatment. Park et al. [11,12] synthesized zeolites using salt mixtures instead of the aqueous solutions as the reaction medium. Hollman et al. [13] two-stage synthesis method produced > 99% pure zeolite products from solutions containing high-Silica. This solution was obtained from extracting silica by light alkaline attack of fly ash and adjusting the Si/Al ratio (Silicon/Aluminium ratio) to obtain the zeolites.

Among these methods for synthesis of zeolites, alkaline fusion followed by hydrothermal treatment has been successfully used by many researchers for the synthesis of X, Y and A zeolites. Shih and Chang [14,15] studied conventional hydrothermal process without/ with fusion and found that the later showed better results for the synthesis of X,Y and A by changing reaction parameters. Molina and Poole [16] studied both conventional hydrothermal technique and the combination of alkaline fusion of fly ash with NaOH prior to a hydrothermal treatment, where the fusion product is mixed with water. In order to optimize the synthesis both processes were evaluated at different conditions of temperature, time and proportion of NaOH : PFA : H₂O. The general reaction scheme described by Ojha et al. [17] for synthesis of X-zeolite is as follows:



(crystal in suspension)

Hui and Chao [18] proposed step-change of synthesis temperature during hydrothermal treatment to reduce the overall synthesis time and maintain a high degree of crystallinity for the samples. Zhao et al [19] reported the effects of ageing and seeding on the formation of zeolite Y from coal fly ash and found that ageing enhances the hydrothermal condition and eliminates the processes of induction and nucleation. During hydrothermal treatment both Si and Al present in the fly ash dissolve into the solution.

In the present work Na-Y was synthesized from coal fly ash. The optimized conditions for high surface area, crystallinity, Si/Al ratio, Na-P

zeolite formation and formation of other phases were discussed.

2. Materials and Methods

2.1. Materials

Raw fly ash was obtained from the cyclone separator of National Thermal Power Corporation, Visakhapatnam, India. The physico-chemical properties of fly ash are shown in Table 1. Commercial Na-Y zeolite was obtained from Sud Chemie Pvt Ltd, Baroda, India. Hydrogen peroxide (30% analytical grade), manganese dioxide, sodium hydroxide pellets (AR) and hydrochloric acid were obtained from RFCL limited (Mumbai), India. Congo red was obtained from LOBA CHEMIE Pvt Ltd Mumbai.

Table 1. EDAX composition of fly ash

Element	Wt%	At%
C	14.09	22.41
O	40.67	48.54
Na	00.15	00.13
Mg	00.29	00.23
Al	14.67	10.38
Si	23.08	15.69
P	00.52	00.32
S	00.27	00.16
K	00.77	00.38
Ca	00.48	00.23
Ba	01.11	00.15
Ti	00.84	00.34
Mn	00.50	00.17
Fe	02.56	00.87

2.2. Zeolite Synthesis

The fly ash was initially screened to eliminate larger particles and calcined at 800±10°C for 2 h to remove the unburnt carbon and volatiles. Fly ash and sodium hydroxide (in powder form) were taken in the ratio of 0.8 to 1.5 (by wt), grinded and mixed to form a homogeneous mixture. The mixture was heated at a slow rate to reach 550°C, and fused at this temperature for 1-2 h. The fused mixture was cooled, grinded and mixed in about 500 ml distilled water and kept stirred for about 10 h (aging). The resulting (sodium aluminate) slurry formed was subjected to hydrothermal crystallization at 90-100°C for 17 h. After crystallization, it was cooled and filtered by Whatman 1 filter paper, washed with distilled

water to remove excess aluminum and dried in an oven at 50-60°C. The zeolite formed was powdered for further use.

2.3. Characterization

The determination of structure of the heterogeneous catalysts were done by X-ray diffractometer (Bruker AXS, Diffractometer D8, Germany) using Cu-K α as a source and Ni as a filter. Goniometer speed was kept at 1°/min and the chart speed was 1 cm/min. The range of scanning angle (2θ) was kept at 3-60°. The intensity peaks indicate the values of 2θ , where Bragg's law is applicable. The formation of compounds was tested by comparing the XRD patterns of the present work with that found by other researchers as well as using JCPDS (Joint Committee of Powder Diffraction Standard) files.

From the XRD plot the values of the intensities were noted for each d-spacing value and compared with the JCPDS powder diffraction file (PDF). The compound and the composition were identified. The percentage crystallinity was calculated as:

% Crystallinity = (sum of the peak heights of unknown material) \times 100/(sum of peak heights of standard material).

The determination of images and composition of catalysts were done by SEM/EDAX QUANTA 200 FEG (specifications: accelerating voltage from 200 V to 30 KV, resolution of 2 mm and magnification up to 1000KX). Scanning for zeolite samples was taken at various magnifications and voltages to account for the crystal formation and size. From EDAX, the composition of the elements in weight percentage and atomic percentage were obtained along with the spectra for overall compositions and particular local area compositions.

Table 2. Zeolite IR assignments from FTIR

Internal tetrahedral	
Asymmetric stretch	1250-950 cm ⁻¹
Symmetric stretch	720-650 cm ⁻¹
T-O bend	420-500 cm ⁻¹
External linkage	
Double ring	650-500 cm ⁻¹
Symmetric stretch	750-820 cm ⁻¹
Asymmetric stretch (Sharp)	1050-1150 cm ⁻¹

The FTIR spectra of the zeolite samples were recorded on a FTIR Spectrometer (Thermo Nicolet, USA, Software used: NEXUS) in the 4000 - 500 cm⁻¹ wave number range using KBr pellets. The internal tetrahedra and external linkage of the zeolites formed were identified and confirmed by FTIR. The IR spectra data was taken from literature [17] shown in Table 2.

BET surface area of the samples was estimated by using Micromeritics CHEMISORB 2720 instrument.

2.4. Analysis

The amount of the dye present in the solution was analyzed by direct reading TVS 25 (A) Visible Spectrophotometer. The visible range absorbance at the characteristic wavelength of the sample at 497 nm was recorded to follow the progress of decolorization.

The COD of the dye solution was estimated by the Standard Dichromator Closed Reflux Method (APHA-1989) using a COD analyzer (Aqualytic, Germany). The color in Pt-Co unit was estimated using a color meter (Hanna HI93727, Hanna Instruments, Singapore) at 470 nm.

3. Results and Discussions

3.1. Factors Affecting the Synthesis of Na-Y Zeolite from Coal Fly Ash

The effect of various parameters on the synthesis of Na-Y zeolite, like heating rate, fusion temperature, mixing time, crystallization time and temperature and acid treatment were evaluated to optimize % crystallization (based on all 35 (JCPDS) peaks), BET surface area and Si/Al ratio.

Effect of Heating Rate

After obtaining the homogeneous mixture of NaOH and fly ash, it was subjected to fusion. The effect of heating rate on crystallinity is presented in Fig. 1. It can be seen that by varying the heating rate between 1.5 to 4°C, the crystallinity was observed in the range of 55 - 99 %. The maximum heating rate 4°C / min with 61.07 % crystallinity was selected for the study.

The effect of heating rate on BET surface area and Si/Al ratio are described in Fig. 2. It can be seen that there were no effect of heating rate on BET surface area and Si/Al. The average value of BET surface area and Si/Al ratio were

found to be $80 \text{ m}^2/\text{g}$ and 1.6 respectively. The maximum values of $89.2 \text{ m}^2/\text{g}$ of BET surface area and 1.92 of Si/Al ratio were obtained at heating rates of $1.428^\circ\text{C}/\text{min}$ and $1.33^\circ\text{C}/\text{min}$.

Figure 1. Effect of heating rate on % crystallinity

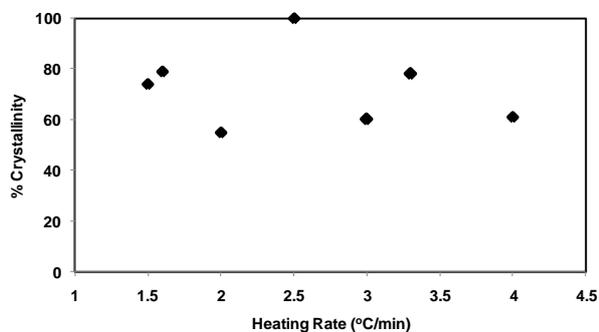
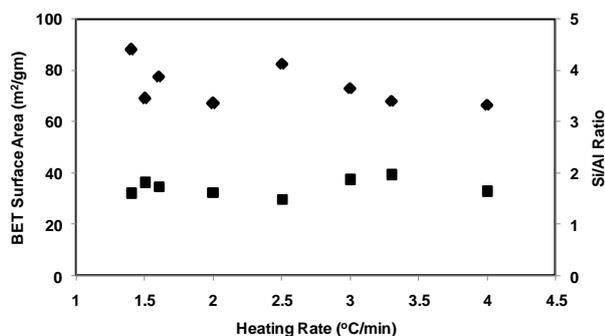


Figure 2. Effect of heating rate on BET surface area and Si/Al ratio of zeolite, \blacklozenge - BET Surface area, \blacksquare - Si/Al ratio



Effect of Fusion Temperature

The silica and alumina present in the fly ash when reacted with NaOH form Na salts soluble in water. Three fusion temperatures; 350°C , 550°C , and 750°C were experimented and the effects studied. The heating rate of $4^\circ\text{C}/\text{min}$ was selected for the study.

Effect of fusion temperature on % crystallinity was observed. As the fusion temperature rises, the crystallinity reaches a maximum value of 65.79% at 550°C and diminishes thereafter. At 350°C , the % crystallinity was 36.87, whereas, at 750°C , the value was 41.59. The optimum BET surface area obtained at optimum fusion temperature of 550°C was $74.39 \text{ m}^2/\text{g}$. The surface area rises with fusion temperature, reaches a maximum at 550°C and thereafter diminishes. The value of surface area at 750°C ($65.68 \text{ m}^2/\text{g}$) was identical to that obtained at 350°C (65.4%).

The Si/Al ratio increased with rise in fusion temperature. Though the maximum value of

Si/Al ratio was 1.94 at fusion temperature of 750°C , the Si/Al ratio at 550°C (1.88) was comparable to that of 750°C . At 350°C , the ratio was 1.61. Fusion temperature of 550°C has also been found to be optimum for synthesis of various zeolites including Y zeolite [20-21].

Effect of Mixing Time

The development of crystal nuclei is related to the aging. It is observed from literature that the aging can considerably reduce the crystallization time at elevated temperatures [22]. The fusion temperature was taken as 550°C . Mixing times of 10 h, 24 h, and 48 h were investigated. The % crystallinity increases linearly with mixing time, attaining 74.96% crystallinity after 48 h.

The BET surface area increases with mixing time. Maximum value of surface area obtained was $78.7 \text{ m}^2/\text{g}$ for the mixing time of 48 h followed by $75.8 \text{ m}^2/\text{g}$ for 24 h and $74.39 \text{ m}^2/\text{g}$ for 10 h. Si/Al ratio initially increases from 1.88 at 10 h, reaching to a maximum of 1.92 at 24 h and decreasing further to 1.817 at 48 h.

The dissolution of Si and Al is a function of mixing time (along with reaction time, heating time for hydrothermal method) and temperature. Murayama et al. [23] explained the relation between Si, Al concentration in liquid phases and reaction time, heating time and heating temperature. The effect of mixing time on % crystallinity and Si/Al at room temperature was studied by Koroglu et al. [24] using hydrothermal treatment method and the results obtained are similar.

Effect of Crystallization Time and Temperature

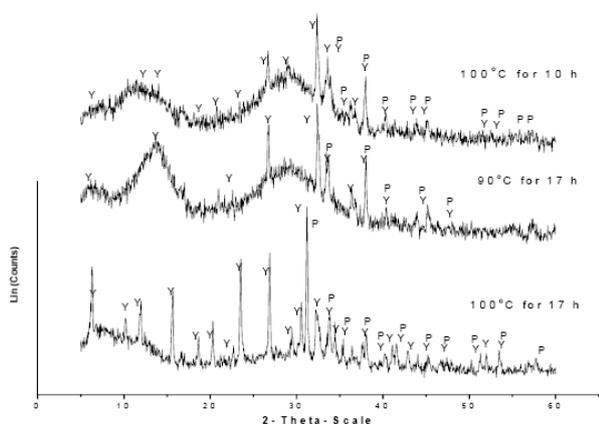
Zeolites X and Y nucleate and crystallize more readily at lower temperature than those having more complicated structure such as mordenite. The recommended crystallization temperature for well developed crystals is reported as 373 K [2].

The aluminosilicate gel formed was subjected to hydrothermal crystallization for various crystallization times: 10 h and 17 h and various temperatures: 90°C and 100°C and the effects were studied. The combined effect helps to optimize crystal size, structure and formation.

At 100°C and 17 h, the crystallinity based on all 35 peaks is less (45.3%) (shows the beginning of formation of crystals). The crystallinity at 90°C for 17 h and 100°C for 10 h

gave better results. Maximum value of 65.79% crystallinity was obtained at crystallization temperatures and times of 100°C for 10 h and also at 90°C for 17 h. XRD pattern for the effect of crystallization time and temperature is shown in Fig. 3. Nugteren et al. [25] reported that an incubation period of 3 h was necessary during which the nucleation of zeolites takes place. Following nucleation, the crystallization yield increases progressively up to 24 h.

Figure 3. XRD pattern for effect of crystallization time and temperature on Na-P formation



The BET surface area value at crystallization time and temperature of 100°C and 10 h was 74.39 m²/g and at 90°C and 17 h was 73.22 m²/g. Zeolite at 100°C and 17 h crystallization time and temperature resulted in maximum surface area of 133.85 m²/g indicating the formation of a perfect crystal. Effect of crystallization time and temperature on Si/Al ratio of zeolite showed an identical pattern as that with BET surface area. A maximum value of 1.88 was obtained for crystallization temperature of 100°C for 10 h. Si/Al ratio for 90°C for 17 and 100°C for 17 h were 1.51 and 1.46 respectively.

Acid Treatment

Table 3. Effect of acid treatment

Treatment	% Crystallinity	Surface area (m ² /g)	Si/Al ratio	% purity	Fe present
NO	45.3	133.85	1.463	74.48	3.28
H ₂ SO ₄	46.37	140.49	1.583	84.38	1.31
HCl	53.15	160.43	1.61	78.85	1.29
HNO ₃	47.19	145.37	1.486	82.1	1.44

Iron present on the surface of fly ash affects the properties of zeolites like ion exchange and binding capacity [28]. The acid treatment conducted was aimed at removing iron

impurities. EDAX was used to find iron content. Table 3 shows that iron removal is with H₂SO₄ showing the removal of other oxides and impurities in the fly ash more than that with

Acid treatment of fly ash (before fusion) with acids HCl (6-7 N), H₂SO₄ (2-3 N), and HNO₃ (6-7 N) for 17 h at 100°C were experimented to remove unwanted materials like Fe and other oxides located mainly in the outer part of the ash particles [26] which hinder the catalytic activity and dealuminate the fly ash in order to increase the activity, acidity and thermal stability for the improved performance as catalyst. Acid treatment is also required to leach some amount of Al₂O₃. It helped in increasing the SiO₂ content of the reaction mixture. After treating fly ash with acids, the fly ash is washed thoroughly with water so that no residual acid was present in fly ash or the pH was nearby 7. If any acid is present, it affects the pH of the solution. pH of the solution has direct effect on crystallization [27]. Table 3 shows that acid treatment increases the crystallinity and is maximum for HCl treated fly ash synthesized zeolite. Maximum value of crystallinity was 53.17% for HCl followed by HNO₃ (47.19%) and H₂SO₄ (46.37%).

Table 3 shows that the HCl treatment gives the maximum surface area of 160.43 m²/g which is followed by HNO₃ (145.37 m²/g) and H₂SO₄ (140.49 m²/g). Si/Al ratio was also more for HCl treated fly ash (shows that HCl dealuminates the fly ash more) followed by H₂SO₄. Maximum Si/Al of 1.61 was obtained with HCl treatment.

The % purity was estimated to see that the final crystals are free from other oxides (other than Na, Al and Si). This was done through EDAX. Table 3 shows that % purity was maximum with H₂SO₄ treated (purity 84.38%). This shows that H₂SO₄ removes other oxides and impurities in the fly ash more than that by HNO₃ (purity 82.1%).

impurities. EDAX was used to find iron content. Table 3 shows that iron removal is with H₂SO₄ showing the removal of other oxides and impurities in the fly ash more than that with

HNO₃. SEM and FTIR images of fly ash, commercial and HCl treated, are shown in Figs. 4 and 5 respectively.

3.2. Formation of Na-P Zeolite, Other Phases in Na-Y and Iron Exchange of Na-Y

When EDAX compositions were compared with the (JCPDS) PDF results, it was found that a little variation is occurring in the compositions. When investigated it was found that in the formation of Na-Y zeolite from fly ash, Na-P zeolite, a competitive phase is also formed [19]. The effect of various parameters affecting the formation of P-zeolite like heating rate, fusion temperatures, mixing time, crystallization time and temperature and acid treatment of fly ash were studied. The formation of P-zeolite was confirmed by XRD analysis.

The variation in heating rate did not show a particular relationship with the amount of Na-P formed (identified by the number of Na-P peaks in XRD and intensity of the peaks). For samples prepared at heating rates of 17, 10, 4, and 2°C/min (7 peaks in each identified), the P zeolite formation is less compared to others. For samples of 3 and 1.33°C/min, more number of peaks were identified (12 peaks) leading to greater formation of Na-P zeolite.

The Na-P zeolite formation slightly decreases with fusion temperature. For highest fusion temperature 750°C, the number of peaks formed in XRD is least (9). For 350°C and 550°C, the number of peaks formed were 11 and 10 respectively.

It has been found that the zeolite prepared at various mixing times 10, 24, and 48 h do not have significant difference. The number of peaks in XRD found are 10, 8, and 9 respectively.

Amongst three different samples, sample crystallized at 90°C for 17 h showed less zeolite P formation (5 XRD peaks). For samples crystallized at 100°C for 10 h and 100°C for 17

h, number of peaks formed were 10 and 11 respectively. XRD pattern for the effect of crystallization time and temperature is shown in Fig. 3.

HCl, H₂SO₄ and HNO₃ were used to treat fly ash. The P-zeolite peaks in XRD were found to be 11 peaks in each case.

Phases and Their Presence in Na-Y Zeolite

The dominant crystalline components in the untreated fly ash are quartz (SiO₂) and mullite (M, Al₆Si₂O₁₃). These phases are still present but to a lower level after synthesis of Na-Y zeolite. The quartz peaks disappeared due to its phase conversion and the major crystalline phase present is zeolite Y. Other crystalline phases that are observed are trace zeolite P and unreacted mullite. These results indicate that most of the crystalline quartz can be effectively converted to zeolite Y, but not the mullite. Zhao et al. [19] observed similar phenomenon with the phases present. The XRD pattern is shown in Fig. 6 and the presence of these phases are shown in XRD identified by PDF (JCPDS).

Exchange of Zeolite with Fe Ion

Both the commercial and synthesized catalysts are compared before and after exchange with Fe. From the EDAX results (Table 4), it is clear that higher amount of iron is exchanged in synthesized catalyst. The XRD results (Fig. 7) also support the same.

Due to the iron present after the exchange process, the Y peaks diminished along with the rise in Fe peaks. Similar phenomena has also been reported by Yee and Yaacob [29] who obtained zeolite iron oxide by adding NaOH and H₂O₂ (drop wise) at 60°C to Na-Y zeolite. XRD pattern (Fig. 7) showed diminishing zeolite peaks along with evolution of peaks corresponding to γ-Fe₂O₃ with increasing NaOH concentration.

Figure 4. SEM images of fly ash, HCl treated synthesized Na-Y and commercial Na-Y

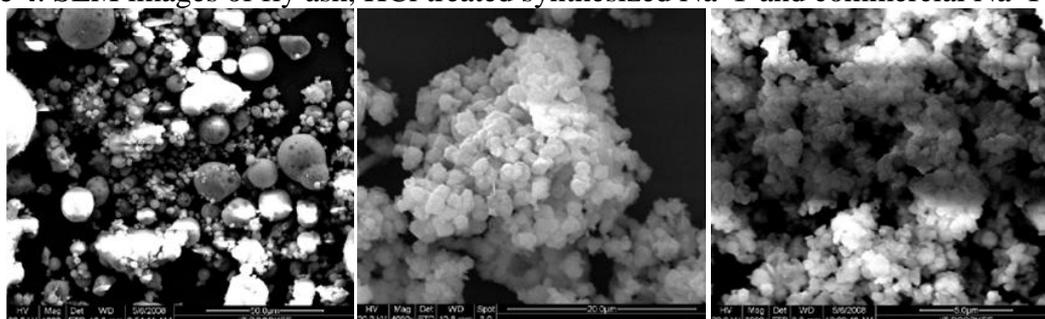


Figure 5. FTIR of fly ash, HCl treated synthesized Na-Y and commercial Na-Y

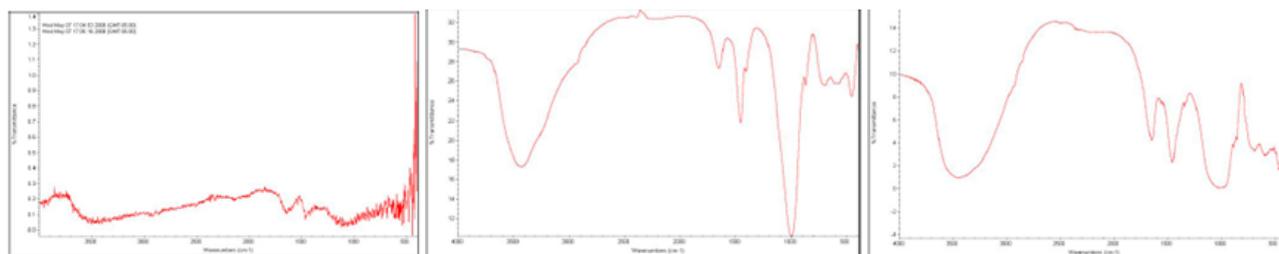


Figure 6. Phases in fly ash and synthesized zeolite

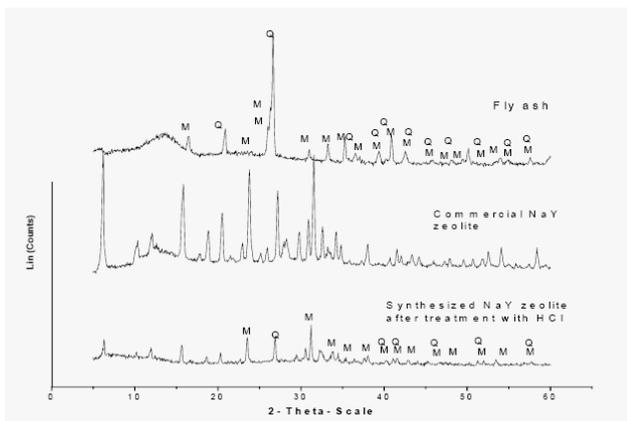
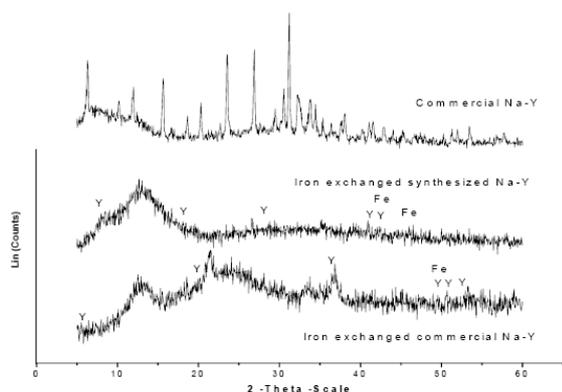


Figure 7. XRD pattern of Iron exchanged commercial and synthesized Na-Y zeolite

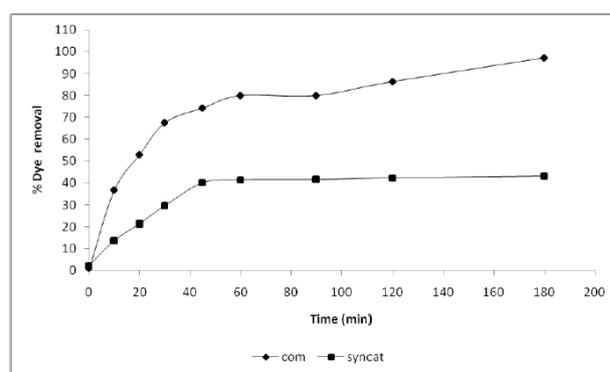


3.3. Effectiveness of the synthesized zeolite as catalyst for the removal of dye

The effectiveness of the synthesized catalyst was tested for the degradation of azo dye (Congo red) by catalytic wet peroxide oxidation using iron exchanged catalysts (commercial as well as synthesized Y zeolite). The operating conditions are evaluated and optimized. The optimum parameters obtained are 90°C, initial pH ($pH_0 = 7$), 1 ml $H_2O_2/350$ ml solution and 1 g/l catalyst. Fig. 8 shows % dye removal as a function of time for both the catalysts. It can be seen that % dye removal performance of iron exchanged commercial catalyst is better in

comparison to the synthesized one. After 1 h of reaction time, the % dye removal obtained were 80% and 43.1% with commercial and synthesized catalysts, respectively.

Figure 8. Comparison of dye removal by Fe Na-Y commercial and Fe Na-Y synthesized zeolites, Temperature = 90°C, $pH_0 = 7$, 1ml $H_2O_2/350$ ml solution and 1 g/l catalyst



The rate of removal is also very high for commercial catalyst (shown by the slope of the curve) compared to synthesized catalyst. After 1 h, the activity of synthesized catalyst did not change, whereas the commercial catalyst was active giving around 97% dye removal after 3 h period.

The Effectiveness of both the catalysts towards color removal has been reported in Fig. 9. The maximum color removal by Fe Na-Y commercial zeolite catalyst was 100% after 3 h and by Fe Na-Y synthesized zeolite it was 50% after the same time. Color removal using synthesized catalyst is nearly 50% after 3 h of reaction time, whereas for commercial catalyst, 100% removal was attained in 3 h. The rate of color removal is higher for commercial catalyst in comparison to the synthesized catalyst i.e. the color removal was 50% in 5 min and 70% in 30 min for commercial catalyst whereas it was 10% in 5 min and 20% in 30 min for synthesized catalyst.

3.4. Effectiveness of Fe-Commercial Na-Y and Fe-Synthesized Na-Y on COD Removal

The results have been shown in Fig. 10. The maximum COD removal by Fe Na-Y commercial zeolite catalyst was 50% after 3 h and by Fe Na-Y synthesized zeolite it was 36% after 3 h. The rate of removal was comparable for both commercial catalyst and the synthesized one.

Figure 9. Comparison of color removal by Fe Na-Y commercial and Fe Na-Y synthesized zeolites, Temperature = 90°C, pH₀ = 7, 1ml H₂O₂/350 ml solution and 1 g/l catalyst

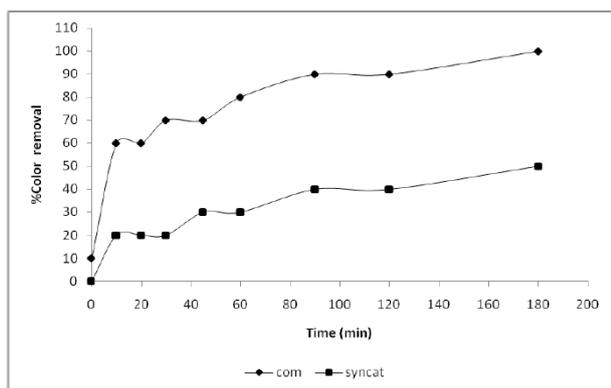
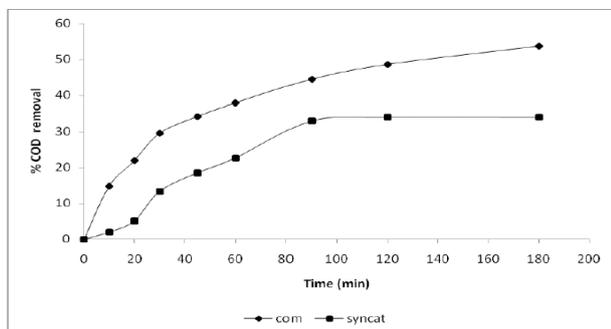


Figure 10. Comparison of COD removal by Fe Na-Y commercial and Fe Na-Y synthesized zeolites, Temperature = 90°C, pH₀ = 7, 1ml H₂O₂/350 ml solution and 1 g/l catalyst



4. Conclusions

Na-Y zeolite was synthesized from coal fly ash by alkali fusion followed by hydrothermal treatment. Characterization of synthesized Y zeolite was done using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and BET surface area. The effect of various factors on the formation of zeolite, such as, fusion temperature, heating rate, ageing time, crystallization time and treatment with acids etc. were studied and the conditions optimized. The maximum surface area of the synthesized zeolite was 160 m²/g at 550°C fusion temperature, 10 h aging time (at room temperature), crystallization at 100°C for

17 h. In another set of experiments the fly ash was pretreated with hydrochloric acid. Formation of Na-P zeolite took place along with Na-Y and the effect of synthesis parameters on the formation of Na-P zeolite, mullite and quartz were discussed. Heating rates of 1 and 3°C/min and fusion temperature of 750°C gave the maximum Na-P zeolite formation. Na-Y zeolite after ion exchange with Fe was tested as a catalyst towards its effectiveness for degradation of Congo red from an aqueous solution.

References

- [1] Bhattacharjee U, Kandpal TC. (2002) Potential of fly ash utilisation in India, *Energy*;27:151-166.
- [2] Breck DW. (1974) Zeolite molecular sieves, John Wiley and Sons, New York.
- [3] Holler H, Wirsching U. (1985) Zeolite formation from fly ash, *Fortschr. Mineral.*;63:21-43.
- [4] Hemni T. (1987) Synthesis of hydroxy-sodalite zeolite from waste coal ash, *Soil Sci. Plant Nutr.*;33:517-521.
- [5] Mondragon F, Rincon F, Sierra L, Escobar C, Ramirez J, Fernandez J. (1990) New perspectives for coal ash utilization: synthesis of zeolitic materials, *Fuel*;69:263-266.
- [6] Shigemoto N, Shirakami S, Hirano S, Hayashi H. (1992) Preparation and characterization of zeolites from coal ash, *Nippon Kagaku Kaishi*;5:484-492.
- [7] Park M, Choi J. (1995) Synthesis of phillipsite from fly ash, *Clay Sci.*;9:219-229.
- [8] Querol X, Umana JC, Plana F, Alastuey A, Soler AL, Medinaceli A, Valero A, Domingo MJ, Rojo EG. (2001) Synthesis of zeolites from fly ash at pilot plant scale: Examples of potential applications, *Fuel*;80:857-865.
- [9] Shigemoto N, Hayashi H, Miyaura K. (1993) Selective formation of Na-X, zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. *J. Mater. Sci.*;28:4781-4786.
- [10] Singer A, Berggaut V. (1995) Cation exchange properties of hydrothermally treated coal fly ash, *Environ. Sci. Technol.*;29:1748-1753.
- [11] Park M, Choi CL, Lim WT, Kim MC, Choi J, Heo NH. (2000) Molten-salt method for

- the synthesis of zeolitic materials I. zeolite formation in alkaline molten-salt system, *Microporous Mesoporous Mat.*;37:81-89.
- [12] Park M, Choi CL, Lim WT, Kim MC, Choi J, Heo NH. (2000) Molten-salt method for the synthesis of zeolitic materials II. characterization of zeolitic materials, *Microporous Mesoporous Mat.*;37: 91-98.
- [13] Hollman GG, Steenbruggena GMJ. (1999) A two-step process for the synthesis of zeolites from coal fly ash. *Fuel*;78:1225-1230.
- [14] Chang HL, Shih WH. (1998) A general method for the conversion of fly ash into zeolites as ion exchangers for cesium, *Ind. Eng. Chem. Res.*;37:71-78.
- [15] Chang HL, Shih WH. (2000) Synthesis of zeolites A and X from fly ashes and their ion exchange behavior with cobalt ions, *Ind. Eng. Chem. Res.*;39:4185-4191.
- [16] Molina A, Poole C. (2004) A comparative study using two methods to produce zeolites from fly ash, *Miner. Eng.*;17:167-173.
- [17] Ojha K, Pradhan NC, Amarnath S. (2004) Zeolite from fly ash: synthesis and characterization, *Bull Mater. Sci.*;27:555-564.
- [18] Hui KS, Chao CYH. (2006) Effects of step-change of synthesis temperature on synthesis of zeolite 4A from coal fly ash. *Microporous Mesoporous Mat.*;88:145-151.
- [19] Zhao SX, Lu GQ, Zhu HY. (1997) Effects of ageing and seeding on the formation of Zeolite Y from coal fly ash, *J Porous Materials*;4:245-251.
- [20] Fan Y, Zhang FS, Zhu J, Liu Z. (2008) Effective utilization of waste ash from MSW and coal co-combustion power plant: Zeolite synthesis, *J. Hazard. Mater.* 153:382-388.
- [21] Rayalu S, Labhasetwar NK, Khanna P. (2000) Process for the synthesis of flyash based zeolite-Y, US Patent 6027708.
- [22] Tatic M, Drzaj B. (1985) *Zeolites* (eds), Drzaj B, Hocevar S, Pejvonik S. Amsterdam: Elsevier Science Publishers.
- [23] Murayama N, Yamamoto H, Shibata J. (2002) Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *Int. J. Miner. Process*;64:1-17.
- [24] Koroglu HJ, Sarioglan A, Tather M, Erdem-Senatalar A, Savascı OT. (2002) Effects of low-temperature gel aging on the synthesis of zeolite Y at different alkalinities, *J. Crystal. Growth*;241:481-488.
- [25] Nugteren HW, Hollman GG, Janssen-Jurkovicova M. (1995) *Proceedings of international ash utilization symposium* (Lexington: University of Kentucky), 224.
- [26] Natush DFS, Taylor DR. (1980) *Environmental effects of western coal combustion: part IV*, Duluth M N: Environmental Research Laboratory.
- [27] Stepto RFT, Szostak R. (1998) *Molecular sieves: principles of synthesis and identification*. Springer, PP.79.
- [28] Rayalu SS, Udhoji JS, Munshi KN, Hasan MZ. (2001) Highly crystalline zeolite A from flyash of bituminous and lignite coal combustion, *J Hazard. Mater.*;88:107-121.
- [29] Yee M, Yaacob II. (2004) Synthesis and characterization of iron oxide nanostructured particles in Na-Y zeolite matrix, *Mater. Res. Soc.*;19:930-936.