Zeolite-X Derived From Fly Ash Collected from Chandrapur Super Thermal Power Station

Ragini Patil*[a]
Department of Applied Chemistry, Namdeorao Poreddiwar College of Engineering & Technology, Gadchiroli-442605, Maharashtra, India.
binnipatil@gmail.com

Rajendra Dongre[a]
Department of Chemistry, Rashtrasant Tukdoji Maharaj Nagpur University, Nagpur-440033, Maharashtra, India.
rsdongre@hotmail.com

***Abstract*—** Zeolite of X-type was synthesized from coal fly ash obtained from Chandrapur Super Thermal Power Station, Chandrapur, (CSTPS) Maharashtra, India by alkali fusion followed by hydrothermal treatment. The quartz main crystalline phase of fly ash can be converted to pure Zeolite X-type at employed treatment conditions. The properties of zeolitic material formed strongly depended upon the treatment conditions and composition of the raw materials. FTIR spectra of zeolite composed of the peaks of vibration of framework and Si–O or Al–O two strong peaks occurring at wavelength number of 1007(ZX-a), 1004(ZX-b). 1001(ZX-c) and 460 cm^{-1} (ZX-a), 448cm^{-1}(ZX-b), 461cm^{-1}(ZX-c) resulted from the asymmetric stretching and bending vibrations of Si–O or Al–O bonds. XRD patterns of different synthesized zeolitic were scanned from 10.330 (2q, where q is angle of diffraction). Various crystalline phase present in samples were identified by six prominent peaks namely at theta value 14.85, 17.60, 24.15, 31.19, 36.62, 54.32 and 70.73.

Keywords- Zeolite, Zeolite-X, Coal fly ash, FTIR, XRD.

*****

I. INTRODUCTION

Fly ash is one of the residues generated in combustion, which comprises of fine particles exit from flue gases (that does not rise is termed bottom ash). Industrially, fly ash produced during combustion of coal, like in thermal plants that gets captured by electrostatic precipitators/particle filtration equipment before the flue gases reach chimneys of coal-fired power plants, and together with bottom ash removed from the bottom of the furnace is in this case jointly known as coal ash. The coal source/makeup/quality being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal-bearing rock strata.

Besides, fly ash closely resembles volcanic ashes used in production of the earliest known hydraulic cements about 2,300 years ago. Those cements were made near the small Italian town of Pozzuoli - which later gave its name to the term "pozzolan." A pozzolan is a siliceous or siliceous / aluminous material that, when mixed with lime and water, forms a cementitious compound. Fly ash is the best known, and one of the most commonly used, pozzolans in the world. Instead of volcanoes, today's fly ash comes primarily from coal-fired electricity generating power plants. These power plants grind coal to powder fineness before it is burned. Fly ash - the mineral residue produced by burning coal - is captured from the power plant's exhaust gases and collected for use. Fly ash is a fine, glass powder recovered from the gases of burning coal during the production of electricity. These micron-sized earth elements consist primarily of silica, alumina and iron. The difference between fly ash and portland cement becomes apparent under a microscope. Fly ash particles are almost totally spherical in shape, allowing them to flow and blend freely in mixtures. That capability is one of the properties making fly ash a desirable admixture for concrete.

The fly ash produced from burning pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones. In general, there are three types of coal-fired boiler furnaces used in the electric utility industry. They are referred to as dry-bottom boilers, wet-bottom boilers, and cyclone furnaces. The most common type of coal burning furnace is the dry-bottom furnace. When pulverized coal is combusted in a dry-ash, dry-bottom boiler, about 80 percent of all the ash leaves the furnace as fly ash entrained in the flue gas.

Coal is composed primarily of carbon and hydrogen, but all coal also contains some mineral matter (for example, clays, shales, quartz, and calcite); the percentage varies by coal type and source. Coal ash is the mineral maner that is collected after the coal is combusted, along with some unburned carbon. The amount of coal ash produced at a power plant depends on the volume of coal burned, the amount of mineral matter in the coal, and the combustion conditions

Table 1: Normal range of chemical composition for fly ash produced from different coal types (expressed as percent by weight).

Sr. No.	Component	Bituminous (%)	Sub-bituminous (%)	Lignite (%)
1	SiO_2	20-60	40-60	15-45
2	Al_2O_3	5-35	20-30	10-25
3	Fe_2O_3	10-40	4-10	4-15
4	CaO	1-12	5-30	15-40
5	MgO	0-5	1-6	3-10
6	SO_3	0-4	0-2	0-10
7	Na_2O	0-4	0-2	0-6
8	K_2O	0-3	0-4	0-4
9	LOI	0-15	0-3	0-5

Raw fly ash has a relatively low specific surface area (2–4 m2 g–1), low porosity, and is hydrophilic; hence, in its raw form it is very poor oil absorbent. To improve oil sorption, the surface of fly ash has to be modified to enhance surface area, porosity, and hydrophobicity. In this paper, we report a novel chemical functionalization process to convert as-received fly ash powder into a zeolite material, which can selectively absorb oil from an oil–water mixture. Zeolites are aluminosilicate minerals primarily used as adsorbents. It has been demonstrated that the glassy aluminosilicate composition of fly ash can be used as a source material for the growth of various zeolite. Several research groups have been reported in zeolite synthesis from fly ash and volcanic rocks. In general, conversions of fly ash to zeolite involve the addition of alkali materials to fly ash at elevated temperature followed by hydrothermal treatment. Recent investigations have shown the potential of fly ash as a raw material for synthesis of various types of zeolites The conversion of fly ash to zeolite has gained importance due to intensive research on zeolite growth in geological material such as volcanic rock & clay minerals. High contents of reactive materials like alumino silicate makes it interesting starting materials for the synthesis of zeolite with a wide range of applications . Various methods of synthesis of zeolite from fly have so far been invented & patented some of the important techniques are alkali fusion followed by hydrothermal treatment slurry method. Fusion method is found to be the most efficient & a general method for synthesis of X-type Y-type & A-type from a large variety of fly ash. A modified fusion process to synthesized zeolite A & X from the fly ash . It was found that the addition of aluminium hydroxide to the fused fly ash solution followed by hydrothermal treatment at 60^0 C produced single phase zeolite A & X depending on the source of the ash received fly ash. The result confirms that the quantity of dissolved aluminium species is critical for the type of zeolite formed from fused fly ashes.

EXPERIMENTAL

I-Material: Zeolite synthesized from fly ash (from CTPS, Chandrapur thermal power station) by hydrothermal treatment.

ISSN: 2321-8169
018– 021

NaOH procured Ranbaxy. All reagents were analytically pure (99%) & used without purification. Fly ash samples contained both amorphous (mainly SiO_2/Al_2O_3) & crystalline components (quartz & mullite). Depending upon source & makeup of coal burned, components of fly ash vary much, but all fly ash includes substantial amounts of SiO_2 amorphous & crystalline & calcium oxide (CaO).

II Zeolite synthesis method: Mixture of NaOH (activator, adjusts sodium contents in starting material) & fly ash (pre-determined ratio) milled & fused in mortal pistal at varied temp for 1 hr and cooled room temperature, griend further & added to water (10g fly ash /100mL water). Slurry agitated mechanically in glass beaker for several hours and kept at around 90^0C for 6 hrs. The resultant precipitate was then repeatedly washed with distilled water to remove NaOH filtered & dried. Mullite & α-quartz present in fly ash sources of aluminium & silicon respectively, for zeolite formation. Steps in zeolite synthesis shown below:

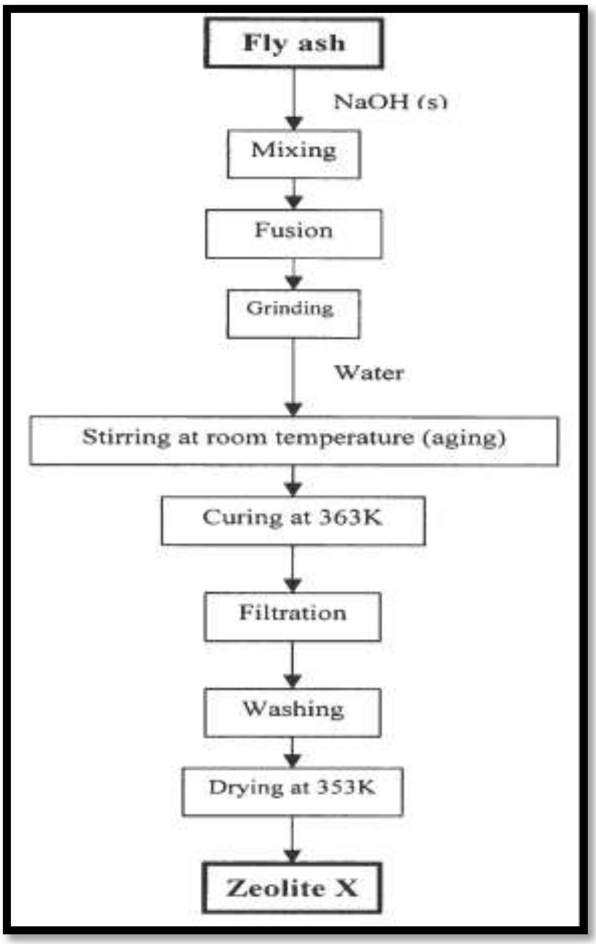

Fig b: Process flow diagram for synthesis of zeolite X-type from fly ash

Table 2: synthesis of zeolite at different temperatures

Zeolite designation	Source of fly ash	NaOH/fly ash	Fusion temperature (K)			Curing time(hrs)
Z-X	CSTPS	01:01.5	600	800	1000	6

RESULTS

1. FTIR: Fourier Transform Infra-Red spectra:

FTIR spectra of various synthesized zeolite-X types shown in Fig. 1a, 1b and 1c. FTIR spectra of zeolite composed of the peaks of vibration of framework and Si–O or Al–O e.g., two strong peaks occurring at wavelength number of 1007(ZX-a), 1004(ZX-b). 1001(ZX-c) and 460 cm^{-1} (ZX-a), 448cm^{-1}(ZX-b), 461cm^{-1}(ZX-c) resulted from the asymmetric stretching and bending vibrations of Si–O or Al–O bonds. The small peak at 629 cm^{-1} (ZX-a), 626cm^{-1}(ZX-b), 630cm^{-1}(ZX-c) is due to the vibration in the external linkage of tetrahedra. No significant broadening/peaks observed beyond 1140 cm^{-1} (attribute to asymmetric stretching vibration of (Si/Al) O_4)

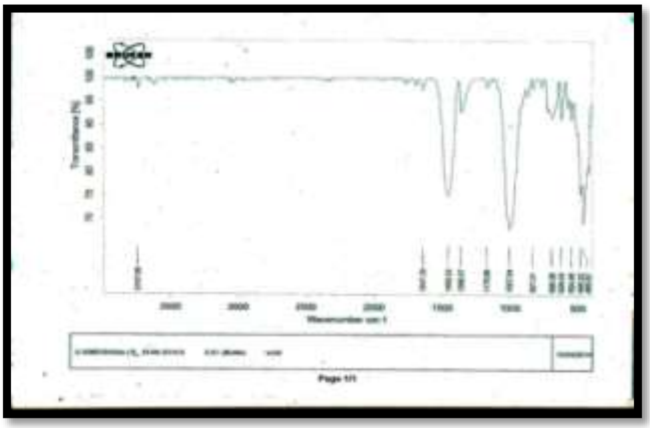

Figure 1a: FTIR of Zeolite X-1

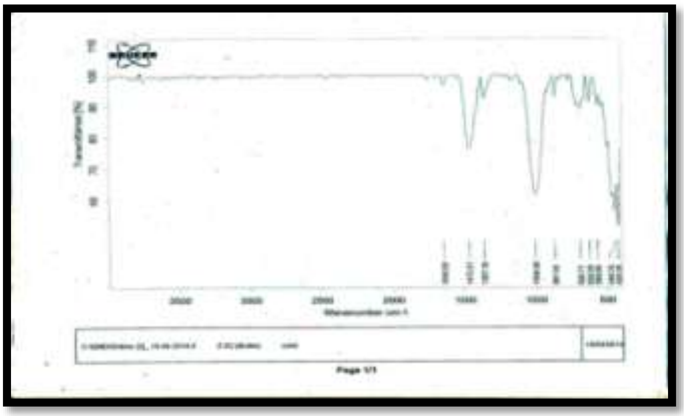

Figure 1b:FTIR of Zeolite X 2

ISSN: 2321-8169
018– 021

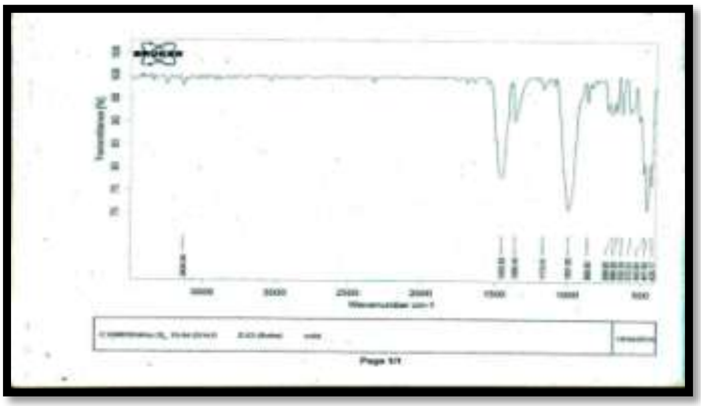

Figure 1c: FTIR of Zeolite X-3

2. X-ray diffraction (XRD): The determination of structure of three synthesized zeolite-X was done by XRD (Bruker AXS, Diffractometer D8, Germany) using Cu-K_ as a source and Ni as a filter as shown in Figure 2 a.

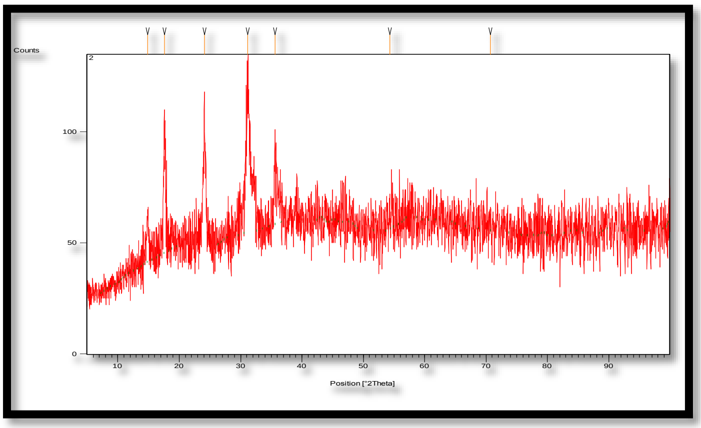

Figure 2 a: X-ray diffraction of zeolite

Table-3 Peak least (Bookmark 1)

Pos. [°2 ThetaΘ]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
14.8572	20.4	0.4896	5.95789	31.64
17.6083	54.36	0.408	5.03274	84.29
24.1523	51.76	0.408	3.68192	80.25
31.1974	64.5	0.4896	2.86465	100
35.6278	28.72	0.4896	2.51793	44.54
54.3214	3.74	1.3056	1.68745	5.8
70.7301	5.43	0.408	1.33089	8.41

The X-ray (powder) diffraction (XRD) pattern of any crystalline material is the fingerprint of its structures. XRD patterns of different synthesized zeolitic were scanned from 10.330 (2q, where q is angle of diffraction). Various crystalline phase present in samples were identified by six prominat peaks namely at theta (Θ) value 14.85, 17.60, 24.15, 31.19, 36.62, 54.32 and 70.73. The major peaks were selected specifically because they are least affected by the degree of hydration of samples & also by others. The percent crystallinity can be calculated as sum of peak height of unknown zeolite divided by sum of peak height of a synthesized zeolite-X that can be assumed 100% crystalline i.e % crystallinity = (sum of the peak heights of unknown material) × 100/ (sum of peak heights of standard material by following formula.

$$\% \text{ Crystallinjty} = \frac{\text{sum of the peak heights of unknown material}}{\text{sum of the peak heights of standard material}} X100\%$$

3. Thermal stability of Synthesized Zeolites: Crystallinity zeolites are more resistive to heat than amorphous materials, the main reason being the geometrical structure of the crystalline framework. However, the effects of silica/alumina ratio & level of cation exchange on thermal stability also cannot be denied. The commercial zeolites having high (SiO_2/Al_2O_3) ratio can resist much higher temperature. The zeolite presently prepared was observed to lose its crystallinity beyond 973K & the crystalline structure was mostly collapsed above 1073.

CONCLUSIONS

Zeolite of X-type was synthesized from coal fly ash (Chandrapur Super Thermal Power Station, Chandrapur, (CSTPS) Maharashtra, India) by alkali fusion followed by hydrothermal treatment. The quartz main crystalline phase of fly ash can be converted to pure Zeolite X-type at employed treatment conditions. The zeolite-X was also successfully synthesized from coal fly ash under certain conditions. The properties of zeolitic material formed strongly depended upon the treatment conditions and composition of the raw materials. The crystallinity of synthesized zeolite changes with fusion temperature and a maximum value was obtained at 1000K. The best conversion of coal fly ash to Na-X zeolite was obtained at the following conditions: NaOH/Fly ash ratio, 1.1.5; fusion temperature, 1000K; aging at 90^0 C for 6 hrs.

ACKNOWLEDGMENT

I wish to thank Prof Jyotsna Meshram, for support and encouragement and Ms Yogita Ashtankar providing the Fly ash sample during this study.

References

[1] Mahmoodi, N. M.; Hayati, B.; Arami, M.; Lan, C.Adsorption of textile dyes on pine cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies *Desalination*2011, 268, 117– 125

[2] Türgay, O.; Ersöz, G.; Atalay, S.; Fross, J.; Welander, U.The treatment of azo dyes found in textile industry wastewater by anaerobic biological method and chemical oxidation*Sep. Purif. Technol.* 2011, 79, 26– 33

[3] Gudelj, I.; Hrenović, J.; Dragičević, T. L.; Delaš, F.; Soljan, V.; Gudelj, H.Azo dyes, their environmental effects, and defining a strategy for their biodegradation and detoxification*Arh. Hig. Rada Toksikol.* 2011, 62, 91– 101

[4] He, H. Y.; Huang, J. F.; Cao, L. Y.; Wu, J. P.Photodegradation of methyl orange aqueous on $MnWO_4$ powder under different light resources and initial pH *Desalination* 2010, 252,66– 70

[5] Parshetti, G. K.; Telke, A. A.; Kalyani, D. C.; Govindwar, S. P.Decolorization and detoxification of sulfonated azo dye methyl orange by Kocuria rosea MTCC 1532 *J. Hazard. Mater.* 2010, 176, 503– 509

[6] Gomathi, D. L.; Mohan, R. K.Enhanced photocatalytic activity of silver metallized TiO_2particles in the degradation of an azo dye methyl orange: Characterization and activity at different pH values *Appl. Surf. Sci.* 2010, 256, 3116– 3121

[7] Teng, M. Y.; Lin, S. H.Removal of methyl orange dye from water onto raw and acid-activated montmorillonite in fixed beds *Desalination* 2006, 201, 71– 81

[8] Ghoneim, M. M.; El-Desoky, H. S.; Zidan, N. M.Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions *Desalination* 2011, 274, 22– 30

[9] Zanjanchi, F.Photo-oxidation of phenylazonaphthol dyes and their reactivity analysis in the gas phase and adsorbed on cellulose fibers states using DFT and TD-D *Dyes Pigm.*2011, 89, 16– 22

[10] Yavuz, Y.; Koparal, A. S.; Öğütveren, Ü. B.Electrochemical oxidation of Basic Blue 3 dye using a diamond anode: evaluation of colour, COD and toxicity removal *J. Chem. Technol. Biotechnol.* 2011, 86, 261– 265

[11] Zahrim, A. Y.; Tizaoui, C.; Hilal, N.Removal of Highly Concentrated Industrial Grade Leather Dye: Study on Several Flocculation and Sand Filtration Parameters *Sep. Sci. Technol.* 2011, 46, 883– 892

[12] Andersen, N. R; Keiding, K.Investigation of filtration conditions for nanofiltration of reactive dye printing wastewater *Filtration* 2007, 7, 75– 81

[13] Koyuncu, I.Direct filtration of Procion dye bath wastewaters by nanofiltration membranes: flux & removal characteristic *J. Chem. Tech. Biot* 2004, 78,1219–24.

[14] Nourouzi, M. M.; Chuah, T. G.; Choong, T. S.Optimisation of reactive dye removal by sequential electrocoagulation-flocculation method: comparing ANN and RSM prediction*Water Sci. Technol.* 2011, 63, 984– 994