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Utilization of Coal Fly Fiery debris as Industrial Waste preparation and characterization of NaX Zeolite

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Abstract

Zeolite is an important class of micro porous material that exhibits excellent molecular sieving capabilities for ion-exchange, catalytic reaction, adsorption, and it is utilized in various processes for environmental protection. Zeolites and zeolite-like materials are micro porous, crystalline materials composed, primarily, of $[SiO_4]_2$- tetrahedral connected to form a framework with 1-, 2-, or 3-dimensional network of pores ranging in diameter from 2 to 10 Å. Zeolite NaX and are the most frequently used zeolites in catalysis. Synthesis of micoporous materials is one of the potential applications of waste fly ash to obtain high value industrial products with environmental technology utilization. The synthesis of such materials from fly ash is of great significance from fundamental as well as commercial point of view which is quite evident from the fact that several researchers are working on this research topic all over the world.

Keywords: CFA,ion-exchange, catalytic reaction, adsorption, IR,XRD, SEM, etc.

1. Introduction

In recent years, various environmentally unsupportive processes in synthesis of bulk and fine chemical industries are being replaced with cleaner catalytic processes. In many industrial processes such as petro chemistry and the manufacture of organic chemicals Solid acid heterogeneous catalyst have been playing an important role as green catalysts and attracted special interest owing to their special features

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such as shape selectivity, controlled variability, their reusability and eco-friendly nature [1-3].

Zeolite is an important class of micro porous material that exhibits excellent molecular sieving capabilities for ion-exchange, catalytic reaction, adsorption, and it is utilized in various processes for environmental protection. Zeolites and zeolite-like materials are micro porous, crystalline materials composed, primarily, of $[SiO_4]_2$- tetrahedra connected to form a framework with 1-, 2-, or 3-dimensional network of pores ranging in diameter from 2 to 10 Å. Zeolite Y and ZSM-5 are the most frequently used zeolites in catalysis.

In such a system, the initial maximum free energy excess must be high with respect to the final stable state. Therefore, the each component in the reacting mixture contributes specific characteristics of the gel and final material obtained. In many instances achieving the right gel often becomes the initial requirements for the crystalline products.

In this study we have repeated the synthesis of zeolite using waste material instead of general chemicals used. Therefore, in the first few attempts of synthesis we have established the synthesis producer only using pure chemicals and then same system is adopted by the use of coal fly ash (CFA) as one of the source of silica[4-6]and number of attempts have been used for crystallization of the NaX zeolite by using CFA. The CFA obtained from thermal power station located near to the Nanded district i.e. One at Parli TPD and Chandrapur TPD. It was observed that we obtained highly crystalline and phase purity of NaX even though we use the silica and alumina from CFA instead of chemicals. Hence the utilization of CFA for synthesis of zeolite not only solves environmental problems but also use to form a value added materials.

2. Experimentation

Synthesis of zeolite NaX with coal fly ash (CFA):
The present section is concerned with the utilization of coal fly ash for synthesis of value added product like Zeolite NaX. The fly ash used zeolites have wide applications in ion exchange, as mole-cular sieves, catalysts, and as adsorbents. The collected CFA from two different TPS contained both amorphous SiO_2, Al_2O_3 and crystalline components quartz and mullite). The compositional similarity of fly ash to the naturally occurring zeolites started the work on the synthesis of zeolites. After this initial work, many patents and technical reports have appeared on different methods of synthesis of zeolite from fly ash and also its several applications were proposed. The physico-chemical properties of the coal fly ash samples discussed here

Prior treatment to coal fly ash (Fuse method)
The fly ash used present investigation is Type "F". The treated Fly ashcollected from Chandrapur TPS and Parali TPS was screened by sieve of 80-mesh size to eradicate the larger particles. The unburnt carbon along with other volatile materials present in CFA was removed by calcination at 800°C for 5h in muffle furnace (shown in Fig1.1.) CFA was then treated with dilute hydrochloric acid to remove iron to a certain extent (if any) or magnetically stirred thereby increasing the activity, thermal stability and acidity of the zeolite.

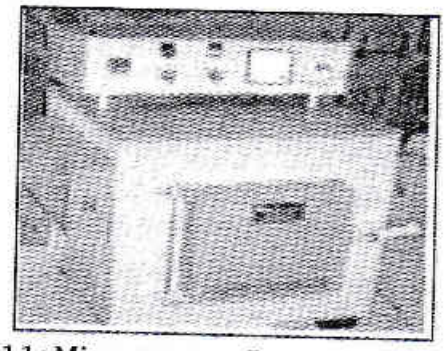

Fig. 1.1 : Micro processor Programmed Furnace

Therefore, before any synthesis treatment, the sample of fly ash (calcined and sieved) was milled and fused in silica crucible with sodium hydroxide in different ratio at 550°C for 1 hour at controlled heating rate (1°C/ min) and cooled by natural convection at room temperature in fused material grind. The ratio of activation solution to coal fly ash (i.e. $NaOH/SiO_2$) along with optimization of temperature, pressure and reaction time results in the formation of various types of zeolite material. An

amorphous SiO^2component in the CFA was used as Si-source for the further investigations.

Chemical Composition of Coal Fly Ash:

The Chemical compositions of fly ash used in the present study are given in Table 1. The chemical composition of samples was established by estimating EDX as well as silicon by gravimetric[7-9]. The qualitative and quantitative analysis results of fly ash, obtained using the FP method, are shown Table 1 and 2. A 3g power sample was directly inserted into a powder-sample container with 5 μm polypropylene adhered to the base.

The 0.5 to 1 g of fly ash was weighed accurately in a pre-weighed platinum crucible. The sample was then ignited on the burner till constant weight. From the difference in the weights, % loss on ignition was calculated. The ignited sample was moistened with the few drops of sulphuric acid to which 5-ml hydrofluoric acid (48 % electronic grade) was added. It was then slowly evaporated till the hydrofluoric acid completely removed[10]. The HF treatment was repeated thrice. After the last HF treatment and removal of H_2SO_4, the sample was ignited strongly on burner. Finally, % SiO_2 was estimated from the difference in the weights (before and after HF treatment).

In the zeolite synthesis method the fly ash precipitates were fused with sodium hydroxide (NaOH) or (KOH) in a different (say 1:1.2, 1:1.5, 1:2 etc.) ratio at 500 to 600°C for about 1-2 h.

The fused product was then mixed thoroughly with distilled water and the slurry was subjected to aging for different hours. After aging the slurry was subjected to crystallisation at 70 to 90°C for 0 h to 12 h. The solid product was recovered by filtration and washed thoroughly with deionised water until the filtrate had a pH of 10-11. The product was then dried at a temperature of 80°C.

Table 1: Chemical Analysis of CFA obtained from Chandrapur and Parli TPS

Chemical Analysis of Fly Ash obtained from Chandrapur Thermal Power Station on % weight basis		Chemical analysis of Fly ash obtained from Parali Thermal Power Station On % Weight	
Fly Ash Content	In Percent	Fly Ash Content	In Percent
Silica (SiO_2)	65.20	SiO_2	70.10
Alumina(Al_2O_3)	21.37	Al_2O_3	20.18
Iron Oxide (Fe_2O_3)	6.68	Fe_2O_3	7.0
(TiO_2)	2.12	Na_2O	0.23
Lime (CaO)	1.56	CaO	1.42
Magnesia (MgO)	0.69	MgO	0.32
Sodium Oxide (Na_2O)	0.24	K_2O	0.40
Potassium Oxide (K_2O)	0.56	Mn_3O_4	0.20
P_2O_5	0.35		
SO_3	0.70		
Total	99.47	Total	100.05
SiO_2/Al_2O_3 = 70.10/20.18 = 3.47 On Mole basis = Si/Al=1.73 Na_2O/Al_2O_3 = 0.11		SiO_2/Al_2O_3 = 65.20/21.37 =3.05 On Molebasis Si/Al=1.525 Na_2O/Al_2O_3=.012	

3. RESULTS AND DISCUSSION:

XRD Pattern of Collected Fly Ash :

The different minerals have different unit cell composition therefore XRD technique allows for qualitive identification of the phases present in the collected mineral. From the fig.1.1, these XRD patterns it can be seen that the major crystalline phases found in the coal fly ash are common mineralogical phases such as quartz, mullite[11] and aluminosilicate glass amorphous material forming during the combustion process.

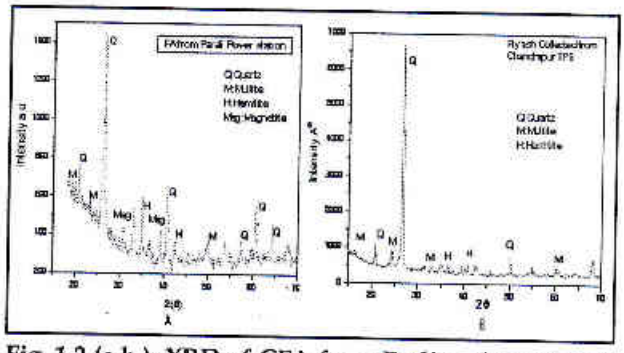

Fig. 1.2 (a,b): XRD of CFA from Parli and Chaddrapur TPS

Fly ash is mainly composed of some oxides derived from inorganic compounds, which remain after combustion of the coal. The amounts of the main components of ash viz. both amorphous (mainly SiO_2, $Al2O_3$) and crystalline components (mainly quartz and mullite) show few variations with the type of coal. The Chemical compositions of fly ash used in the present study are given in Table 1and 2. The compositional similarity of fly ash to the naturally occurring zeolites started the work on the synthesis of zeolites from this waste material. After this initial work, many patents and technical reports have appeared on different methods of synthesis of zeolite from fly ash and also its several applications were proposed. The ratio of activation solution to coal fly ash (i.e. $NaOH/SiO_2$) along with optimization of temperature, pressure and reaction time results in the formation of various types of zeolite material

Infrared spectroscopy:

FTIR spectra provide valuable information about the basic characteristics of the molecule, namely, the nature of atoms, their spatial arrangement and their chemical linkage forces. Infrared spectroscopy[12-14] has been extensively used for identifying the various functional groups of the support, as well as identifying the various functional groups of the active component. The mid infrared region of the spectrum contains the fundamental frame work vibration of $Si(Al)O_4$ grouping. The absorption band in between the wave numbers 980-1320 cm^{-1} in IR spectrum of fly ash and treated fly ash represent the presence of substitutated Al atoms in the tetrahydral forms of silica frame work.

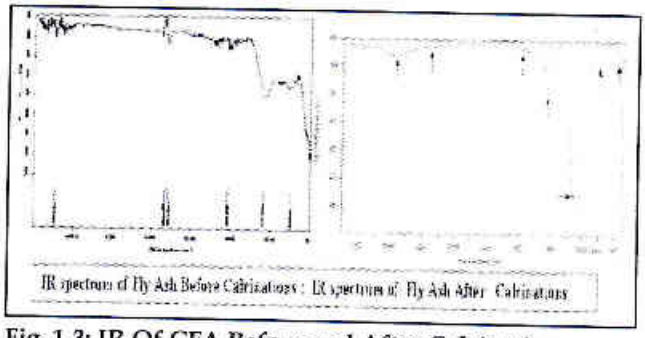

Fig. 1.3: IR Of CFA Before and After Calcination

SEM:

For SEM analysis, solid fly ash samples (from Parali and Chndrapur TPS) were set into an epoxy resin and polished to give a smooth cross section of particles for the morphological structure of the raw fly ash.

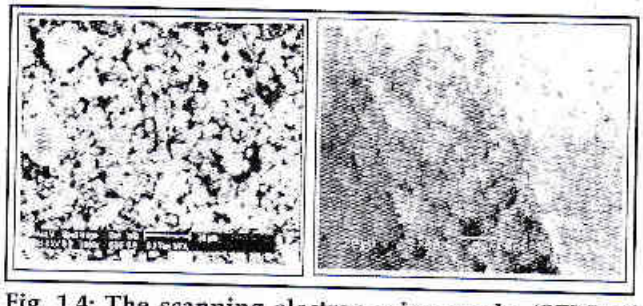

Fig. 1.4: The scanning electron micrographs (SEM) of the original and treated CFA

The bulk composition was also estimated from SEM by indirect method. The elemental composition of samples

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was first determined from SEM and from these data the percentage of oxides was calculated. It can be seen that there is significant chemical and mineralogical variation between different ash particles and even within a single particle.

The effect of Fusion Temperature:

The properties of synthesized zeolite NaX are also affected by fusion temperature (FT). The effect of fusion temperature on SiO_2/Al_2O_3 ratio was studied, the ratio first increases with fusion temperature and then attains the maximum value again it decreases with increase in the temperature. During fusion, the silica and alumina present in the fly ash react with the NaOH and form Na-salts which is soluble in water. Therefore crystallinity was also found to change with fusion temperature.

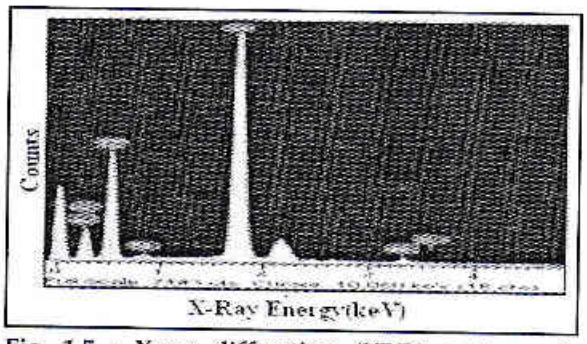

Fig. 1.5 : X-ray diffraction (XRD) pattern of NaX synthesized with CFA.

The X-ray powder diffraction (XRD) patterns of sample were recorded to ascertain the phase purity and also to detect the change in crystallinity during the different synthesis runs and modification treatments by ion exchange. The XRD patterns were collected over 2θ range of 5° to 40° using Ni filtered CuK (λ= 1.54041 Å) radiation by step scan with a 0.05° step and a 5.0 s. counting time, using a Rigaku D Max-III VC X-ray diffractometer. The most crystalline with no impurity sample was treated as parent or reference sample in the system.The degree of crystallization of the solid product was estimated from the formula

% Crystallization= Peak Area' of the product ÷Peak area' of the reference sample

('Peak Area of prominent peak between 2θ= 5-40°)

Table 2 : XRD data of Na-X

NaX data with CFA	
d(Å)	(I/I_0)
14.51	100
8.92	25
7.60	24
5.77	54
4.74	17
4.43	30
4.24	4
3.96	15
3.82	89
3.67	20
3.61	11
3.38	76

Effect Synthesis Temperature on NaXcrystallinity:

The XRD pattern of three synthesis temperature 70, 80, 90°C is reported in the Figure 1.6. The percent crystallinity of the samples drawn at different three temperature 70, 80, 90°C was calculated based on the ratio of the sum of the areas of prominent peaks (with 2θ 6.0, 9.9, 11.6, 15.3, 18.3, 20.0, 23.3, 26.6, 29.2, 30.3, 30.9, 31.9, 32.6, 33.6,34.2 and 37.3 values). These patterns shows the typical progressive development of the zeolite NaX phase obtained from CFA after 8 h of crystallization period. The characteristic peaks of zeolite NaX starts appearing after the two hour and the fully crystalline phase is obtained at 8 hr. This unusual shorter crystallization period may be due to ultrasonic treatment given to reaction gel. Perhaps higher reactivity of the $SiO_2/NaOH$ ratio at the time of fusion of Fly ash may also responsible for this.

The fig.1.6 also illustrated that absence of impurity peaks and amorphous halo region in powder XRD profiles of NaX sample of 8 h. indicated highly pure and crystalline nature of the samples. This most crystalline sample in the system was arbitrarily assumed to be 100 % crystalline. It also observed from the powder XRD profiles that obtained characteristics peaks were closely matches with the chemically produced NaX data in above Table 2.3.

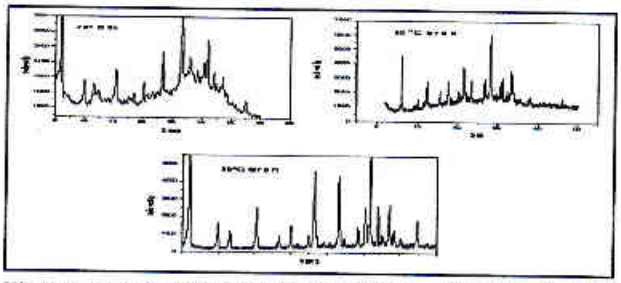

Fig.1.6 :powder XRD of NaX at Temp. 70, 80 and 90°C.

The obtained values crystallinity for 70, 80 and 90 °C were calculated and they are 30 %, 80 % and 100 % crystalline .The Scanning Electron Microscope (SEM) picture of the samples obtained after 8 h at 90 ° C shown in Fig. 1.7. and it was found to be fully crystalline (free from amorphous impurities) as revealed by the XRD. The crystal habit is nearly spherical in shape with 2-3 μm in size. The crystal morphology is often influenced by different synthesis parameters.

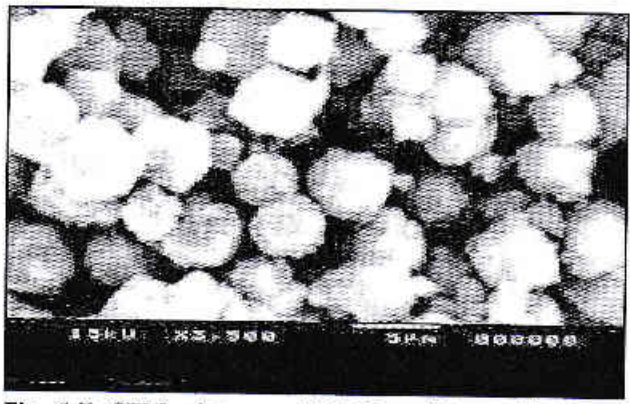

Fig. 1.7: SEM pictures of NaX zeolites with 100 % crystallinity

4. Conclusion

The synthesis parameters and crystallization of micro-porous material like feujasite family member like zeolite NaX. In the synthesis process instated of chemicals, CFA as a source of silica was used. Therefore, to optimise the synthesis parameters the number of synthesis runs has been attempted. After finalizing the value of parameters in hydrothermal synthesis process were optimised and repeated to get 100% crystanalline and phase purity of the synthesised samples. It is observed that the final product of NaX zeolite having 100% carnality was obtained at temperature between 60 to 180°C, synthesis time between 4 to 8 hours, pH>10 and Si/Al ratio =1.15.

All the characterization techniques performed in this study reveals that well orderedmesoporous material of uniform hexagonal array can be synthesized very conveniently and in a very short span of time from an industrial waste coal fly ash Coal Fly Ash. Even after their post modification, no marginal changes are found in their structural morphology i.e. the structure of NaCsX remained more intact. Hence, these modified forms may be used in basic or acidic catalytic reactions.

Conflicts of interest: The author stated that no conflicts of interest.

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