Reflux-Assisted Synthesis of ZSM-5 Zeolite from Coal Fly Ash: A Sustainable Waste-to-Resource Approach

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ABSTRACT

The coal fly ash (CFA) is produced on large scale in India by thermal power plant. CFA is the waste material having aluminosilicate as the major portion. Zeolite is the aluminosilicates microporous crystalline material. So CFA can be used as a source material for the synthesis of ZSM5 zeolite. In the present study ZSM5 zeolite is synthesized from CFA by reflux method. The synthesized zeolite is characterized by XRD, IR, SEM, EDAX and TG-DTA.

Keywords: CFA, Zeolite, Reflux, ZSM, SEM

INTRODUCTION

In developing countries like India power generation is most important requirement for economic and social development. Coal is currently the most commonly used fuel for generating electricity in the world, because of its low cost, widespread availability and ease of storage. Coal fired generation plays an important role in stabilizing electricity prices everywhere. Out of total production of electricity in India, 70% electricity is produced from coal. The average content in Indian coal used in thermal power plants is about 35%. The generation of 1MW power with Indian coal results in cogeneration of nearly 1800t of fly ash. Out of this, nearly 20% (300t) is coarser bottom ash and about 80% (1500t) is fly ash.

Coal Fly Ash (CFA) is a by-product from coal based thermal power plants. It has been generally considered a waste material in the past and disposal of which has posed numerous ecological and environmental problems. [1-4] However, recent researches have shown that CFA has potential to act as invaluable ingredient in cement and concrete if used within the framework of prescribed specifications and quality systems. [5] The CFA is now considered as a resource material rather than waste in civil engineering and material science. [6-8] In addition fly ash can be gainfully used for various other applications. [9-10]

CFA originates from the inorganic fraction of combusted coal. At the macro-structural level, coal fly ash consists of a heterogeneous mixture of different mineral phases, the most important of which are aluminosilicate glass, mullite, quartz, iron oxides such as magnetite, hematite, salts and earth-alkali oxides (CaO, MgO). Glass and mullite are formed from the aluminosilicates phases present in coal. [11-12].

Zeolites are crystalline aluminosilicates with a framework based on a three dimensional network of oxygen ions with Si^{4+} and Al^{3+} ions occupying the tetrahedral sites formed by the oxygen's. CFA contains a major part of aluminosilicate so it can be used as a base material for the synthesis of ZSM5 zeolite.

MATERIAL METHODS

The main raw material, CFA samples were collected from Deep Nagar Thermal Power Plant, Bhusawal. The samples contained both amorphous (mainly SiO_2, Al_2O_3) and quartz and mullet. The unburnt carbon along with other volatile materials present in fly ash was removed by calcinations at high temperature for 2 hrs. Then 10g fly ash was taken and added with NaOH solution as 1:1.2 Proportions. The resultant mixture was stir at 300K for different time period. Then the mixture was filtered and washed and dried at 353K. [13]

Characterization

The synthesized zeolite is characterised by XRD, IR SEM, EDAX and TG-DTA and compare with CFA for its morphological study. The diffractograms were recorded using Cu-Kα radiation at a scanning speed of 1.2 degree per min. The zeolite material is scanned in the 2θ range of 0^0 to 60^0. The XRD pattern was obtained at 30kV and 15mAon Philips (3710pw/1710) X-Ray Diffractormeter system. The X-ray diffractogram of CFA and ZSM5 zeolite are shown in figure 1 and 2 respectively.

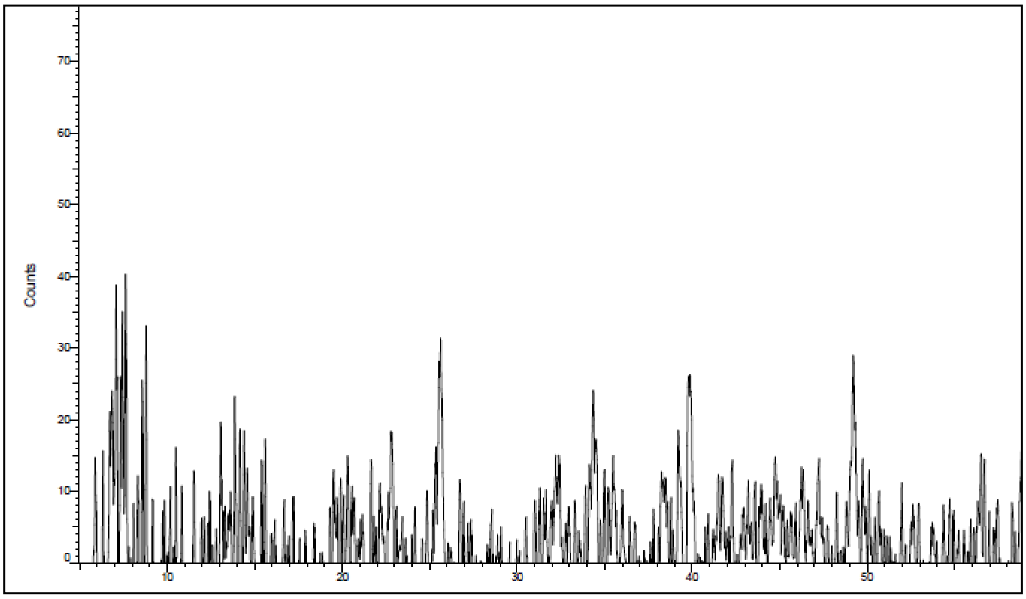

Figure 1. XRD of Coal Fly Ash (CFA)

In the XRD of coal fly ash multiple sharp diffraction peaks indicating crystalline phases of quartz, mullite, and possibly iron oxides. A significant amorphous phase contributing to the baseline. This is a typical class F fly ash pattern (high in silicates and alumina, low in calcium).

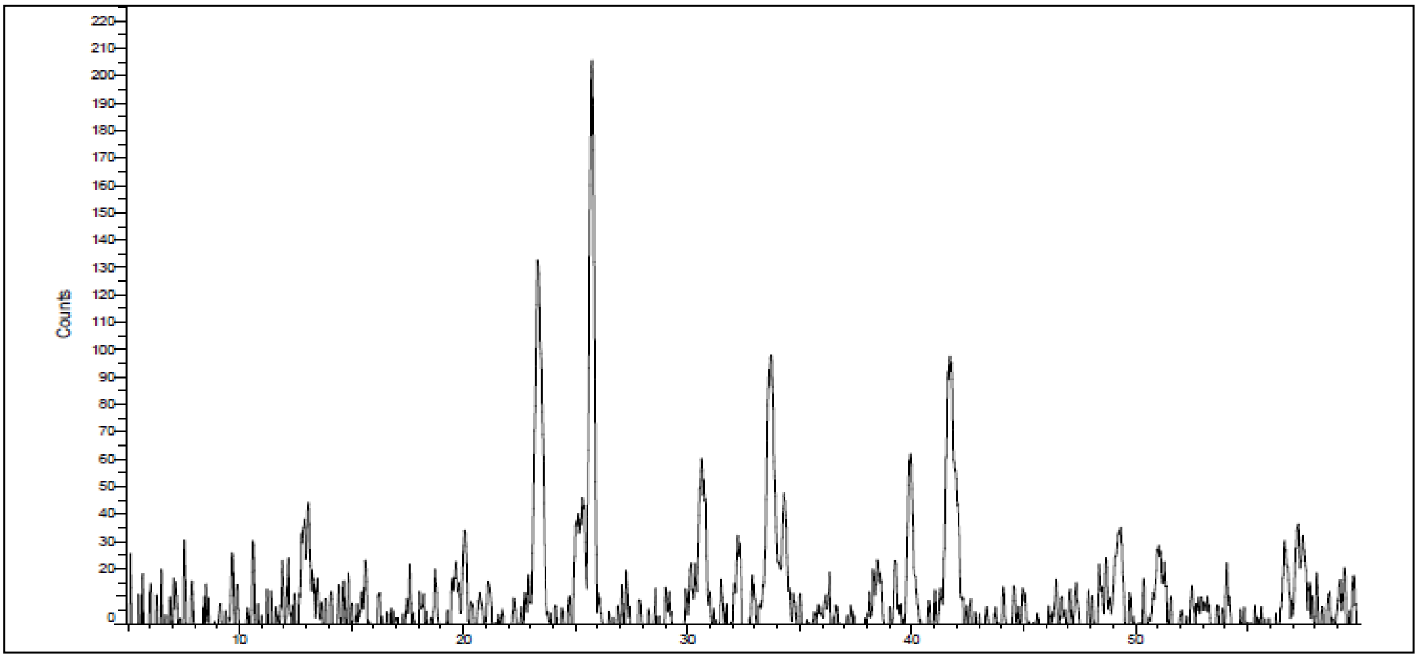

Figure 2. XRD of ZSM5 zeolite.

The XRD pattern of the synthesized ZSM-5 zeolite shown in Figure 2 exhibits numerous sharp and intense diffraction peaks, evidencing the formation of a highly crystalline structure. Prominent reflections appearing at 2θ values around 22–25° are characteristic of the MFI framework of ZSM-5 [14] . Relative to fly ash, the disappearance of the amorphous hump and the development of well-defined diffraction peaks indicate a substantial structural transformation from an amorphous aluminosilicates precursor to an ordered zeolitic framework. Moreover, the absence of diffraction peaks corresponding to quartz or mullet suggests the effective conversion of fly ash constituents into phase-pure ZSM-5 zeolite.

Infrared spectrograms of fly ash and modified ZSM5 zeolite are shown in figure 3 and 4. These were recorded on Perkin-Elmer FT-IR spectrophotometer in the frequency range 400-4000 cm^{-1} by using KBr pellet technique.

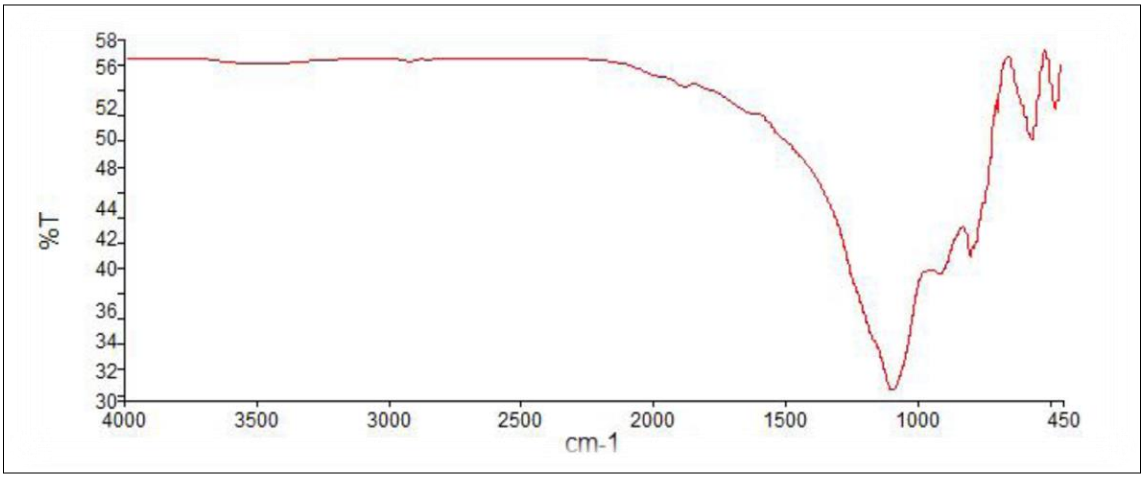

Fig.3 IR of Coal Fly Ash (CFA)

The spectrum is dominated by a series of strong, broad absorption bands primarily in the mid-infrared region, indicative of the material's mixed amorphous and crystalline composition. The most prominent feature is the very intense, broad band centred near 1000 cm^{-1}, which is the definitive signature of the asymmetric stretching vibrations of Si–O–Si and Al–O–Si bonds within the tetrahedral aluminosilicate network that forms the glassy matrix of the fly ash. This band's breadth and intensity confirm the predominance of amorphous silicate phases. A distinct secondary band is observed near 400-500 cm^{-1}, which is attributed to the bending modes of O–Si–O and O–Al–O linkages. The data also shows significant absorption in the 1500-1600 cm^{-1} range, which typically indicates the presence of carbonate species (CO_3^{2-}), likely from minor calcite ($CaCO_3$) or residual unburned carbonates. The absence of a strong, sharp O-H stretching band around 3400-3600 cm^{-1}, suggests a relatively low content of free moisture or hydroxyl groups in this sample, which is common for processed or dried fly ash. Overall, this IR spectrum is classic for Class F fly ash [15].

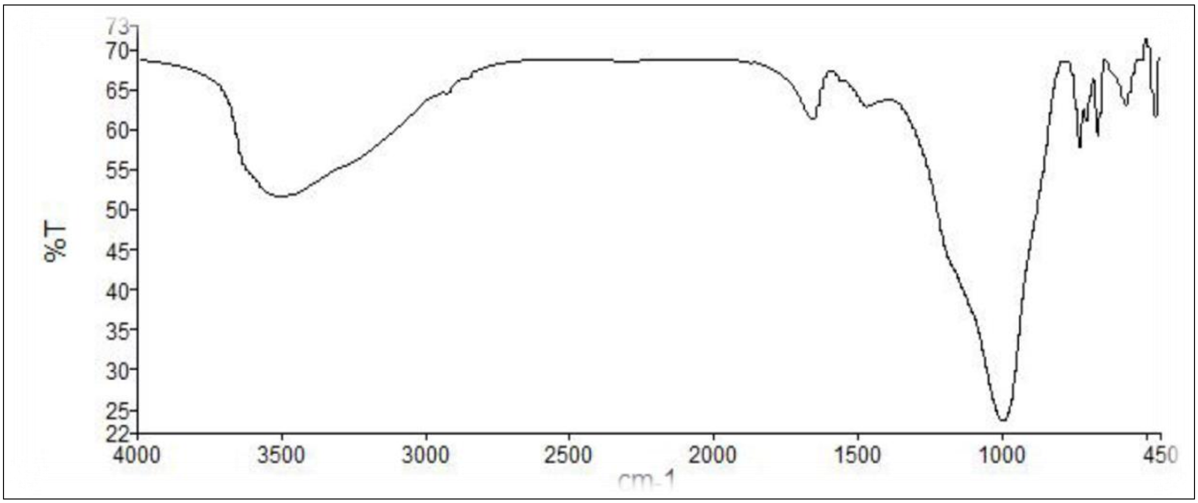

Fig.4 IR of ZSM5 Zeolite

The most significant absorption occurs at 1000 cm⁻¹, where the transmittance value of 25.0 indicates strong absorption, which corresponds to the asymmetric stretching vibration of T–O–T bonds (where T = Si or Al) within the zeolitic framework. This band confirms the primary aluminosilicate structure of ZSM-5. The presence of a weak but noticeable shoulder around 450 cm⁻¹ is attributed to T–O bending modes, further supporting the zeolite lattice integrity. A pronounced absorption band is observed in the region around 1500 cm⁻¹, which is unusually strong for a pure ZSM-5 sample. The strong absorption in the range of 3000–4000 cm⁻¹ is also significant. The relatively low transmittance value at 3500 cm⁻¹ paired with higher values at 3000 cm⁻¹ and 4000 cm⁻¹ suggests a broad, asymmetric O–H stretching band, characteristic of hydrogen-bonded silicon (Si–OH) groups. Overall, the IR spectrum confirms the presence of the ZSM-5 aluminosilicate framework.

The thermo gravimetric analysis was carried out on T.A. instrument (U.S.A.) SDT-2960 with reference material Al_2O_3 in nitrogen atmosphere. The TGA analyses were recorded for ZSM5 zeolite and it is shown in figure 5. The ZSM-5 sample, reveals a multi-stage mass loss profile characteristic of zeolitic materials, particularly those containing organic templates or adsorbate. The analysis begins at room temperature (~29.3°C) with an initial sample mass near 98.0%, indicating a minor pre-analysis mass adjustment. The primary mass loss event occurs in the low-to-mid temperature range (30–200°C), where the weight decreases from ~98% to ~86–90%. This significant drop of approximately 8–12% is attributed desorption of physically adsorbed water from the external surface and within the zeolite's microporous channels. ZSM-5 is highly hydrophilic, and this stage reflects the removal of loosely bound moisture.

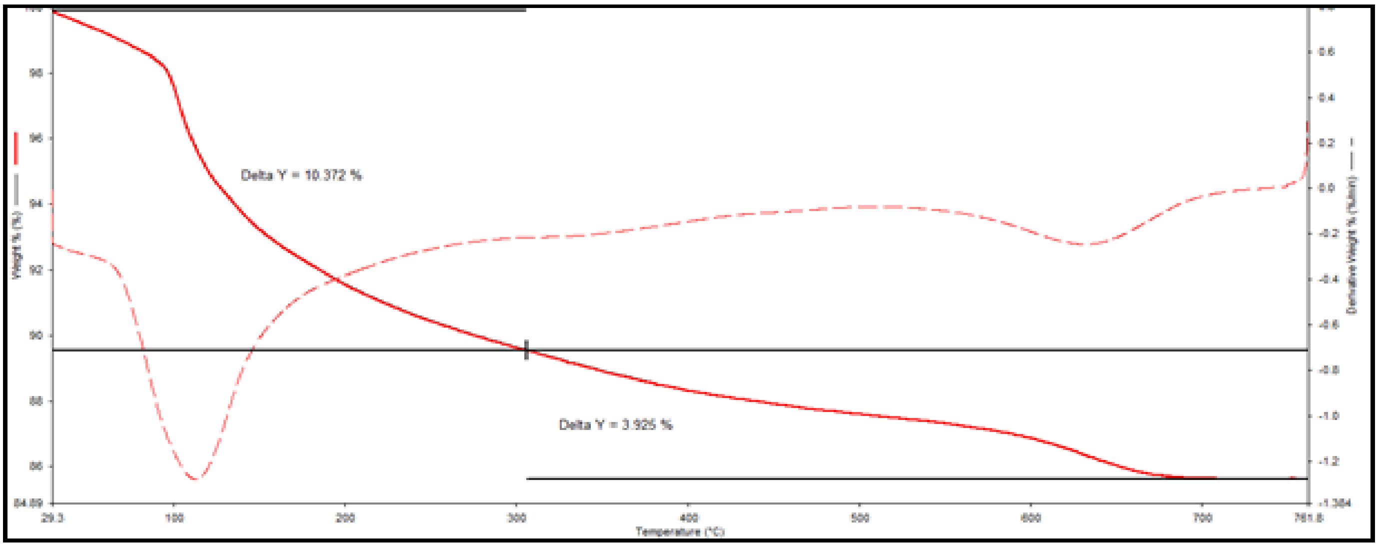

Fig. 5 TGA of ZSM5

A second, more gradual mass loss is observed from 200°C up to approximately 500°C. In this region, the weight continues to decline from ~90% to about 87–93.5%, depending on the dataset. This sustained loss is typically associated with the combustion or decomposition of residual organic template molecules or internal (Si-OH) groups. Above 500°C, the mass stabilizes significantly, with only minimal further loss up to 761.8°C, where the residual mass is approximately 84.8–99.5%. The high-temperature stability confirms the robust thermal integrity of the ZSM-5 aluminosilicate framework, which does not decompose within this range. The final plateau indicates the complete removal of volatile components, leaving behind the anhydrous, template-free zeolite.

The fly ash and zeolite sample was analysed using a Hitachi S-4800 scanning electron microscope at a 15.0 kV accelerating voltage, 8.5 mm working distance, with a magnification of 30,100x to 90,000x is shown in figure 6 and 7 respectively. The detector used was the secondary electron (SE) detector in upper mode, providing high-resolution topographical contrast. The image scale bar indicates 1.00 µm. At this high magnification, fly ash particles typically reveal their characteristic microstructure and morphology. Fly ash particles are generally spherical (cenospheres) due to surface tension effects during rapid cooling of molten mineral droplets in the flue gas.

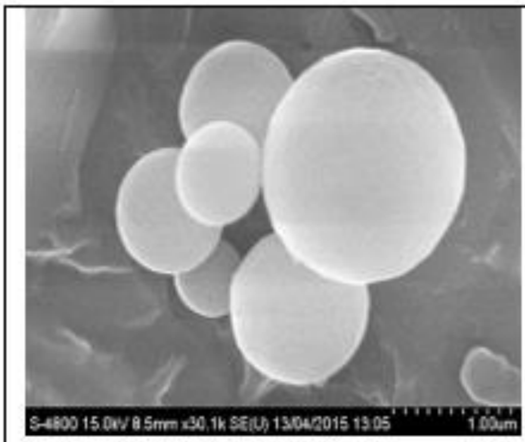	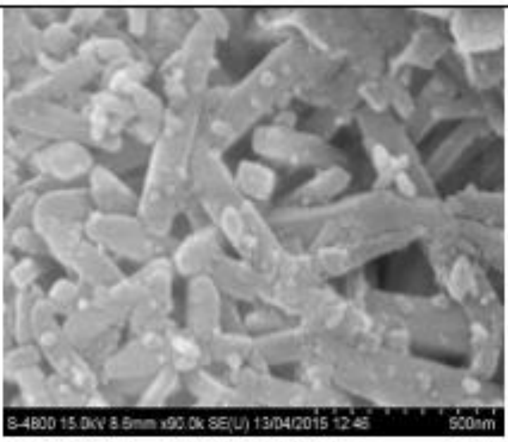
Fig 6. SEM of Fly Ash	Fig 7. SEM of ZSM5

The spherical morphology is a key indicator of the pozzolanic reactivity of the ash, as the glassy, amorphous aluminosilicate spheres contribute to strength development in concrete through reaction with calcium hydroxide. Some particles may also appear irregular or agglomerated, which could indicate unburned carbon, crystalline mineral phases (e.g., quartz, mullite), or smaller particles adhering to larger ones. Surface features such as porosity, smoothness, or micro-cracks on the spheres may also be visible, offering insight into the combustion conditions and cooling history [16].

ZSM-5 typically crystallizes in the form of inter grown, coffin-shaped or hexagonal prismatic crystals with well-defined facets. The image likely reveals these individual Nano crystals or aggregates, with crystal sizes often ranging from 50 nm to several µm. The micrograph is expected to show a uniform, polycrystalline texture with clearly visible crystal edges, smooth faces, and possibly some surface roughness. The absence of amorphous debris and the presence of well-faceted, discrete crystals would indicate a highly crystalline, phase-pure ZSM-5 material synthesized under controlled hydrothermal conditions. The scale bar of 500 nm suggests that many of the individual crystals or primary particles are likely in the sub-micron to nanoscale range, which is advantageous for maximizing accessible active sites in reactions.

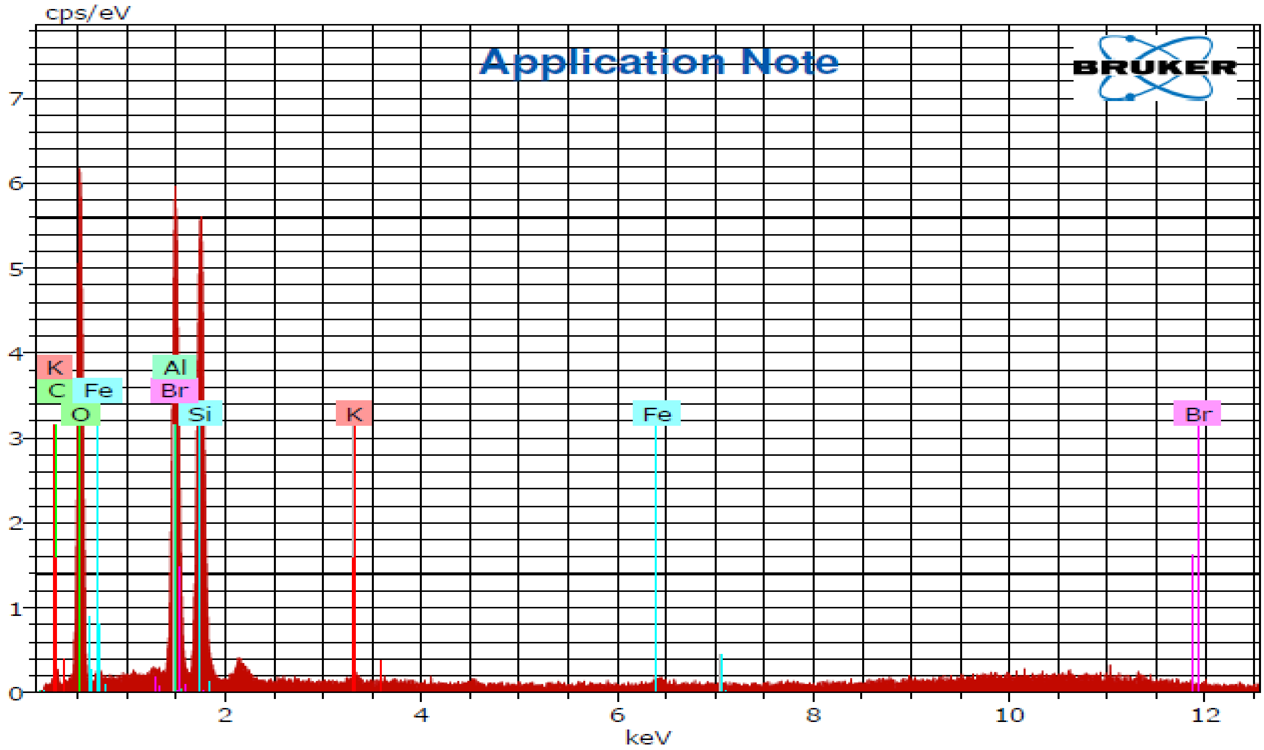

Fig.8 EDAX of fly ash

The spectrum is dominated by the silicon (Si) peak at 1.74 keV, confirming silicon as a primary component, consistent with the quartz (SiO_2) and aluminosilicate glass matrix of fly ash [17]. The aluminium (Al) peak at 1.49 keV is also prominent, indicating a significant aluminium content, which is characteristic of the mullite ($3Al_2O_3 \cdot 2SiO_2$) phase and amorphous aluminosilicates. The presence of iron (Fe), shown by the peak at ~6.4 keV, is common in fly ash and typically originates from iron oxides such as magnetite (Fe_3O_4) or hematite (Fe_2O_3), contributing to the material's often grayish colour. Notably, the data shows a strong signal for potassium (K)**,** with peaks at ~3.31 keV and ~3.59 keV. This suggests a notable alkali metal content, which can influence the ash's fusibility and its behavior in cementations systems.

Table 1 Elemental analysis of Fly Ash

Element	Atomic Wt.	Series	Normal Wt%	Atomic Wt%
C	6	K-series	3.67	7.07
O	8	K-series	44.58	64.51
Al	13	K-series	4.01	3.44
Si	14	K-series	18.68	15.40
K	19	K-series	0.50	0.30
Fe	26	K-series	8.10	3.36
Br	35	L-series	20.46	5.93

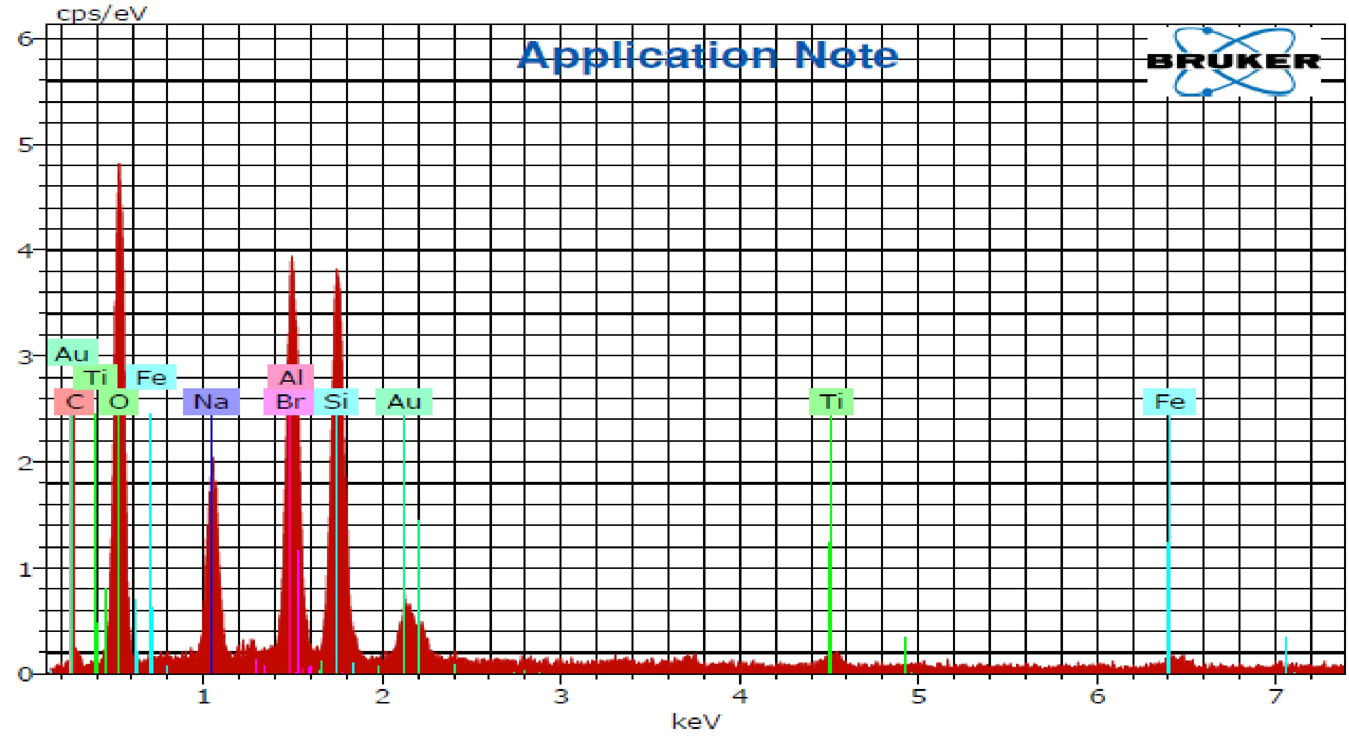

Fig. EDAX of ZSM5

Table 2 Elemental analysis of ZSM5

Element	Atomic Wt.	Series	Normal Wt%	Atomic Wt%
C	6	K-series	4.61	9.56
O	8	K-series	37.40	58.18
Na	11	K-series	7.28	7.89
Al	13	K-series	0.56	0.52

Si	14	K-series	14.78	13.10
Ti	22	K-series	2.58	1.34
Fe	26	K-series	4.44	1.98
Br	35	L-series	20.82	6.49
Au	79	M-series	7.51	0.95

Based on the provided EDAX spectral data presented as a list of detected elemental peaks with their corresponding energies (keV), the analysis of the ZSM-5 zeolite sample reveals a composition that includes both expected framework elements and several unexpected, potentially spurious signals. The presence of Silicon (Si) at ~1.74 keV and Aluminium (Al) at ~1.49 keV confirms the fundamental aluminosilicate (SiO_2 and Al_2O_3) framework of the ZSM-5 zeolite. These are the primary structural components. The detection of Oxygen (O at ~0.53 keV) is also consistent with the oxide composition of the zeolite.

CONCLUSION

Coal fly ash was effectively transformed into highly crystalline ZSM-5 zeolite by alkaline activation followed by hydrothermal treatment. The XRD results verified the successful formation of the MFI-type ZSM-5 structure, accompanied by the disappearance of quartz, mullite, and the amorphous phases originally present in the raw fly ash. FTIR analysis further confirmed the development of an ordered aluminosilicate framework through the appearance of characteristic T–O–T vibrational bands. Thermo gravimetric studies showed that the synthesized zeolite possesses good thermal stability, with an initial weight loss due to moisture removal and only minor changes at elevated temperatures. SEM observations indicated a distinct morphological shift from spherical fly ash particles to well-defined zeolitic crystals, while EDAX data confirmed the predominance of Si–Al–O as the main framework components.

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