

# Cu (II), V (IV) and Co (II) complexes of 2-picolinic acid encapsulated in fly ash based zeolite, their characterization and catalytic activity towards hydroxylation of phenol

<sup>[1]</sup> S. Sheeba Thavamani, <sup>[2]</sup> T. Peter Amaladhas

<sup>[1][2]</sup> P.G and Research Department of Chemistry, V.O. Chidambaram College, Thoothukudi, Tamil Nadu, India

**Abstract-** Fly ash is a major residue generated from coal fired power plants. Owing to the environmental threats posed by fly ash, several attempts have been made for gainful utilization of fly ash. In this work, the possibility of synthesizing high value added products such as zeolites from fly ash has been explored. Fly ash based zeolite (FAZ) has been synthesized from fly ash by hydrothermal treatment. The formation of FAZ has been confirmed by FT-IR, XRD, TGA, SEM, XRF and BET surface area analysis. The cation exchange capacity of FAZ has been determined. Cu(II), V(IV) and Co(II) complexes of 2-picolinic acid have been encapsulated in the pores of FAZ by flexible ligand method. The zeolite encapsulated complexes were characterized by FT-IR, SEM, AAS, TGA, XRD and UV-Vis spectrophotometry. M-O stretching has been observed at 767 cm<sup>-1</sup> for the encapsulated metal complexes. The encapsulated metal complexes thus prepared have been screened for catalytic activity using hydroxylation of phenol as a test reaction, the products identified to be hydroquinol and catechol by GC-MS. The extent of the reaction has been monitored as a function of time. A maximum conversion efficiency of 73.10% has been observed. Such heterogeneous catalysts offer the advantage of easy separation of the catalyst and reusability.

**Keywords:-** Fly ash zeolite, flexible ligand method, 2-picolinic acid.

## I. INTRODUCTION

Thermal power stations play a key role in power production. Fly ash is a major residue generated from coal-fired power plants which is related with environmental hazards and health risks. Disposal of fly ash poses threats related to environmental concern which led to the utilization of fly ash in the manufacture of cement, tiles, bricks, concrete, blocks, etc. Utilization of fly ash for the synthesis of zeolites is studied by many researchers but to best our knowledge this is the first report where fly ash from Tuticorin Thermal Power Station (TTPS) is used for the synthesis of zeolite. Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework, cations and water molecules. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 1.83 makes fly ash a suitable candidate for the synthesis of low silica zeolites. Low silica zeolites have the highest cation exchange capacity and find applications as ion exchange agents. Transition metal complexes of 2-picolinic acid are encapsulated in the FAZ by flexible ligand method. Encapsulation of transition metal complexes in the pores of FAZ offers the advantage of heterogeneous catalysis including easy separation of products and reusability of the catalyst. This work involves (i) Conversion of fly ash to FAZ by hydrothermal method (ii) Synthesis of Cu(II), Co(II) and V(IV) exchanged FAZ (iii) Complexation of the metal ions in FAZ with 2-picolinic

acid to yield Cu(II), Co(II) and V(IV) complexes of 2-picolinic acid encapsulated in FAZ (M-PIC-FAZ) (iv) Assessment of catalytic activity of the encapsulated complexes towards hydroxylation of phenol

## II. EXPERIMENTAL

### 2.1. Materials

F-type fly ash collected from the electrostatic precipitators of Tuticorin Thermal Power Station (TTPS) was used for the study. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and VOSO<sub>4</sub>·5H<sub>2</sub>O of 99% purity manufactured by E.Merck were used for preparing metal exchanged zeolite. 2-picolinic acid of 99% purity of ReagentPlus grade manufactured by Sigma-Aldrich was used. Phenol of assay 99.0% purchased from Chemspure, Chennai, India was used for catalytic activity studies. Hydrogen peroxide solution manufactured by E.Merck of assay 30-32% W/V was used. Acetonitrile and dichloromethane (HPLC grade) of 99.5% purity were used as solvents. 40% solution of HF (Sigma-Aldrich) was used to dissolve the zeolite encapsulated metal complexes for AAS analysis.

### 2.2. Physical measurements

FT-IR spectra were recorded as KBr pellet on Perkin-Elmer FT-IR spectrophotometer model-spectrum 100 optica in the frequency range 400-4000 cm<sup>-1</sup> with a resolution of 0.1 cm<sup>-1</sup>. The structural crystallinity of the encapsulated complexes

was confirmed by recording the XRD patterns in PANalytical model X'pert PRO using CuK $\alpha$  (2.2 KW Max.) source and X'celerator (semiconductor) detector. Ni filtered CuK $\alpha$  radiation was used with a curved graphite crystal monochromator and NaI scintillator. UV-Vis spectra were recorded from 190 to 1000 nm using JASCO, V-530 model spectrophotometer. 25 mg of metal complex encapsulated zeolite was heated with 20 mL of dilute sulphuric acid to facilitate leaching of the metal complex. The metal contents in the zeolite encapsulated metal complexes were measured using Varian, Model Spectraa 220 Atomic Absorption Spectrometer in the flame of acetylene-air mixture. 50 mg of the encapsulated metal complex was dissolved in 20 mL of HF (40%) and the metal contents in the solution were analysed using Atomic Absorption Spectrometer. GC analysis was carried out to identify the products obtained from the hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> (catalysed by the encapsulated metal complexes) in GC-MS Hewlett Packard HP 5890 instrument fitted with FID detector and RTX 502.2 column of length 60 m, 0.25 ID using He as the carrier gas. The initial temperature was maintained at 70 °C for 12 minutes and the temperature was increased at the rate of 10 °C per min up to a temperature of 250 °C. 0.5 microlitre of the sample was injected.

### 2.3. Synthesis of Fly ash zeolite (FAZ):

F-type fly ash was collected from Tuticorin Thermal Power Station and subjected to hydrothermal treatment for the synthesis of X-type zeolite [1]. The prepared FAZ has been found to have a cation exchange capacity of 457 meq/100g. The surface area and pore volume of the prepared zeolite have been reported to be 172.82 m<sup>2</sup>/g and 0.1412 cm<sup>3</sup>/g respectively [2].

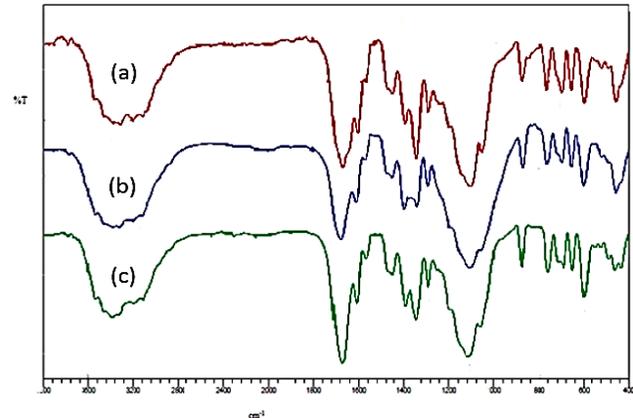
### 2.4. Encapsulation of Cu(II), Co(II) and V(IV) complexes of 2-picolinic acid in FAZ:

Cu(II), Co(II) and V(IV) ions were exchanged with Na<sup>+</sup> ions of zeolite by stirring with the corresponding metal salt solution. The metal ion exchanged zeolite was thoroughly washed with distilled water and dried for 15 hours at 150 °C in an air oven. The change in colour indicates the loading of metal ions in the pores of zeolite. About 1 g of the metal exchanged zeolite was further refluxed with 2.5 g of 2-picolinic acid and 50 mL acetonitrile while stirring magnetically. The ligand has been reported to have the ability to diffuse freely through the zeolite pores, and can co-ordinate with the transition metal cations to form metal complexes which is too large to exit. The zeolite encapsulated metal complexes were subjected to Soxhlet extraction to remove any uncomplexed ligand and metal complex adhered to the surface of the zeolite.

## III. RESULTS AND DISCUSSION

### 3.1. FT-IR studies:

The FT-IR spectra of the encapsulated metal complexes of 2-picolinic acid are presented in fig. 1.



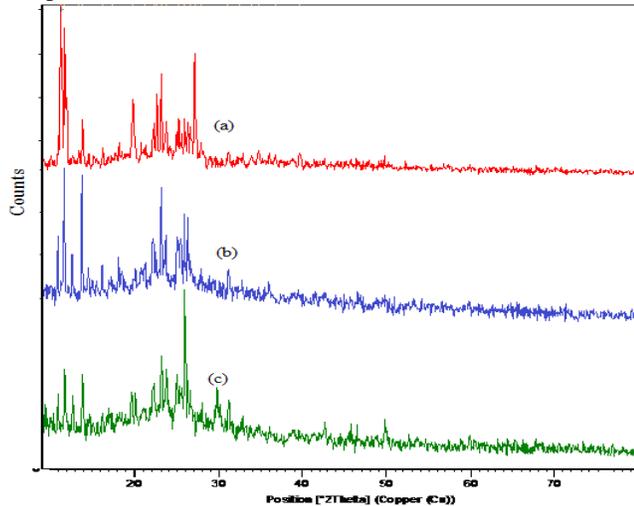
**Fig. 1: FT IR spectra of (a) Cu-PIC encapsulated FAZ; (b) V-PIC encapsulated FAZ; (c) Co-PIC encapsulated FAZ**

The intense band at 983 cm<sup>-1</sup> corresponds to Si-O-Al asymmetric stretching [3]. The band at 1216 cm<sup>-1</sup> shows the presence of substituted Al atoms in the tetrahedral forms of zeolite framework [4]. The band centred on 3400 cm<sup>-1</sup> is due to the asymmetric and symmetric -OH stretching vibrations which indicates the presence of hydrated aluminosilicates. >C=O stretching is observed at 1676 cm<sup>-1</sup> [5]. The peak at 1610 cm<sup>-1</sup> is attributed to C=C stretching and the hump observed at 1452 cm<sup>-1</sup> is attributed to C-C. The peaks located at 1396 cm<sup>-1</sup> and 1344 cm<sup>-1</sup> correspond to C-O stretching and O-H stretching respectively. The peak at 1290 cm<sup>-1</sup> is attributed to C-N stretching [6]. The M-O stretching has been observed at 767 cm<sup>-1</sup> for all the zeolite encapsulated metal complexes [7]. The FT-IR spectra of the zeolite encapsulated metal complexes show peaks similar to that of their corresponding neat complexes which can be considered as a direct evidence for bis-(picolinate) structure [8]. The peak positions are influenced due to the distortion of the encapsulated complexes inside the zeolite super cages or by a difference in coordination by the -OH groups of the zeolite.

### 3.2. XRD analysis:

The X-Ray diffraction patterns of the encapsulated metal complexes of 2-picolinic acid are presented in fig. 2. The XRD pattern of FAZ matches with that of zeolite - X [9]. Comparison of XRD patterns of the encapsulated complexes with that of the parent zeolite shows no change in the peak positions. This ensures that the crystallinity of zeolite framework has been preserved after the encapsulation

process [10] and also indicates the poor loading of the metal complexes in the cavities of FAZ [11].



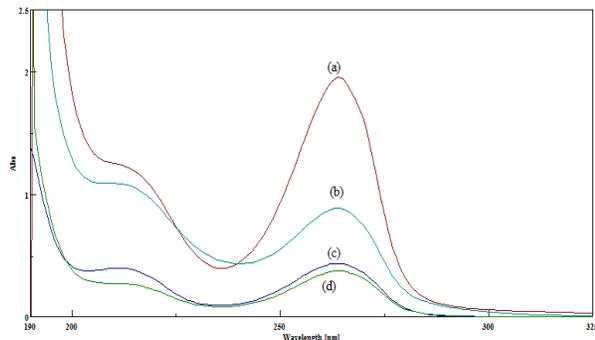
**Fig. 2:** XRD patterns of (a) Cu-PIC encapsulated FAZ; (b) Co-PIC encapsulated FAZ; (c) V-PIC encapsulated FAZ

**3.3. Atomic Absorption Spectrometry**

50 mg of each metal complex encapsulated zeolite was dissolved in 20 mL hydrofluoric acid (40%) and was analysed by atomic absorption spectrometer. The report shows the presence of the corresponding metal ions, (Cu: 87.77 ppm, V: 32.03 ppm and Co: 34.15 ppm), in the solution which further proves the encapsulation of the metal complex in the zeolite.

**3.4. UV-Vis. spectral analysis:**

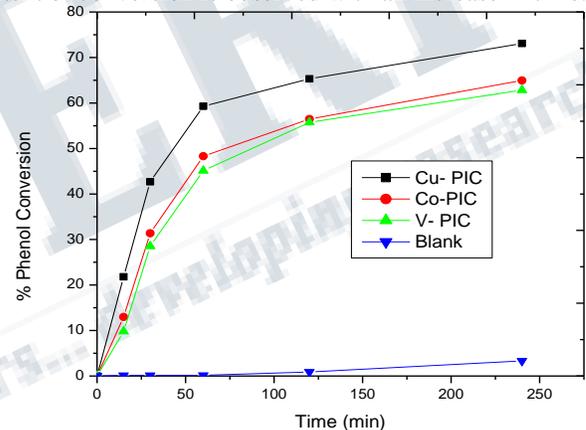
The UV-Vis spectra of the leachate of the metal complexes are presented in fig. 3. UV-Vis spectra of the leachate of the metal complexes show two peaks around 264 nm and 211 nm which arises as a result of ligand based  $\pi-\pi^*$  transition [12]. Due to the low concentration of the metal complexes in the leachate, d-d transitions could not be observed [13].



**Fig. 3:** UV-Vis spectra of (a) V-PIC encapsulated FAZ; (b) Co-PIC encapsulated FAZ; (c) PIC ligand; (d) Cu-PIC encapsulated FAZ

**3.4. Catalytic activity studies of encapsulated metal complexes of 2- picolinic acid:**

Hydroxylation of phenol was carried out using the different metal complex encapsulated zeolites as solid heterogeneous catalysts. An aqueous solution of 30% H<sub>2</sub>O<sub>2</sub> (1.6 mL, 53.38 mmol) and phenol (0.54 g, 6.16 mmol) were mixed in 5 mL CH<sub>3</sub>CN. 0.02 g of zeolite encapsulated metal complex of 2-picolinic acid was added and the reaction mixture was refluxed for the stipulated time. After the reaction, the product mixture was cooled to room temperature and made up to a definite volume. The products were analysed by GC-MS and identified to be hydroquinol. The amount of unreacted phenol in the reaction mixture was estimated by quantitatively substituting with bromine [9]. The % phenol conversion to hydroquinol for the encapsulated complexes varies with time in the order: Cu-PIC > Co-PIC > V-PIC. Fig. 4 shows that the extent of phenol conversion increases with time. A blank experiment was also performed and compared with the performance of the catalysts. A higher extent of conversion is observed with an increase in time.



**Fig. 4:** Variation of % phenol conversion as a function of time for M-PIC encapsulated complexes

The variation of catalytic activity of the different M-PIC encapsulated complexes was monitored as a function of time towards the hydroxylation of phenol and the results are tabulated in table 1.

**Table-1:** % conversion of phenol as a function of time for M (PIC)-X

Sample	15 min	30 min	60 min	120 min	240 min
Co- PIC-X	12.97	31.37	48.32	56.46	64.95
V-PIC-X	9.79	28.53	45.13	55.75	62.83
Cu-PIC-X	21.81	42.69	59.29	65.31	73.10
Blank	21.81	42.69	59.29	65.31	73.10

#### IV. CONCLUSION

The encapsulation of transition metal complexes in the pores of FAZ has been proved beyond doubt using sophisticated analytical techniques. The catalytic activity of the encapsulated metal complexes have been monitored as a function of time towards the hydroxylation of phenol. This provides a high-tech route for utilisation of fly ash. The activity of the prepared complexes can be monitored towards other industrially significant reactions.

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