Encapsulation of *N,N*-ethylenebis(salicylamide) metal complexes in fly ash based zeolite, characterization and catalytic activity

T. Peter Amaladhas*, S. Sheeba Thavamani

PG and Research Department of Chemistry, V. O. Chidambaram College, Thoothukudi 628008, Tamil Nadu, India

*Corresponding author. Tel: (+91) 461 2310876; Fax: (+91) 461 2310275; E-mail: peteramaldhast@yahoo.co.in

ABSTRACT

Coal fly ash has been used to synthesize X-type zeolite by alkali fusion followed by hydrothermal treatment. The synthesized fly ash based zeolite (FAZ) has been characterized by various analytical techniques. Copper(II), Nickel(II) and Zinc(II) complexes of N,N′-ethylenebis (salicylamide) encapsulated in the supercages of FAZ have been prepared by flexible ligand method and characterized by Fourier Transform infra red spectroscopy (FTIR), X-ray diffraction (XRD) analysis, Scanning electron microscopy (SEM), Atomic absorption spectrometry (AAS), Ultra Violet – Visible spectroscopy and Thermo gravimetric analysis (TGA). These complexes have been found to catalyze the liquid phase hydroxylation of phenol with hydrogen peroxide to yield catechol. It appears to be the first report of catalysis of metal complex encapsulated in fly ash based zeolite. Copyright © 2013 VBRI press.

Keywords: Fly ash; zeolite; encapsulation; flexible ligand method.

T. Peter Amaladhas has received his Ph.D. degree in Chemistry from University of Rajasthan, Jaipur, India in 1991. He has 8 years industrial experience as Research and Development Manager and Quality Assurance Manager in various fine chemical industries. He worked as a Faculty of Chemistry in Department of Applied Sciences, Higher College of Technology, Muscat, Sultanate of Oman for 3 years. Currently he is working as a faculty of Chemistry in V.O.Chidambaram College, Thoothukudi, India. His fields of interest are material chemistry and biosynthesis and applications of nanoparticles. He has authored 9 research papers in various international journals.

S. Sheeba Thavamani obtained her post graduate degree in Chemistry from The American College, Madurai and M.Phil. in Chemistry from Manonmaniam Sundaranar University. She has eight years of teaching experience and is working as a faculty of chemistry in V.O. Chidambaram College, Thoothukudi, India. Presently, she is perusing her research under the guidance of Dr. T. Peter Amaladhas. Her title of research is encapsulation of metal complexes in fly ash based zeolites and assessment of their catalytic activity.

Introduction

With the rapid hike in human population and developmental activities, a great threat is caused to the environment due to the industrialization and urbanization. Although thermal power plants are important for generating electricity, they produce huge quantities of fly ash. Fly ash is considered as a hazardous waste and disposed in special landfills. Dumping of fly ash in land produces a great threat to the environment endangering soil, surrounding vegetation as well as ground water around disposal ponds [1]. However it is becoming increasingly difficult to obtain more land for land filling purpose due to high population density. The composition of fly ash varies depending on the source and type of coal used. It has considerable surface reactivity due to its large specific surface and consists of unburnt carbon, high content of combined silica and alumina [2, 3]. For sustainable development of the thermal power projects in India, one of the main considerations should be on efficient disposal of ash and its utilization to avoid environmental pollution and reduce land requirement.

Fly ash contains more than 85% of silica and alumina and hence considered to be the most suitable and convenient raw material for the synthesis of zeolites. Zeolites are naturally occurring hydrated aluminosilicate materials. They belong to the class of materials known as 'tectosilicates'. The structures of zeolites consist of three dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The

Aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} and Al^{3+} produce a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (Sodium, Potassium or Calcium) [4].

Though the production of fly ash based zeolite is not a complete solution to fly ash menace, it will definitely provide cost-effective alternative to commercial zeolite in applications where zeolite purity could be compromised. The synthesis of zeolites from fly ash is expected to resolve the problem of disposal of fly ash at least partially and thereby minimize its impact on the environment. Several environmental and energy technologies can emerge with substantial benefits from zeolite based materials which include reduction in waste improved energy efficiency, environmentally benign composite structures, waste remediation and energy conservation [5]. In the past fly ash based zeolites have been synthesized in many ways such as hydrothermal method [6, 7], alkali fusion method [8], microwave method [9] and molten salt method [10]. The encapsulation of transition metal complexes into the framework sites of the zeolite has attracted considerable attention as the preparation of novel catalysts, owing to which possess the advantages of both homogeneous catalysis as the metal ion in the solution and heterogeneous catalysis as the molecular sieve in the polyphase system. Enhanced selectivity and ease of separation and purification of reactants and products would accompany its activity in solution phase. Since the encapsulated complexes are reported to have catalytic activity, this explores a new channel of catalysts which can be used in fine chemical industries. The present work describes (i) the synthesis of zeolites from the fly ash using hydrothermal method [11, 12], (ii) encapsulation of transition metal complexes of Cu(II), Ni(II) and Zn(II) in the cages of zeolite using flexible ligand method [13] and (iii) screening of catalytic activity of the transition metal complexes encapsulated in fly ash zeolite for the liquid phase hydroxylation of phenol to catechol. Though encapsulation of several metal complexes have been reported in commercial zeolites [14, 15] to the best of our knowledge this is the first report that involves the encapsulation of metal complexes in fly ash based zeolites. This work is significant since it suggests a catalyst for fine chemical industries and also envisages an alternative route for the utilization of FA which presents potential risks to the environment.

Experimental

Materials

The main raw material, F-type coal fly ash sample was collected from electrostatic precipitators of Tuticorin Thermal Power Station (TTPS), Thoothukudi, Tamil nadu, India. The sample contained both amorphous (mainly SiO_2 and Al_2O_3) and crystalline components (mainly quartz and mullite). Methyl salicylate (AR) and 1,2-diaminoethane (AR), were obtained from E. Merck, Mumbai, India. Analytical reagent grade metal nitrates ($Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$ and $Zn(NO_3)_2.6H_2O$) were also procured from E. Merck, Mumbai, India. LOBA Chemie, Mumbai, India, 30% H_2O_2 and AR grade Acetonitrile, Fischer,

Chennai, India were used to study the catalytic activities. 1,2-bis(2-hydroxybenzamido)ethane (H_2hybe) was prepared as reported in literature [16].

Physical methods of analysis

The metal contents in the zeolite encapsulated metal complexes were measured using Varian Model Spectra 220 Atomic Absorption Spectrometer. IR spectra were recorded as KBr pellet on a Perkin-Elmer FT-IR spectrometer model spectrum 100 optica. The structural crystallinity of the encapsulated complexes was confirmed by recording the XRD patterns in PANalytical model X'pert PRO using Cu K (2.2 KW Max.) source and X'celerator (semiconductor) detector at CECRI, Karaikudi. GC analysis was carried out to monitor the catalytic activity of the encapsulated metal complexes towards hydroxylation of phenol in GC-MS Hewlett Packard HP 5890 instrument fitted with FID with RTX 502.2 column of length 60 m, 0.25 ID using He as the carrier gas. Temperature program: Initial Temperature 70^0C for 12 minutes and increased at the rate of 10^0C per min up to a temperature of 250^0C. Injection volume - 0.5 microlitre. Thermo grams were recorded in a Perkin - Elmer Thermo gravimetric analyzer TGA7 with a vertical furnace and vertical sample gas flow at a heating rate of 10^0C per minute. To study the surface morphology, SEM images were recorded using Punta 200, FEI instrument.

Zeolite synthesis

X-type zeolite was synthesized from F-type fly ash using a method reported in literature [17]. A typical procedure is given below. The raw fly ash sample was first screened through a sieve of 80-mesh size, to eliminate the larger particles. The unburnt carbon (3%) along with other volatile materials present in fly ash were removed by calcination at $800(\pm10^0C)$ for 2 hours. The calcined fly ash sample was further treated with hydrochloric acid to increase its activity, thermal stability and acidity of the zeolite, all aiming for better catalytic applications.

A mixture of sodium hydroxide and fly ash (calcined and HCl treated) in the 1:1 ratio (by weight) was milled and fused in a silica crucible at 550^0C for 1hour. The resultant fused mass was then cooled to room temperature, ground further and added to water (10g fly ash / 100 mL water). The slurry thus obtained was agitated mechanically in a glass beaker for 8 hours. It was then kept at 90^0C in an oven for 6 hours without any disturbance. The resultant precipitate was repeatedly washed with water to remove excess NaOH, filtered and dried. The sodium hydroxide added to the sample not only acts as an activator but also adjusts the sodium content of the starting material. Mullite and α-quartz present in fly ash are sources of aluminium and silica respectively for zeolite formation. **Fig. 1** describes various steps involved in the preparation of FAZ.

Preparations

The metal complex encapsulated zeolites were prepared by flexible ligand method. The metal ion was exchanged with the Na+ ions of the FAZ which were further treated with the ligand. In this approach, the flexible ligand must be able to diffuse freely through the zeolite pores, where it coordinated to the previously exchanged transition metal

cations to form the encapsulated complex. This method involves the diffusion of a multidentate ligand into the zeolite pores; where upon complexation with a metal ion becomes too large to exit.
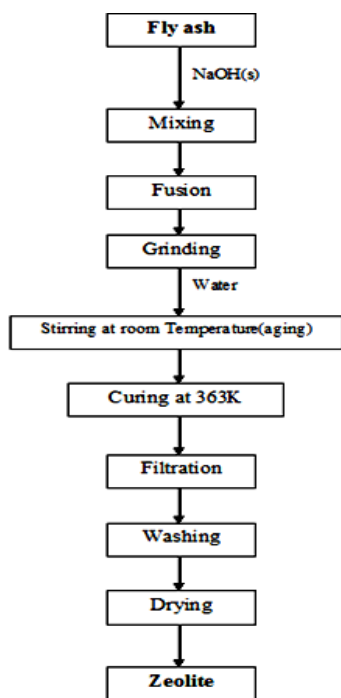

Fig. 1. Process flow chart for synthesis of zeolite from fly ash.

Preparation of metal exchanged zeolite, M-Y; [M=Cu(II), Ni(II) and Zn(II)]

About 1.0 g of fly ash zeolite (FAZ) was suspended in 100 mL of 0.1 M metal nitrate solution. [Nitrates of Cu(II), Ni(II) or Zn(II)]. The reaction mixture was magnetically stirred for 24 hours. The solid was filtered, washed with distilled water till the filtrate was free from the metal ion on the surface of the zeolite and then dried for 15 hours at 150^0C in an air oven.

Preparation of [M (hybe)-Y]

The encapsulated complexes were prepared by flexible ligand method. About 1.0 g of metal ion exchanged zeolite [M= Cu(II), Ni(II) or Zn(II)] and 2.5g of H_2hybe were mixed in 50 mL acetonitrile in a flask and the reaction mixture was heated at reflux for ca.15 hours while stirring magnetically. During this period, the ligand can slowly enter the zeolite pores and form complexes with the metal ion. After cooling, the slurry was Soxhlet extracted with methanol (ca.48 hours) till the complex was free from unreacted ligand and any free metal complex on the surface of the zeolite. The uncomplexed metal ions on the surface were removed by exchanging with aqueous 0.01M NaCl. Finally, the encapsulated complexes were filtered and washed with hot distilled water till no precipitation of AgCl was observed on treating the filtrate with $AgNO_3$ solution. The coloured solids (colourless in the case of Zn(II)) were

dried at 150^0C for five hours till constant weight was achieved.

Results and discussion

The formation of zeolite from fly ash occurs in three steps-viz., dissolution, deposition and crystallization. The dissolution takes place in the heating process. The amorphous aluminosilicate gradually deposits on the particle surface of coal fly ash in the heating process. The zeolite crystals are conspicuously formed at 90^0C in the reaction time of 6 h. As the zeolite crystallization progresses, the surface of the coal fly ash is covered with deposited zeolite in the alkaline solution [18]. **Fig. 2** represents the structure of the ligand 1,2-bis(2-hydroxybenzamido)ethane (H_2hybe) which co-ordinates with the metal ion that has been exchanged for Na^+ in the zeolite.
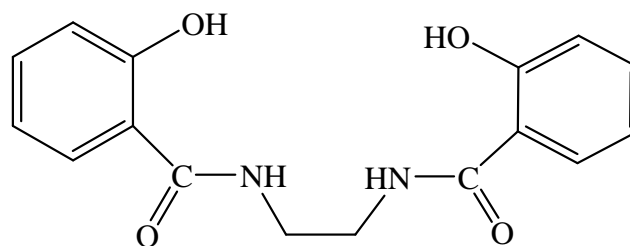

Fig. 2. Structure of 1,2-bis(2-hydroxybenzamido)ethane (H_2hybe).

Fourier transform infra-red spectroscopy

Infra-red spectroscopy can yield information concerning structural details of the zeolite. It is a good tool to characterize the encapsulated metal complexes in the cavity of the zeolite. In general, the IR spectrum can be split into two groups of vibrations (i) internal vibrations of framework TO_4 units which are insensitive to the structural vibrations and (ii) vibrations related to the external linkages of the TO_4 units in the structure which are sensitive to structural vibrations. The common features observed in the infra red pattern of zeolites are asymmetric and symmetric stretch, double ring vibrations and T-O bending modes. The frequency regions where different kinds of vibrations are located in zeolites are summarized in **Table 1**.

Table 1. Zeolite IR assignments [common for all zeolites].

Internal tetrahedral:	
Assymetric stretch	$1250\text{-}950\,cm^{-1}$
Symmetric stretch	$720\text{-}650\,cm^{-1}$
External linkage:	
Double ring	$650\text{-}500\,cm^{-1}$
Symmetric stretch	$750\text{-}820\,cm^{-1}$
Asymmetric stretch (sharp)	$1050\text{-}1150\,cm^{-1}$

The FTIR spectrum of the as prepared FAZ is given in the **Fig. 3**. The stretching and bending modes of the zeolite and that of the ligands can be located in the FTIR spectra of the metal complexes encapsulated FAZ which is a clear evidence for the loading of the complexes in the pores of the zeolite. The most intense band at 968 cm^{-1} is assigned to an asymmetric stretching of Si-O-Al [19, 20]. The mid infra red region of the spectrum contains the fundamental framework vibration of Si(AlO$_4$) groupings. The band at 1216 cm^{-1} (980 cm^{-1}-1320 cm^{-1}) represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks. All these observations confirm the formation of zeolites on alkali treatment of fly ash. The band at 3337cm^{-1} (weak to medium) is attributed to the asymmetric and symmetric stretching vibrations υ(O-H) suggesting the presence of possibly hydrated aluminium silicates. The weak band at 2371cm^{-1} is attributed to hydrogen bonds of ligated water molecules or to the contribution of stretching over bending vibrations. The band at 1646 cm^{-1} is attributed to the bending mode of water molecules [17].
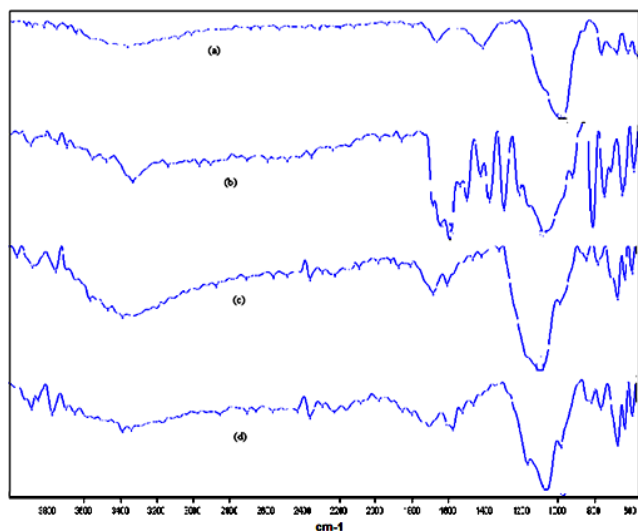
Fig. 3. FT-IR spectra of (a) FAZ (b) Cu-hybe complex encapsulated FAZ (c) Ni-hybe complex encapsulated FAZ (d) Zn-hybe complex encapsulated FAZ.

The peak at 1637 cm^{-1} is due to the N-H out of plane stretching frequency of R-CO-NH-R attached to a six – membered ring in the ligand. The band at 1597 cm^{-1} is due to aromatic C-C stretch. The peak at 1243 cm^{-1} is attributed to aromatic C-O stretching frequency. The C-N stretching frequency is observed at 1159 cm^{-1}. The band at 751 cm^{-1} is attributed to ortho di substituted C-H out of plane stretching frequency.

The IR spectrum of the ligand shows three sharp peaks at 1641, 1547 and 1252 cm^{-1} due to amide I, II and III modes respectively [21]. Amide I band arises because of υ(C=O) mode, while amide II and III arise because of υ(C-N) and υ(N-H) bending modes. All the three bands are shifted to a lower frequency in the encapsulated complexes indicating the coordination of amide nitrogen to the metal ion. The υ(N-H) peak at 3377cm^{-1} for the free ligand is shifted to a lower frequency for the encapsulated metal complexes which shows the formation of metal complexes [22]. A broad band appearing at 2300-2600 cm^{-1} in the ligand due to intramolecular hydrogen bonding between the

phenolic OH and amide CO is absent in the complexes. This shows that there is breaking of hydrogen bonding during complex formation.
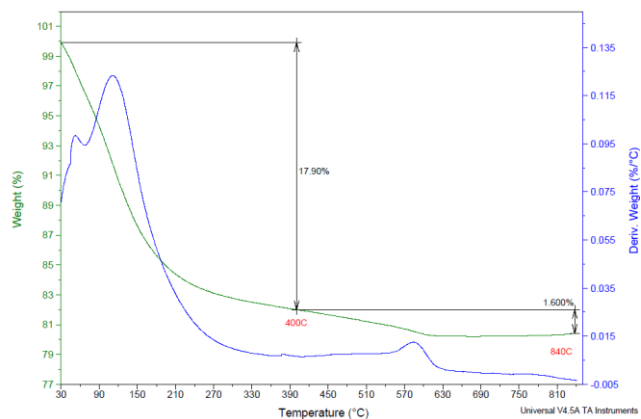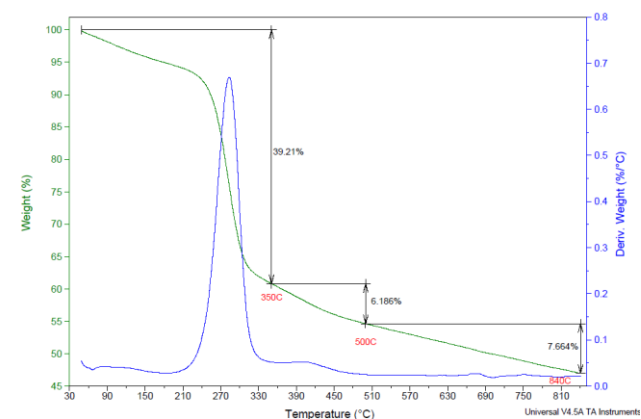

Fig. 4. Thermo gram of FAZ.

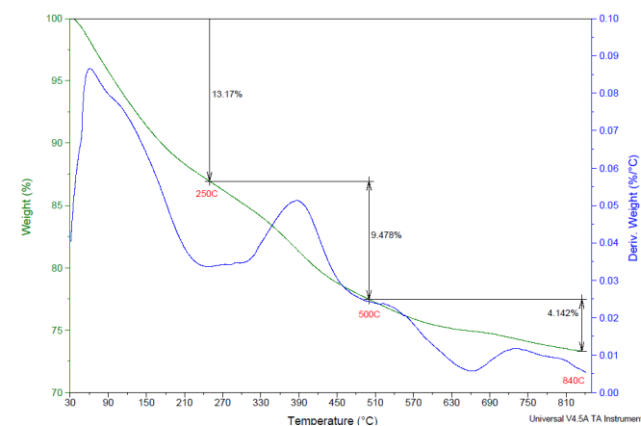**Fig. 5.** Thermo gram of Cu-hybe encapsulated FAZ.

Fig. 6. Thermo gram of Ni-hybe encapsulated FAZ.

Cation exchange capacity (CEC)

The CEC was calculated as per the method reported in literature [23]. The zeolite prepared has high cation exchange capacity. The CEC of raw fly ash was found to be 0 meq/100g while that of FAZ was estimated consistently to be 457 meq/100g which is a high value when compared with literature [24, 25]. The process of zeolitization

improves the CEC of fly ash drastically which enables a hike in the exchange of metal ions.

Thermal studies

Thermo gravimetry is a better tool to confirm the loading of the complexes in the zeolite cavities. The thermo grams of FAZ and that of the metal complexes encapsulated FAZ are given in **Fig. 4-7**. The TGA data of the encapsulated complexes along with the percentage weight loss at different steps and their assignments are summarized in **Table 2**.
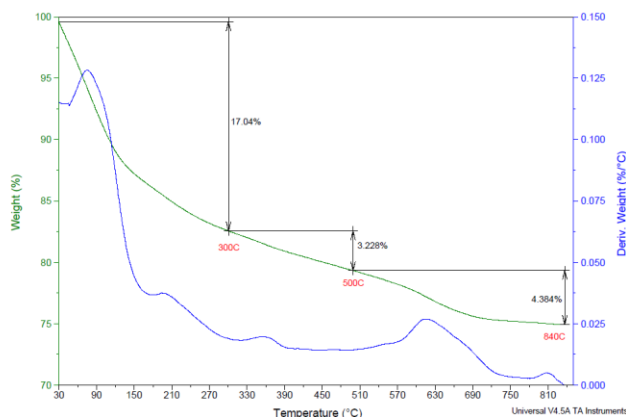

Fig. 7. Thermo gram of Zn-hybe encapsulated FAZ.

Table 2. Thermo gravimetric analysis data of metal complex encapsulated FAZ.

Catalyst	Temperature range(^{0}C)	Loss (weight %)	Group lost
FAZ	100-400	17.9	nH_2O
	300-500	-	-
[Cu(hybe)]-Y	100-350	39.21	nH_2O + Coordinated water molecule in the complex
	350-500	6.19	Ligand
	500 -840	7.66	Structural OH group
[Ni(hybe)]-Y	99-300	17.04	nH_2O
	300-500	3.23	Ligand
	500 -840	4.38	Structural OH group
[Zn(hybe)]-Y	99-300	17.04	nH_2O
	300-500	3.23	Ligand
	500 -840	4.38	Structural OH group

The thermal decomposition of the complexes occurs in two major steps. The first weight loss of 13-39% occurs in the temperature range 100-350^{0}C owing to the presence of intra-zeolite water [**26**]. Though all the complexes were dried at 150^{0}C for constant weight, it is expected that even at this temperature intra-zeolite water will remain in the complexes. The weight loss of 3-10% starts immediately after the first step and is due to the slow decomposition of the ligand. A very small percent weight loss indicates the presence of only a small amount of the metal complex in the zeolite matrix. This is in agreement with the low

percent metal content estimated by atomic absorption analysis. This second weight loss due to the decomposition of the complex is absent in the thermo gram of the zeolite which is further evidence for the encapsulation of the metal complexes. The third weight loss which is observed around 500-840^{0}C for the encapsulated metal complexes corresponds to % weight loss of structural hydroxyl group [**27**].

Scanning electron microscopy

The scanning electron micrographs (SEM) of the zeolite encapsulated complexes indicate the presence of well defined zeolite crystals without any shadow of metal ions or complexes present on their external surface. The prominent difference in SEM image of the zeolite from that of the metal complex encapsulated zeolite is further an evidence for the encapsulation of metal complexes. The representative photographs are shown in **Fig. 8**.
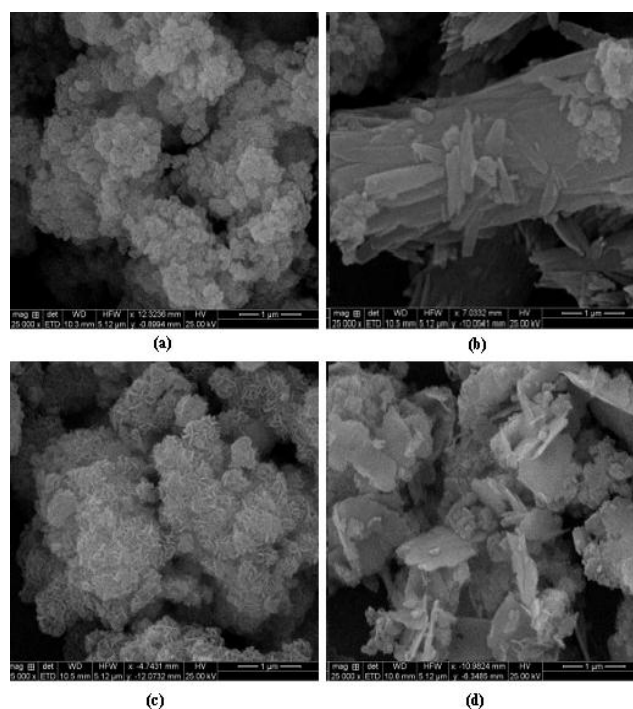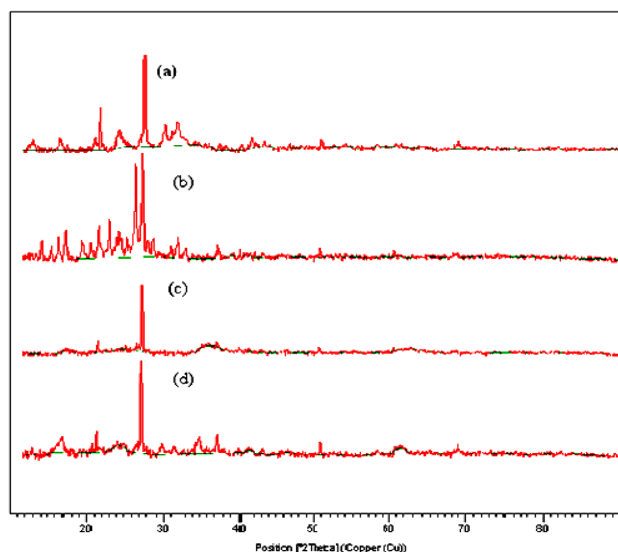

Fig. 8. Scanning electron micrographs of a) fly ash zeolite (b) Cu- hybe encapsulated FAZ (c) Ni- hybe encapsulated FAZ and (d) Zn- hybe encapsulated FAZ.

The SEM image of FAZ shows agglomeration of rough spheres of undefined shape with no observation of crystal formation confirming the formation of zeolites from fly ash [**28-30**]. An uniform orientation and morphology can be observed. **Fig. 8b** shows the encapsulation of sheet like Cu - hybe complexes amidst the rough spherical agglomeration of zeolites. **Fig. 8c** and **8d** show the inclusion of knitted spherical Ni - hybe complex and leaf – like Zn - hybe complexes in the spherical agglomeration of the zeolite. The sizes of the spherical structures remain unaffected indicating that there is no change in the zeolite framework after the encapsulation of the complexes.

X-ray powder diffraction study

The X-ray powder diffraction (XRD) patterns of zeolite, and the complexes of M-hybe [M=Cu(II), Ni(II) and Zn(II)] were recorded at 2θ values between 0 and 90^0 and are represented in **Fig. 9**. The FAZ and the complexes have main peak at 2θ value ~26.60. Some additional peaks are observed in the metal complexes encapsulated zeolites. The changes in XRD patterns are attributed to the loading of the complexes in the structural framework of zeolites which is reflected in the change in the position of the peaks. Similar diffraction patterns are observed for all the encapsulated complexes, except little change in the relative peak intensities. This indicates that the crystallinity of the zeolite matrix remains intact and does not suffer any major structural modifications upon encapsulation of the metal complex [**31**]. Due to the poor loading of the complexes during encapsulation no intense new peaks are detected [**32, 33**] and the frame work remains intact.

The 3 prominent peaks observed in XRD in the order of intensity are given in **Table 3**. It is difficult to exactly identify the peaks due to the presence of many metal oxides although it was reported [**14**] to be X- type zeolite.

Fig. 9. XRD pattern of a) fly ash zeolite; b) Cu- hybe encapsulated FAZ; c) Ni- hybe encapsulated FAZ and d) Zn- hybe encapsulated FAZ.

Table 3. Prominent peaks in XRD.

Complex	2θ values
FAZ	26.73, 20.79, 29.41
Cu-hybe	26.58, 25.60, 22.18
Ni-hybe	26.62, 20.83, 50.20
Zn-hybe	26.66, 20.89, 36.57

UV-Vis spectroscopy

The absorbance of the different complexes was measured by leaching the complex with dil. H_2SO_4 and presented in **Fig. 10**. The electronic spectrum of the ligand shows two bands at 303 and 239 nm due to n→Π* and Π→ Π* transitions of the phenolic group respectively. In the encapsulated metal complexes these bands appear at a relatively lower wavelength which suggests the association of the ligand with the metal ions [**33**]. The band around 217 nm is due to φ → φ* transition which is attributed to the presence of benzene ring. These three bands that are characteristic for the free ligand are observed after leaching the metal complexes from the zeolite matrix [**34**]. The band due to LMCT or d-d transition could not be located. The same trend has been reported in literature in the case in the case of commercial zeolites [**21**].

Atomic absorption spectrometry

500 mg of each metal complex encapsulated zeolite was dissolved in 20 mL hydrofluoric acid (40%) and was analyzed by atomic absorption spectrometer. The report shows the presence of the corresponding metal ions, (Cu: 92.57 ppm, Ni: 417.88 ppm and Zn: 325.53 ppm), in the solution which further proves the encapsulation of the metal complex in the zeolite.
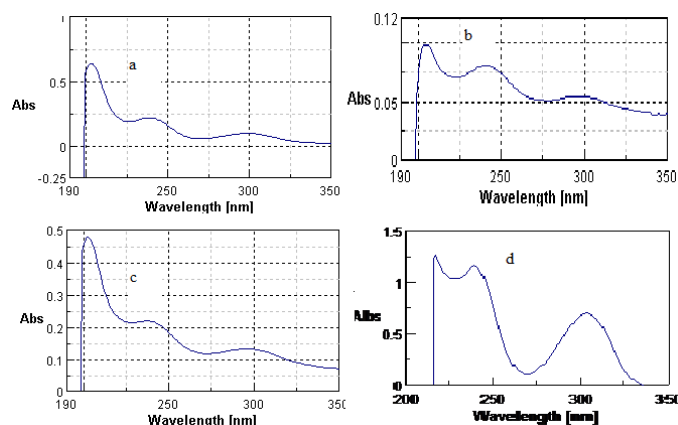

Fig. 10. UV-Vis Spectra of a) Cu- hybe complex b) Ni- hybe complex d) Zn- hybe complex and d) hybe ligand.

Catalytic activity studies

The catalytic activity towards the hydroxylation of phenol was carried out in a 50 mL flask fitted with a Liebig condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (5.67g, 0.05mol) and phenol (4.7g, 0.05mol) were mixed in 2 mL CH_3CN and the reaction mixture was heated at 80^{0}C with continuous stirring in an oil bath [**35**]. An appropriate catalyst (0.025g) was added to the reaction mixture. The products were identified to be catechol using GC auto integrated with Mass Spectrometer. Catechol had a retention time of 33.25 while phenol had a retention time of 77.52 [**36**]. The % phenol conversion to catechol for the encapsulated complexes is in the order: Cu-hybe : 71.89 > Ni- hybe : 56.62 > Zn- hybe : 38.34.

Conclusion

Fly ash zeolite was synthesized from coal fly ash and metal complexes have been successfully encapsulated in this zeolite and characterized by FT-IR, XRD, TGA, SEM, UV-Vis and AAS. All these reports clearly show the encapsulation of metal complexes in the framework of the zeolite. These encapsulated complexes have been further

used as a catalyst in the hydroxylation of phenol and the product has been identified by Gas Chromatography. This work paves a new space for the utilization of fly ash and this catalyst can be used in fine chemical industries.

Reference

1. Adriano, D.C.; Weber, J.; Bolan, N. S.; Paramasivam, S.; Bon-Jun Koo; K. S. Sajwan. *Water, Air, Soil Pollut.,* **2002**, *139,* 365.
   DOI: 10.1023/A:1015895922471
2. John H. B.; McCarthy, M.J. *Energy Fuels*, **2006**, *20 (6)*, 2580.
   DOI: 10.1021/ef0603028
3. Shoude, W.; Lingchao, L.; Xin, C. *Adv. Mat. Lett.,* **2011**, *2(1)*, 12.
   DOI: 10.5185/amlett.2010.9163
4. Erdem, E.; Karapinar, N.; Donat, R. *J. Colloid Interface Sci.,* **2004**, *280*, 309.
   DOI: 10.1016/j.jcis.2004.08.028
5. Rayalu, S.S.; Bansiwal, A.K.; Meshram, S.U.; Labhsetwar, N.; Devotta, S**.** *Catal. Surv. Asia,* **2006***, 10(2)*, 74.
   DOI: 10.1007/s10563-006-9011-z
6. Singer, A.; Berkgaut, V. *Environ. Sci. Technol*., **1995**, *29*, 1748.
   DOI: 10.1021/es00007a009
7. Shiegemoto, N.; Sugiyama, S.; Hayashi, H.; Miyaura, K. *J. Mater. Sci.*, **1995**, *30*, 5777.
   DOI: 10.1007/BF00356720
8. Mishra, T.; Tiwari, S. K. *J. Hazard. Mater. B,* **2006**, *137*, 299.
   DOI: 10.1016/j.jhazmat.2006.02.004
9. Inada, M.; Tsujimoto, H.; Eguchi, Y.; Enomoto, N.; Hojo, J. *Fuel*, **2005**, *84*, 1482.
   DOI: 10.1016/j.fuel.2005.02.002
10. Park, M.; Choi, C.L.; Lim, W.T.; Kim, M.C.; Choi, J.; Heo, N.H. *Micropor. Mesopor. Mater.*, **2000**, *37*, 91.
    DOI: 10.1016/S1387-1811(99)00195-X
11. Querol, X.; Umana, J. C.; Plana, F.; Alastuey, A.; Solder, A. L.; Mcdinaceli, A.; Valero, A.; Domingo, M. J.; Rojo, E. G. *Fuel*, **2001**, *80*, 857.
    DOI: 10.1016/S0016-2361(00)00156-3
12. Ojha, K.; Pradhan, N. C.; Samanta, A. N. *Bull. Mater. Sci.*, **2004**, *27*, 555.
    DOI: 10.1007/BF02707285
13. Chandra, R. J.; Saji P. V; Ratnasamy; P. *Appl. Catal., A*, **1998**, *168(2)*, 353.
    DOI: 10.1016/S0926-860X(97)00365-7
14. Abraham, R.; Yusuff, K. K. M. *J. Mol. Catal. A: Chem.*, **2003**, *198*, 175.
    DOI: 10.1016/S1381-1169(02)00687-8
15. Maurya, M. R.; Saklani, H.; Kumar, A.; Chand, S. *Catal. Lett.*, **2004**, *93*, 121.
    DOI: 10.1023/B:CATL.0000016959.93948.d7
16. Das, N. N.; Satapathy, P. K.; Dash, S. C.; Mohanty, P. *React Kinet Mech Cat***, 2011,** *102(2)*, 367.
    DOI: 10.1007/s11144-011-0282-7
17. Charles A. G. *Eur J Mineral,* **2012***, 24(3),* 439.
    DOI: 10.1127/0935-1221/2012/0024-2176
18. Murayama, N; Tanabe, M; Yamamoto, H; Shibata, J. *Mater. Trans,* **2003***, 44(12),* 475.
    DOI: 10.2320/matertrans.44.2475
19. Davidova, M.; Nachtigallova, D; Bulanek, R; Nachtigall, P. *J. Phys. Chem. B*, **2003**, *107 (10)*, 2327.
    DOI: 10.1021/jp026989o
20. Gupta, N.; Kushwaha, A.K.; Chattopadhyaya, M.C. *Adv. Mat. Lett.*, **2011**, 2(4), 309-312
    DOI: 10.5185/amlett.indias.201
21. Maurya, M. R.; Titinchi, S. J. J.; Chand, S. *Catal. Lett.*, **2003**, *89*, 219.
    DOI: 10.1023/A:1025706529969
22. Maurya, R. C.; Rajput, S. *J. Mol. Struct.*, **2004**, *687***,** 35.
    DOI: 10.1016/j.molstruc.2003.08.023
23. Kolay, P.K.; Singh, D.N.; Murti, M.V.R. *Fuel*, **2001**, *80*, 739.
    DOI: 10.1016/S0016-2361(00)00135-6
24. Amrhein, C.; Haghnia, G. H.; Kim, T. S.; Mosher, P. A.; Gagajena, R. C.; Amanios, T.; Torre, L. D. L. *Environ. Sci. Technol.*, **1996**, *30*, 735.
    DOI: 10.1021/es940482c
25. Berkgaut, V.; Singer, A. *Appl. Clay Sci.*, **1996**, *10*, 369.
    DOI: 10.1016/0169-1317(95)00033-X
26. Ren, Y. W.; Li, J.; Zhao, S. M.; Zhang, F. X. *Struct. Chem.*, **2005**, *16*, 439.
    DOI: 10.1007/s11224-005-6353-5
27. Hemvichian, K; Laobuthee, A.; Chirachanchai, S; Ishida, H. *Polym. Degrad. Stab.*, **2001**, *76(1)*, 1.
    DOI: 10.1016/S0141-3910(01)00260-9
28. Mimura, H.; Yokota, K.; Akiba, K.; Onodera, Y. *J. Nucl. Sci. Technol*., **2001**, *38(9)*, 766.
    DOI: 10.1080/18811248.2001.9715093
29. Belviso, C.; Cavalcante, F; Fiore, S. *Waste Manage. (Oxford)*, **2010**, *30(5),* 839.
    DOI: 10.1016/j.wasman.2009.11.015
30. Pengthamkeerati, P.; Satapanajaru, T.; Chularuengoaksorn, P. *Fuel*, **2008**, *87*, 2469.
    DOI: 10.1016/j.fuel.2008.03.013
31. Modi, C.K.; Parthiv M. T. *Adv. Mat. Lett.* **2012**, *3(2)*, 149.
    DOI: 10.5185/amlett.2011.10313
32. Kozlov, K.; Asakura; Iwasawa, Y. *J. Chem. Soc., Faraday Trans.*, **1998**, *94*, 809.
    DOI: 10.1039/a706679a
33. Chavan, S. A..; Srinivas, D.; Ratnasamy, P. *Chem. Commun.*, **2001**, *12*, 1124.
    DOI: 10.1039/b102016c
34. Hu; Xile; Meyer; Karsten *Inorg. Chim. Acta*, **2002**, *337*, 53.
    DOI: 10.1016/S0020-1693(02)01079-4
35. Seelan, S.; Sinha, A.K. *Appl. Catal., A*, **2003**, *238*, 201.
    DOI: 10.1016/S0926-860X(02)00350-2
36. Maurya, M.R.; Titinchi, S.J.J.; Chand S., Mishra I.M. *J. Mol. Catal. A: Chem.*, **2002**, *180*, 201.
    DOI: 10.1016/S1381-1169(01)00435-6