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Synthesis, characterization and catalytic activity of transition metal complexes of ascorbic acid encapsulated in fly ash based zeolite

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ABSTRACT

A new route for the utilization of fly ash has been formulated. X-type zeolite has been synthesized from fly ash by alkali fusion followed by hydrothermal treatment. Ascorbic acid was used as a ligand for the synthesis of metal complexes of copper, nickel and vanadium encapsulated in the super cages of fly ash based zeolite (FAZ) by flexible ligand method and characterized by FTIR, XRD, Atomic Absorption Spectrometry (AAS), Ultra Violet–Visible spectroscopy and Thermo gravimetric analysis (TGA). The additional peaks corresponding to that of the complex have been observed which confirms the loading of the metal complexes in the zeolite cavities. The shifting of C=C-O stretching frequency found at 682 cm^{-1} in ascorbic acid to 601 cm^{-1} confirms the co-ordination of the ligand resulting in the formation of the metal complex. The thermo grams show deflation in three regions corresponding to the loss of the intra-zeolite water, metal complexes and the structural –OH group respectively. The catalytic activity of these complexes towards the liquid phase hydroxylation of phenol with hydrogen peroxide has been established. The extent of the reaction as a function of time has been investigated. Vanadium-ascorbate complex had the highest conversion of 78%. The product was identified as hydroquinol by GC-MS. This study reports a highly attractive catalytic method for the preparation of hydroquinol from phenol using aqueous hydrogen peroxide as the oxidising agent which is industrially significant. Copyright © 2013 VBRI press.

Keywords: Fly ash; zeolite; hydrothermal treatment; flexible ligand method; hydroxylation of phenol.

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Introduction

The whole world is aiming at a cleaner technology for power production as an alternative to coal-fired power plants. Though nuclear technology has been developed to produce power, disposal of nuclear wastes is still a hazardous issue and the risks involved with nuclear power production is alarming. Hence, coal fired power stations are in the run and they generate a very huge amount of ultra-fine fly ash as waste **[1]**. In India, fly ash is being generated at the rate of 120 million tonnes per annum and 65,000 acres of land being occupied by ash ponds. Fly ash has been utilized in many ways such as concrete production, as a substitute material for Portland cement and sand **[2]**, in embankments and other structural fills usually for road construction, waste stabilization and solidification, cement clinkers production (as a substitute material for clay), mine reclamation **[3],** stabilization of soft soils, as aggregate substitute material in brick production, and so on. Though fly ash has been utilized in so many ways, still huge amounts of fly ash are being dumped in landfills **[4]** and utilization of fly ash is a pressing issue. Fly ash has been utilized in the synthesis of zeolites since they contain silica and alumina **[5].** 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]**. Zeolites are aluminosilicates that consist of AlO_4 and SiO_4 tetrahedra connected by mutual sharing of oxygen atoms and characterized by pore openings of uniform dimension. Zeolites have wide application as molecular sieves **[11]**, soil conditioners **[12]**, in water purification **[13]**, as catalysts **[14]**, and adsorbents **[15]**.

Several reports focus on the conversion of fly ash to zeolite by hydrothermal treatment. Hydrothermal treatment involves the dissolution of highly polymerised Si and Al present in fly ash in an alkaline solution, followed by crystallisation to form the ring like structures that are necessary for zeolite construction. The high percentage of aluminosilicates in fly ash makes them a cheap and readily available source of Si and Al for zeolite synthesis. The low Si/Al ratio of fly ash allows for the synthesis of low Si zeolites, which have a high cation exchange capacity, high affinity towards polar molecules and a large pore volume **[16]**.

Homogeneous catalysts can offer high molar catalytic efficiencies and rates under mild conditions, tolerance to many types of organic functionality and high selectivity in reactions that allow formation of specific desired reaction product. Heterogeneous catalysts are usually more robust (insensitive to air and moisture), easy to handle and can be completely removed from the reaction easily. An ideal catalyst would possess the beneficial aspects of both homogeneous and heterogeneous systems. Towards this objective, significant work has been expanded in an attempt to develop homogeneous catalysts that have been anchored to a solid support though it is associated with multiple practical difficulties. Encapsulation of transition metal complexes in zeolites and related materials has gained much attention since they possess both homogeneous and heterogeneous catalytic characters. The rigid inorganic zeolite framework defines the reaction cavity surrounding the active sites of the transition metal complexes. Though the encapsulation of transition metal complexes in zeolites have been established as good catalysts, the replacement of commercial zeolites by FAZ has gained only little attention. Recently, encapsulation of N,N′-ethylenebis(salicylamide) metal complexes in fly ash based zeolite was reported and these complexes have been found to catalyze the liquid phase hydroxylation of phenol with hydrogen peroxide **[17].** Up to now, hydroxylation of phenol with hydrogen peroxide as the oxidant has become the most general way to obtain diphenols owing to its environmental acceptability. The activity of the encapsulated transition metal complexes is different from that of the neat complexes since the selectivity is altered in a constrained environment [**18-20**]. Results from the present study seems promising enough to introduce the transition metal complexes encapsulated zeolites as catalysts for the liquid phase hydroxylation of phenol. However, more investigations are recommended to confirm the industrial applicability of the obtained results, especially concerning the total efficiency and economics.

This work involves the (i) the synthesis of zeolite from fly ash (ii) characterization of the synthesized FAZ (iii) encapsulation of transition metal-ascorbate complexes in the zeolite cavities by flexible ligand method (iv) characterization of the encapsulated metal complexes using various analytical techniques (v) establishment of the catalytic activity of the encapsulated metal complexes towards hydroxylation of phenol as a function of time.

Experimental

Materials

F-type coal fly ash sample was collected from electrostatic precipitators of Tuticorin Thermal Power Station (TTPS), Thoothukudi, Tamilnadu, India. The sample contained both amorphous (mainly SiO_2 and Al_2O_3) and crystalline components (mainly quartz and mullite). L- Ascorbic acid of 99.5% assay was purchased from Spectrochem, Mumbai, India. Metal nitrates $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$ of 99.0% assay were obtained from Fischer, Chennai, India. $VOSO_4.5H_2O$ of 98% assay was obtained from Ottokemi, Mumbai, India.

Physical methods of analysis

FTIR spectra were recorded as KBr pellet on a Perkin-Elmer FT-IR spectrophotometer. XRD patterns were recorded in PANalytical model X'pert PRO using CuKα (2.2 KW) source and X'celerator (semiconductor) detector. The metal contents were measured using Varian Model Spectraa 220 Atomic Absorption Spectrophotometer. GC analysis was carried out in GC-MS Agilent 6890 instrument fitted with FID dector and DB-35MS (30mx0.25mmx0.25µm), capillary column using He as the carrier gas at a constant flow rate of 2.0 mL/min. The initial temperature was maintained at 100^0C for 2 minutes and raised at the rate of 10^0C per minute up to a temperature of 310^0C. The injection volume was 2.0 µL. 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 100C per minute. To study the surface morphology, SEM images were recorded using ESEM Quanta 200, FEI instrument. XRF analysis was carried out using Alcatel X-ray Fluorescence Spectrometer Model ASM 100 T instrument at National Geophysical Research Institute, Hyderabad. The textural properties of the FAZ were determined by Nitrogen Adsorption isotherms measured on a Carlo–Erba sorptometer (Model 1800). Prior to the adsorption measurements, the sample was activated at 373K for 12 h, in high vacuum. After evacuation, the samples was cooled at room temperature and weighed. The sample was cooled to 78K using liquid Nitrogen and then Nitrogen was allowed to adsorb on them. The volume of Nitrogen adsorbed (at STP) and the BET surface areas were then measured.

Synthesis of zeolite

X-type zeolite was synthesized from F-type fly ash based zeolite was synthesized from F-type fly ash using hydrothermal method of synthesis **[21].** This involves the dissolution of Al-Si bearing fly ash phases with NaOH and subsequent precipitation of the zeolitic material. The composition of fly ash was established by XRF analysis. The high silica and alumina content of fly ash revealed the possibility of synthesising zeolite from fly ash. The following methodological conditions were applied. The raw fly ash samples 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(±10^{0}C) for 2 hours. Fly ash samples were further treated with hydrochloric acid to increase its catalytic activity in in zeolite formation. A mixture of sodium hydroxide and fly ash (calcined and HCl treated) in the 1:1 ratio (by weight) was ground and fused at 550^{0}C for 1 hour in a silica crucible. The product obtained after the fusion process were cooled to room temperature, ground further and dissolved in water (10g fly ash / 100 mL water). The slurry thus obtained was agitated mechanically for 8 hours. Crystallisation of the sodium aluminosilicate gel thus obtained was then performed under static condition of 90^{0}C in an oven for 6 hours without any disturbance. The resultant precipitate was washed several times with distilled 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.

Preparation of metal exchanged zeolite, M-X; [M=Cu(II), Ni(II) and V(IV)]

About 1.0 g of fly ash zeolite [FAZ] was suspended in 100 mL of 0.1 M metal salt solutions [Nitrates of Cu(II), Ni(II) and Vanadyl sulphate]. 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 3 hours at 150^{0}C in an air oven.

Preparation of [M (Asc)-X]

The encapsulated complexes were prepared by flexible ligand method. About 1.0 g of metal ion exchanged zeolite [M= Cu(II), Ni(II) or V(IV)] and 2.5 g of ascorbic acid were mixed in 50 mL acetonitrile in a flask and the reaction mixture was heated at reflux for ca.15 hours while stirring magnetically. After cooling, the slurry was Soxhlet extracted with dichloromethane (ca.48 hours) to leach out any free ligand or metal complex adhering to the surface of the zeolite. The uncomplexed metal ions on the surface were further 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 metal complexes of Cu(II), Ni(II) and V(IV) with ascorbic acid[Cu-Asc, Ni-Asc and V-Asc] were dried at 150^{0}C for 5 hours till constant weight was achieved.

Results and discussion

The silica and alumina present on fly ash exist as soluble sodium aluminosilicates after the fusion with sodium hydroxide and subsequent treatment with water. Formation of zeolite is highly dependent on the temperature and the concentration of alkali medium used. Crystallisation of zeolitic material occurs through nucleation of aluminosilicate ions and crystal growth. Nucleation depends on alkalinity; therefore high concentration of alkali is used in the zeolitisation process to ensure the complete dissolution of silica and alumina of coal fly ash.

In aqueous solution ascorbic acid **(Fig. 1a)** behaves as a weak dibasic acid, which dissociates in two steps: $H_2Asc \leftrightarrow H^+ + HAsc^-$; $HAsc^- \leftrightarrow H^+ + Asc^{2-}$. The dissociation constants of ascorbic acid have been reported as $K_1=6.77x10^{-5}$ ($pK_1=4.17$) and $K_2=6.2x10^{-5}$ ($pK_2=11.57$) **[22]**. At pH 9 of the reaction mixture, ascorbic acid mainly exists as $HAsc^-$. Ascorbic acid was reported to coordinate with the metal ions through oxygen atoms at C-2 and C-3 positions **[23]** and also through C-2 and C-5 positions **[24]**. Spectroscopic evidences suggest that in aqueous solution, ascorbate anion chelates with metal ions through the O-3 and O-2 atoms of ascorbic acid **[25]**. The enolised form of ascorbic acid acts as a bidentate ligand **[26]**. Literature reveal six- coordinate geometries (octahedral) for metal ascorbic acid complexes **[27]**. The bidentate nature of ascorbic acid **[28]** ensures coordination through the carbonyl group and the oxygen atom of carbon 2-enolic group. The remaining two axial positions are expected to be loosely bound by two silanolic-OH groups from the zeolite matrix. Thus a distorted octahedral geometry is expected.

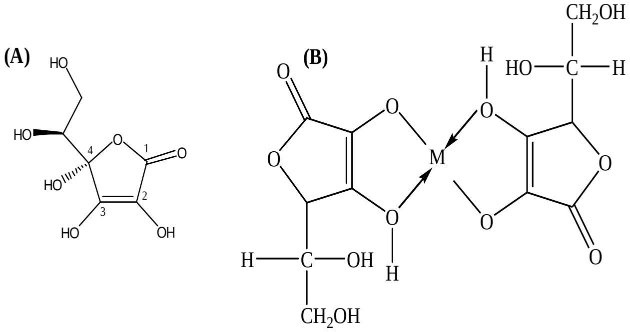

Fig. 1. (A) Structure of ascorbic acid and (B) Structure of metal-ascorbate complex.

Fourier transform infra-red spectroscopy

Infra-red spectroscopy can yield information concerning structural details of the zeolite. The IR spectrum of zeolites 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 FTIR spectra of the as prepared FAZ and the corresponding zeolite encapsulated metal complexes are presented in the **Fig. 2**. The most intense band at 983 cm^{-1} is assigned to an asymmetric stretching of Si-O-Al **[29, 30]**. The mid infra red region of the spectrum contains the fundamental framework vibration of $Si(AlO_4)$ groupings. The band at 1112 cm^{-1} (980 cm^{-1}-1320 cm^{-1}) represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks. The band at 3337 cm^{-1} (weak to medium) is attributed to the stretching vibrations of O-H group suggesting the presence of possibly hydrated aluminium silicates. The bands at 1651 cm^{-1} and 1404 cm^{-1} are attributed to the bending mode of water molecules **[31, 32].** All these observations confirm the formation of zeolites on alkali treatment of fly ash.

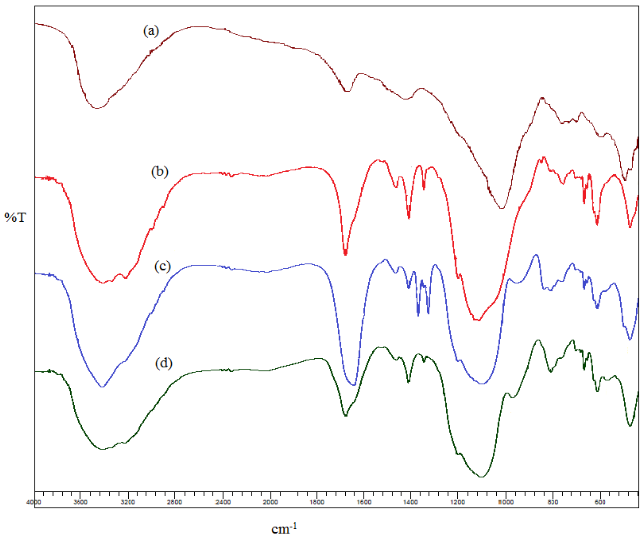

Fig. 2. FT-IR spectra of (a) FAZ (b) Cu-Asc encapsulated FAZ (c) Ni-Asc encapsulated FAZ (d) V-Asc encapsulated FAZ.

The loading of the metal complexes in the pores of zeolites can be confirmed by the additional peaks observed in their FT-IR spectra. Three additional peaks are observed around 3400 cm^{-1} region in the spectra due to the incorporation of –OH groups from metal ascorbate complex in the zeolite. The vibration around 1668 cm^{-1} along with a hump at 1653 cm^{-1} is due to the C=C stretching frequency of the five membered ring **[33],** this frequency is less than that in the ascorbic acid (1674 cm^{-1}) indicating the involvement of enolic -OH group in the formation of metal complexes. The peak at 1336 cm^{-1} is due to the C-O stretching frequency in ascorbic acid **[34].** The most intense band at 968 cm^{-1} is assigned to an asymmetric stretching of Si-O-Al for FAZ which has merged with the C-C and C=C stretching of ascorbic acid which has been confirmed by the broadening of the band **[35]**. The C=C-O stretching frequency found at 682 cm^{-1} in ascorbic acid has shifted to 601 cm^{-1} due to the co-ordination of ascorbic acid with the metal ion to form the metal complex. All the bands of ascorbic acid have shifted to a lower frequency in the encapsulated complexes indicating the coordination of ascorbic acid to the metal ion **[36].**

Cation exchange capacity (CEC)

The CEC was calculated as per the method reported in the literature **[37]**. 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 to be 457 meq/100g which is a high value when compared with literature **[38, 39].** Zeolitisation of fly ash has gained considerable attention owing to the enormous increase in cation exchange capacity.

Surface area and pore size distribution of fly ash zeolite

Typical Nitrogen adsorption isotherm along with the pore size distribution has been presented in **Fig. 3**. The adsorption/desorption isotherm of Nitrogen for FAZ represents Type I **[40].** Since adsorption increases within a range, it indicates a definite growth in the number of micropores, which is one of the defining features of zeolitic materials.

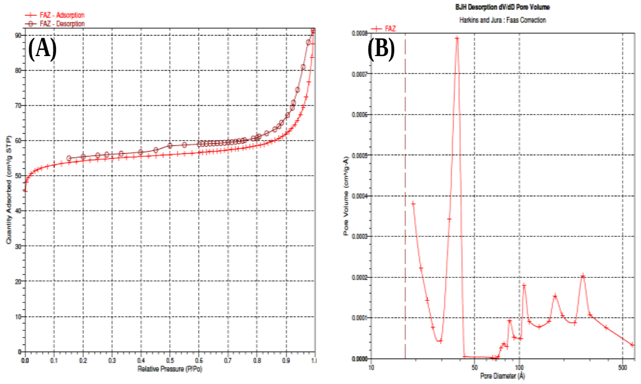

Fig. 3. (A) BET isotherm linear plot and (B) BJH desorption dA/dlog(D) Pore area.

Table 1. XRF analysis of fly ash and FAZ.

Constituent	Fly ash	Fly ash zeolite
SiO_2	57.23	50.28
Al_2O_3	31.30	22.98
Fe_2O_3	4.72	3.83
MnO	0.02	0.03
MgO	0.62	1.14
CaO	1.19	1.16
Na_2O	0.56	14.56
K_2O	1.34	1.36
TiO_2	1.84	2.56
P_2O_5	0.93	0.03

The inflection in the Nitrogen isotherm around P/P_0= 0.8-1.0 becomes sharper indicating narrower and uniform pore size distribution. The surface area and pore diameter have been acquired from the Nitrogen adsorption isotherm data. A surface area of 172.83 m^2/g and pore volume of 0.014 cm^3/g clearly indicates that the material has a high order pore system. On the basis of the above mentioned data and in reference to the SEM images, it can be further conjectured that the pores in the zeolites are uniform and can facilitate complexation in them. The crystallinity of the zeolites is reflected by the high surface area of the zeolites **[41].**

XRF analysis

The analysis of major and trace elements in fly ash zeolite by X-ray fluorescence is made possible by the behaviour of atoms when they interact with radiation. The sample was additionally pulverised, homogenised and pressed into pellet with chromatographic cellulose as binder. XRF analysis data of fly ash and FAZ are tabulated in **Table 1**.

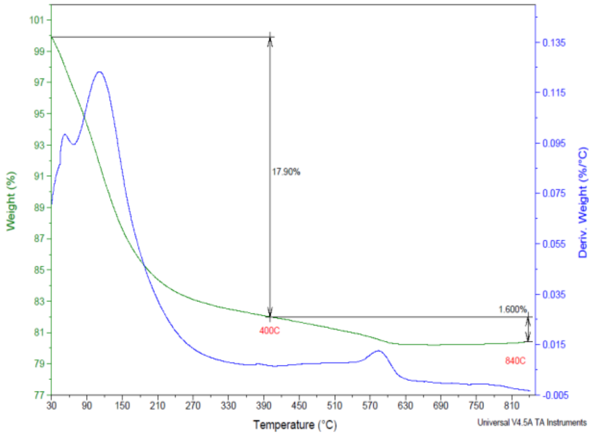

Fig. 5. Thermo gram of FAZ.

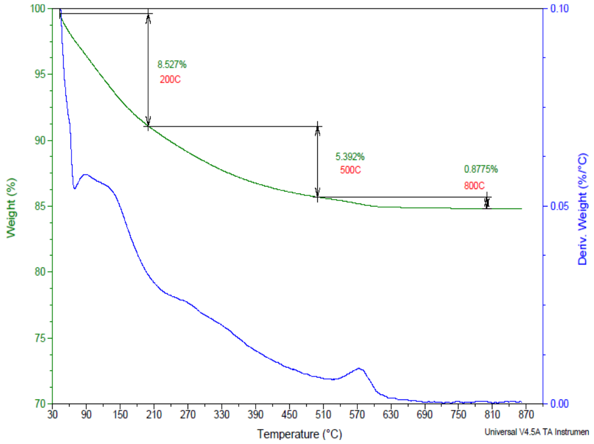

Fig. 6. Thermo gram of Cu-Asc encapsulated FAZ.

Thermal studies

The thermo grams of FAZ and all the encapsulated complexes are given in the **Figs. 5-8**. The thermal decomposition of the complexes occurs in two major steps. The first weight loss of up to 10% occurs in the temperature range 100-200^{0}C owing to the presence of intra-zeolite water **[42].** 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 5-17% starts immediately after the first step is due to the slow decomposition of the metal complex encapsulated in the zeolite matrix. 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 an evidence for the encapsulation of the metal complexes. The decomposition of ascorbic acid has been reported around 220^{o}C **[43].** The second weight loss is observed between 200-500^{o}C which clearly shows the decomposition of ascorbic acid in this temperature range. The third weight loss which is observed around 500 to 800^{0}C for the encapsulated metal complexes corresponds to % weight loss of structural hydroxyl group **[44].**

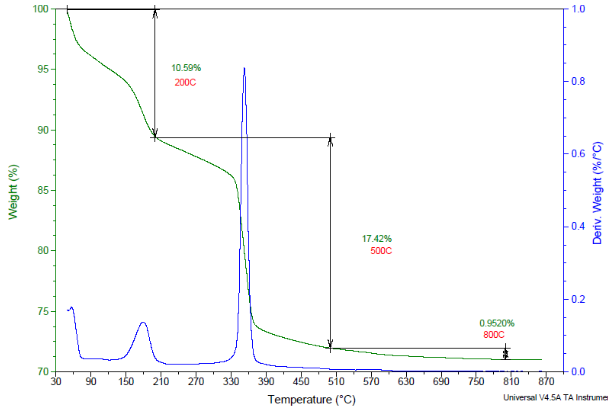

Fig. 7. Thermo gram of Ni-Asc encapsulated FAZ.

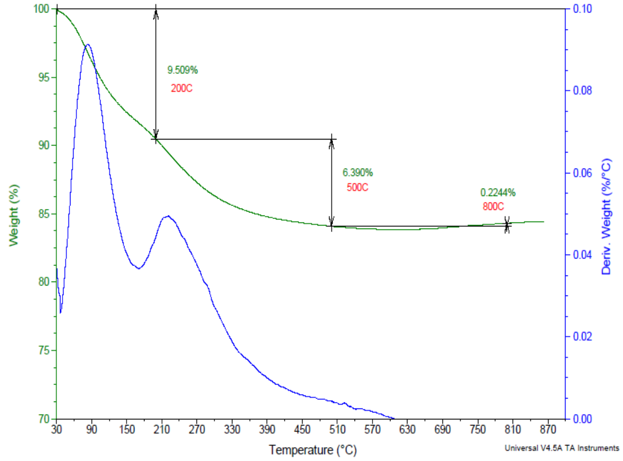

Fig. 8. Thermo gram of V-Asc encapsulated FAZ.

X-ray powder diffraction study

The X-ray powder diffraction (XRD) patterns of zeolite, and the complexes of M-Asc [M=Cu(II), Ni(II) and V(IV)] were recorded at 2θ values between 0 and 90^{0}. The XRD pattern of FAZ is represented in **Fig. 9.** It reveals an amorphous-crystalline nature. A mild amorphous plateau and intensive diffraction reflections of crystalline phases can be observed. It is established that the crystalline portion is dominant. The characteristic peaks of the following crystalline phases could be identified by comparing the literature diffraction data. The most intensive peak on the zeolite diffractogram at 2θ=26.739^{o} (d=3.334Å) and the peak at 2θ=20.081^{o} (d=4.421Å) are attributed to α-SiO_2. Hematite (α-Fe_2O_3), has diffraction peak at 2θ=36.614° (d=2.454Å). Mullite ($Al_6Si_2O_{13}$) is characterized with main diffraction peaks at 2θ=23.306° (d=3.813Å), 2θ=40.882° (d=2.207Å) and 2θ=18.259° (d=1.373Å). The reflexes situated above 55° could be addressed to mullite. As the characteristic reflexes of the different constituents are situated very closely, it is difficult to associate them undoubtedly to an exact compound **[45].** The weight losses that occur in three different regions are tabulated in **Table 2**.

Table 2. Weight losses of the FAZ encapsulated complexes in %.

Complex	100-200°C	200-500°C	500-800°C
Cu-Asc	8.52	5.39	0.87
Ni -Asc	10.59	17.42	0.95
V-Asc	9.50	6.390	0.22

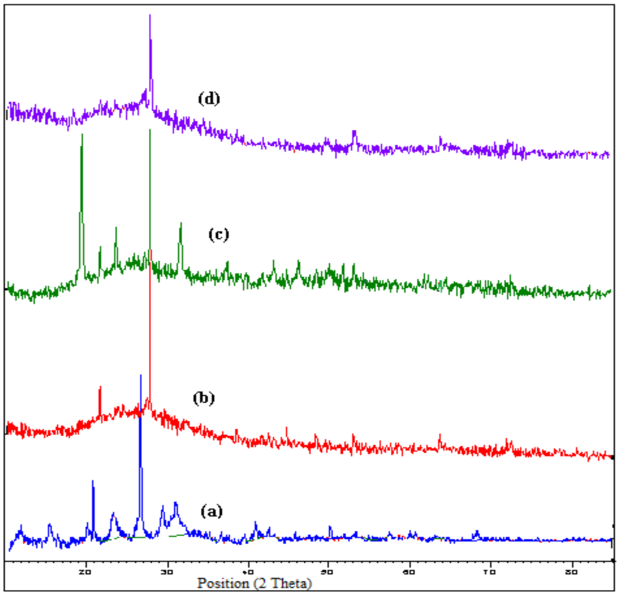

Fig. 9. XRD patterns of (a) FAZ (b) Cu-Asc encapsulated FAZ (b) Ni-Asc encapsulated FAZ (c) V-Asc encapsulated FAZ.

In the diffraction pattern, background is lower within the range 15 to 35(2θ). This phenomenon is related to crystallisation of zeolitic phase mainly from aluminosilicate glass. The XRD pattern of FAZ matches with that of Zeolite - X **[46].** XRD measurements show that the encapsulation of the metal complexes of ascorbic acid in the cavities of zeolites shows no strong influence in the structure of the zeolitic matrix which remains intact **[16].** The minor 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. Due to the poor loading of the complexes during encapsulation, no intense new peaks are detected **[47-49].**

Scanning electron microscopy

The representative SEM images are shown in **Fig. 10**. The agglomeration of rough spheres of undefined shape confirms the formation of zeolites from fly ash **[50-52].** A uniform orientation and morphology with single phase formation can be observed.

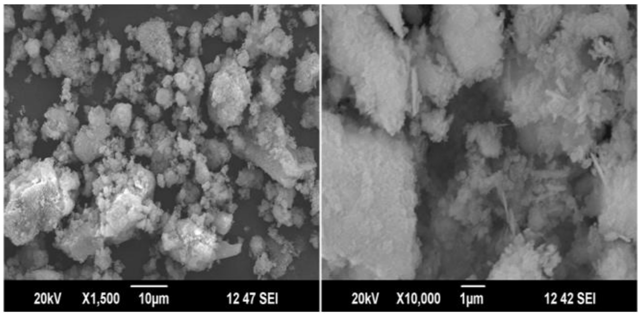

Fig. 10. SEM images of FAZ.

UV-Vis spectroscopy

The electronic spectra of the different complexes were measured by leaching the complex with dil. H_2SO_4 **(Fig. 11)**. The leached solutions are coloured due to electronic transitions by absorption of light. The bands between 200 and 250 nm are due to charge transfer transitions in the metal complexes **[53]** which is absent in the case of the ligand. Ascorbic acid shows a peak at 249 nm due to n→π^* transition of the carbonyl group. A blue shift is observed in the peak due to the complexation of the ligand **[54].**

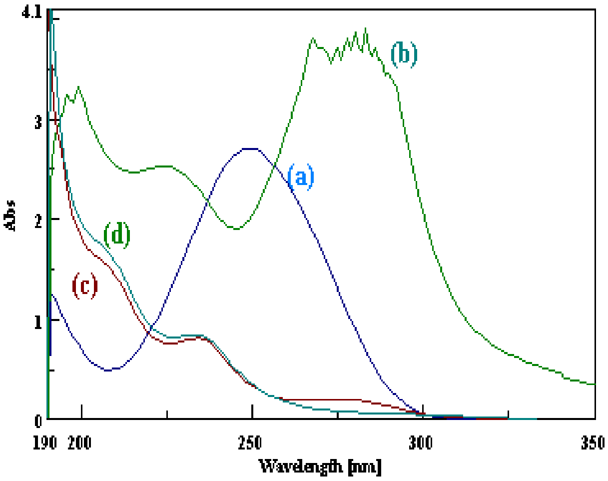

Fig. 11. UV-Vis Spectra of a) ascorbic acid ligand b) Cu-Asc complex c) Ni- Asc complex d) V-Asc complex.

The absorbance around 190 nm is due to the $\pi \rightarrow \pi^*$ transition of the C=C group. The n→ π^* transition due to the C-O in the five-membered ring is observed at 209 nm. The hump that appears around 277 nm in the case of encapsulated metal complexes arises due to the intra ligand transition **[55]**. The band due to d-d transition could not be located; the same trend is reported in the case of commercial zeolites also **[56]**.

Atomic absorption spectrometry

50.0 mg of each metal complex encapsulated zeolite was dissolved in 20 mL hydrofluoric acid (40%) and was analyzed by atomic absorption spectrophotometer. The report shows the presence of the corresponding metal ions, (Cu: 65.7 ppm, Ni: 510 ppm), in the solution which further prove the encapsulation of the metal complex in the zeolite.

Catalytic activity studies

The catalytic activity towards the hydroxylation of phenol was carried out in a 100 mL flask fitted with a Liebig condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (1.6 mL, 53.38 mmol) and phenol (0.54g, 6.16 mmol) were mixed in 5 mL CH_3CN. An appropriate catalyst (0.020g) was added to the reaction mixture and was refluxed for the stipulated time. The colour of the reaction mixture was changed to dark brown within 5 minutes before refluxion in the case of Cu-Asc and V-Asc complexes; whereas the appearance of colour was observed only after 15 minutes refluxion in the case of Ni-Asc. The products were analyzed by GC-MS and identified as hydroquinol **[57].** The amount of unreacted phenol in the reaction mixture was estimated by quantitatively substituting with bromine produced from bromide and bromate in acid solution. The unreacted bromine was estimated by adding excess potassium iodide and back titrating the liberated iodine with standard sodium thiosulphate solution **[58].** The % phenol conversion to hydroquinol for the encapsulated complexes varies with time (**Fig. 12).** A higher conversion is observed with an increase in time. Maximum phenol conversion up to 78% has been observed in V-Asc complex where as 7% conversion was observed in the absence of catalyst signifying the high potential of these catalysts in industry.

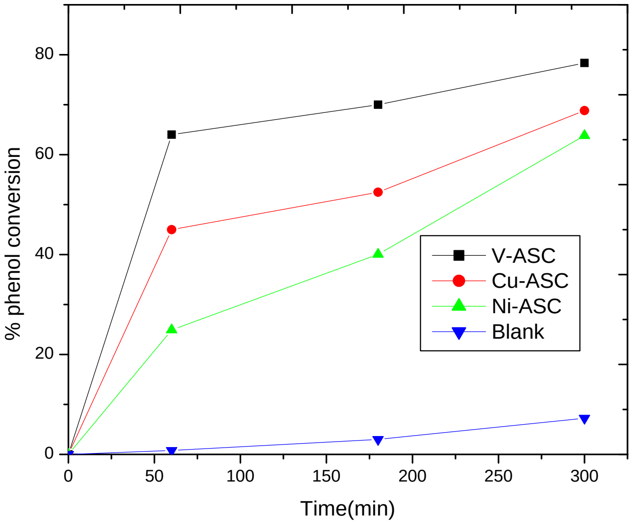

Fig. 12. Variation of % phenol conversion as a function of time.

The following criteria highlight attention to be drawn towards this catalyst: (i) The catalyst is easily and economically immobilised (ii) the immobilised catalyst displays high catalytic activity towards the postulated transformation (iii) the immobilised catalyst operates under mild conditions (iv) the catalyst is robust and (v) the catalyst can be removed efficiently from the reaction mixture easily.

Conclusion

Fly ash zeolite was synthesized from coal fly ash and metal complexes of ascorbic acid have been successfully encapsulated in this zeolite and characterized using modern analytical techniques. 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 heterogeneous catalyst in the hydroxylation of phenol and the product has been identified by Gas Chromatography. The reaction time has a strong effect on the catalytic performance and acetonitrile is the solvent of choice. This work paves a new space for the utilization of fly ash and this catalyst can be used in fine chemical industries. Despite the low volume utilisation of fly ash for zeolite production technology compared to other utilization techniques; this production technology has advantages of value addition, offering an edge over other fly ash utilisation techniques currently used. This system is likely to find wide application in both research and manufacturing aspects. However, more investigations are recommended to confirm the industrial applicability of the obtained results, especially concerning the total efficiency and economics.

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