

Synthesis of Zeolites and Their Applications in Heavy Metals Removal: A Review

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Abstract Over 800 million tonnes of coal fly ash are produced worldwide every year posing an environmental threat due to disposal problems. Nowadays the increasing interest in the synthesis of zeolites from low cost materials has prompted extensive studies on their conversion into zeolites as one of promising coal fly ash utilization methods. Zeolite synthesized from coal fly ash is a minor but interesting product, with a number of environmental applications. This paper provides an overview on the methodologies for zeolite synthesis from coal fly ash, and a description of conventional alkaline conversion processes, of synthesis of different zeolitic products and their methods of characterisation. The examination of the studies presented by different authors reveal that one of the main potential applications of zeolite materials is the uptake of heavy metals and organic pollutants such as dyes from polluted waste waters and nearly all zeolite synthesis have been driven by environmental concerns.

Keywords characterization, coal fly ash, heavy metal removal, structure, zeolites

Introduction

Zeolites are crystalline microporous materials that show interesting properties in catalysis, gas separation, and other important technological applications [1] (Corma et al, 2008). Combustion of coal in thermal power stations produces over 800 million tonnes of fly ash worldwide annually [2,3,4]. Hence disposal of such huge quantities of ash has become a problem [5,6]. The production of zeolites is one of the potential applications of fly ash in order to obtain high value industrial products with environmental technological utilization [6,7].

Presently, there are several strategies for utilisation of fly ash available which include among others cement/concrete industry and civil engineering/construction industry, [5] but most of them are leading to low volume of fly ash usage. The cost implications especially associated with transportation make it logistically difficult for fly ash to compete with other traditional raw materials in various applications [7]. Non-use of fly ash endangers surrounding surfaces and ground waters

as it can release different and potentially toxic trace and major elements during and after its transport to the dump. The coal fly ash in the environment is exposed to various influences, and solubilisation processes take place, sometimes transforming almost insoluble metals to soluble species, and leading to pollution of water and soil. Other cost effective methods of disposing coal fly ash need to be developed [9]. Fly ash is a product of burning finely ground coal in a boiler to produce electricity. It is removed from the plant exhaust gases primarily by electrostatic precipitators or bag houses and secondarily by scrubber systems [10]. Fly ash is the finest of coal ash particles formed from the mineral matter in coal, consisting of the non combustible matter in coal plus a small amount of carbon that remains from incomplete combustion.

Heavy metals in waste water have emerged as the focus of environmental remedial efforts because of their toxicity and threat to human beings. Due to rapid growth of industrialization and urbanization with new technological advancement, the existing water resources are contaminated by discharging waste water containing organics, colour, heavy metals and so on hence, removal of toxic and heavy metal contaminates from wastewater is one of the most important environmental and economic issues [2,7,11,12]

Coal fly ash constituents vary significantly between any two producers depending mainly on the geology of the coal mine. Fly ash properties can be divided into two sets; (i) chemical, and (ii) physical. The chemical properties of fly ash are a function of both its composition and mineralogy. Fly ash mineral phases are mullite and quartz [13].

2. Zeolites synthesis from coal fly ash

Coal fly ash as a raw material for zeolite synthesis has several advantages varying from its fine particulate nature requiring no crushing or grinding, rich in aluminium and silicon present in the glass phase, hence no calcinations required as in clays. It is a low value raw material and is a largely available resource with significant unused piled reservoirs.

Many different methods of zeolite synthesis have been developed but all these methods are based on the hydrothermal alkaline conversion of fly ash where variations lead to several types of methods [10] like (i) classical alkaline conversion of fly ash; the method is based on the combination of different activation solutions /fly ash ratios, temperature, pressure and time (ii) the application of microwave to the conventional synthesis parameters which allow reduction in reaction time and (iii) a two stage synthesis procedure which allows the synthesis of greater than 90% purity zeolite products from high Si solutions resulting from a light alkaline attack of coal fly ash. [10], (iv) confined space synthesis [14].

2.1 Structure of zeolites

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals: principally sodium, potassium, magnesium, lithium, barium and calcium [15]. Zeolites are inorganic porous materials having a highly regular structure of pores and chambers that allow molecules to pass through and cause others to be either excluded or broken down. Their framework is crystalline and three dimensional networks of tetrahedra silica or alumina anions strongly bonded at all corners. The very regular structure and pore sizes give these materials a sponge-like appearance. Their pores hold water and or other molecules. Differences in zeolites arise from pore diameter, pore shape and the way these pores are interconnected. The pore size plays a significant role in the use of zeolites: allowing or prohibiting the entrance of the molecules to the system.

Following their discovery zeolites were found to be characterized by the following properties [16]. catalytic properties; high hydration propensity; stable crystal structure when dehydrated; low density and high void volume when dehydrated; and cation exchange and sorption properties. Synthesized zeolites compared to natural zeolites have several advantages such as purity, uniform pore size and better ion exchange abilities [17].

2.2 Studies on zeolite synthesis

Hollman et al., (1999) used a method by which part of the silicon in fly ash can be used for the synthesis of a maximum of 85 g of pure zeolite per kg of fly ash prior to the residual being converted into zeolite by the traditional method [18]. The cation exchange capacities ranged from 3.6 to 4.3 meq/g for the pure zeolites and from 2.0 to 2.5 meq/g for the zeolite containing residual coal fly ash. In the research by [19] hydrothermal syntheses of zeolites from coal fly ash were carried out using NaOH and KOH as an alkali source in order to clarify the reaction mechanism of zeolitization. The physical properties such as surface structure, crystal structure and cation exchange capacity (CEC), and the ion exchange properties were measured for the zeolites synthesized by hydrothermal treatment. The zeolite P and K-CHA had a large exchange capacity [20] used coal fly ash to synthesize X-type zeolite by alkali fusion followed by hydrothermal treatment. The synthesized zeolite was characterized using various techniques such as X-ray diffraction, Scanning Electron

Microscopy, Fourier Transform Infrared Spectroscopy and BET method for surface area measurement. The synthesis conditions were optimized to obtain highly crystalline zeolite with maximum BET surface area. The crystallinity of the prepared zeolite was found to change with fusion temperature. The cost of synthesized zeolite was estimated to be almost one-fifth of that of commercial 13X zeolite available on the market.

Mishra and Tiwari, (2006) used fly ash collected from a thermal power plant for study[21].The zeolite was prepared by modified alkali fusion method. A mixture of 24 g NaOH and 20 g of fly ash was milled and fused in a tray at 500-600 °C for one hour and it was analysed using by XRD and BET . The prepared zeolites had a surface area of 430m²/g. A method for the synthesis of NaP1-type zeolite and analcime from Polish fly ash derived from hard coal combustion in pulverized-fuel boilers was applied by Adamczyk and Baelecka, (2005)[22]. The NaP1-type zeolite and analcime were produced at 120°C. The NaP1-type zeolite content rose with rise in temperature and for temperatures the analcime share in the synthesis products became significant of 200 to 320°C.

The effects of NaOH concentration on the crystal structure and the reaction rate of the zeolite synthesized from fly ash with a hydrothermal treatment method were studied .The fly ash was hydrothermal treated using NaOH aqueous solutions of various concentrations. It was found out that the reaction rates increased consistently with the NaOH concentration [5]. Conventional alkaline activation granular zeolitic material from a commercially-unusable fine-fraction of a lightweight aggregate building material produced from coal fly ash was done to produce NaP1 zeolite, K-F zeolite, K-Phillipsite and K-chabazite were synthesised. The process was optimised by combining four reaction parameters (temperature, alkali concentration, solution/fly ash ratio and reaction time). Zeolitic materials with the highest zeolite yields and cation exchange capacities were selected for future application in environmental processes [6].

Nano-porous zeolite A and MCM-41 materials were also synthesized from coal fly ash by novel and fast methods [24]. This novel production method allowed a reduction by half of the total production time while maintaining a high degree of crystallinity of zeolite A. This approach took 24 h at 25 °C to produce 9 g of MCM-41 materials from 30 g of the coal fly ash. This was the shortest time and lowest reaction temperature required to produce pure and ordered MCM-41 materials compared to the values reported in the literature. Performance evaluation of the produced zeolite A and MCM-41 materials in wastewater treatment and air pollution control were also done. In another study, the effect of CFA crystallinity towards lead adsorption capacity was investigated. The result showed that using NaOH to treat CFA caused crystallinity of quartz and mullite decrease. At higher NaOH concentration the quartz and mullite crystallinity were damaged followed by crystal formation of hydroxysodalite zeolite [25].

Synthesis of single phase zeolite A from South African coal fly ash using mine water as a substitute for ultra pure water

and the effect of ultrasound during the aging step prior to hydrothermal synthesis was investigated and it was found that sonication reduced the synthesis time of pure zeolite A to one hour [19]. The fusion method for synthesis by mixing NaOH with CFA and treating under various temperatures yielded zeolites with surface area in the range of 49-69 m²/g compared to the surface area of CFA of 17 m²/g [26].

In a study by Koukouzas et al., (2011) two coal fly ashes underwent a hydrothermal activation with 1M NaOH solution applying two different FA/NaOH solution/ratios (50, 100 g/L) for each sample. This led to the formation of several zeolitic materials. Experimental products were characterized by means of X-ray diffraction XRD and energy dispersive X-ray coupled scanning electron microscope and while X-ray fluorescence (XRF) was applied for the determination of their chemical composition. Zeolite formation was confirmed effectively.

2.3 Potential applications of zeolites

Zeolites can be used for gas purification and separation, ion exchange, catalysis, lightweight construction materials, waste water treatment media, radioactive waste treatment, pool filtration media, fertilizer and feed additive fillers, aquaculture [27]. and gases, and as replacements for phosphates in detergents [27,28].

2.4 Heavy metals removal

There are three traditional fields for zeolite application namely separation, purification and environmental treatment process; petroleum refining, petrochemical, coal and fine chemical industry. One major area of concern where zeolites have found much application is the removal of heavy metals [2,29]. Adsorption is a special characteristic of zeolites. The amount of metal adsorbed is affected by conditions like the nature and concentration of counter ions, pH, and metal solubility. Heavy metals ions such as Cu²⁺, Pb²⁺ and Cd²⁺ can be easily removed by zeolites [29].

2.5 Zeolite application in wastewater remediation

The cation exchange capacities range from 3.6 to 4.3 meq/g for the pure zeolites and from 2.0 to 2.5 meq/g for the zeolite containing residual fly ash. Tests showed that the pure zeolites are suitable for the removal of ammonium and heavy metal ions from waste water. [18,10].

Removal of heavy metals by newly formed zeolites depend on selectivity of different ions, the composition of the water and temperature. Samples were taken from metallurgical industrial waste and treated with newly synthesised zeolite and there was great reduction in heavy metals in the effluent. For example Fe²⁺ changed from 124 ppm to 0.95 ppm and Zn²⁺ from 583 ppm to 0.31 ppm [2]. Products of hydrothermal syntheses of zeolites from coal fly ash have a large exchange capacity as cation exchangers making them efficient in removing heavy metals in aqueous solutions.

Most studies done show that the resultant zeolites have a high efficiency of metal uptake as compared to coal fly ash examples being in the case of Cu²⁺, Co²⁺ and Ni²⁺ at different

pH and temperature with Indian ash [21], Cr (III) from aqueous solution [30], Cu²⁺, Cd²⁺, and Pb²⁺ [30,31], Zn, Cu Mn, and Pb in which the sorption capacity rose between 2 and 25 times after zeolitisation [36]. Origin of coal fly ash also has an effect on the adsorption capacity of the resultant zeolite [33]. Other scholars argue that the condition, under which the fly ash is made has a greater effect on the properties of the fly ash hence the zeolites that results thereof [34]. Dosage has also been seen to affect the performance of both zeolites and fly ash [33,34,35].

A number of studies focused on the isotherms to describe the mechanism of adsorption and adsorption was better described by Freundlich and Langmuir models which suggest suitability of both heterogeneous and homogeneous surfaces of both the zeolites and fly ash [9,32,33,35]

The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e. anthracite, bituminous, and lignite) and characteristics of fly ash produced varies with source and zeolites that are synthesised from different types of coal fly ashes [3,9,20,22,30] It is important to study coal fly ashes from different parts of the world to get a better understanding of zeolite synthesis. Thus there continues to be many studies on zeolite synthesis from coal fly ash.

3. Characterisation of the synthesized zeolites and fly ash

3.1 X-ray Diffraction

X-ray Powder Diffraction technique is the best method to define the crystallographic and hence the mineralogy of zeolite. Each zeolite has their own specific pattern that can be used as references for the determination of solid crystal phase and it is used as fingerprint for every zeolite. This technique can signify whether the solid sample is amorphous or crystalline phase, the degree of crystallinity and identification of phase present. The purity of solid crystal is measured by comparing the X-ray diffractogram pattern of sample with X-ray diffractogram pattern of standard that can be obtained from International Zeolite Association (IZA). The presence or absence of some peaks of the diffractogram indicates the existence of other crystal phases or zeolites [37]. Amorphous phases produce no diffraction line at all and small particles will produce broad diffraction lines but crystalline particles give a sharp and strong diffraction lines. Grounded 1g solid samples of zeolites and CFA is usually mounted into sample holder and lightly pressed using slide glass to get smooth surface of thin layer. X-ray diffractogram is recorded in the 2θ scale of 2° to 100°. The X-Ray Diffraction patterns of fly ash and synthesised zeolites is done to show the major crystalline phases of mineral composition as well as type of zeolite synthesised using the JCPDS (Joint Committee on Powder Diffraction Standards) files and compared [2,26]

3.2 Scanning Electron Microscopy (SEM)

The morphological structure of raw fly ash and synthesised zeolites material is usually obtained using SEM to

evaluate the chemical and within chemical and between the fly ash particles to see if there are any transformations after zeolite formation in comparison with coal fly ash [2,38]. This method is also essential in elucidating the elemental composition as well as the bulk composition of the zeolites [20].

3.3 X-ray Fluorescence (XRF)

XRF is used to find the chemical composition of both fly ash and zeolites to compare the differences in amount of oxides like Na_2O since it is supposed to increase with zeolite formation as it becomes incorporated. Such analyses is helpful in obtaining the the bulk elemental composition there by augmenting the SEM analyses [13,24].

3.4 Fourier Transform Infrared (FTIR)

Infrared spectroscopy is commonly used to study the silica aluminate framework, hydroxyl group and also adsorbed molecules in zeolite. Zeolite infrared interplanar spacing dhkl vibration can be divided into two forms of vibration, the internal vibration and external vibration. The internal vibrations occur from the vibration of the TO4 tetrahedron, which is insensitive to the structure changes and present in each zeolite framework and silica [37]. The shifting of these stretching to higher wave number occurs when the aluminium contents in the framework decrease hence can show whether zeolitisation has occurred. The increase of wave number with the decreased aluminium content is related to change of bond length and bond orders. The powder is used to make transparent disk and analysed on the FTIR from 4000 to 400 cm^{-1} .

3.5 BET

The synthetic zeolites and raw fly ash is subjected to N_2 adsorption to measure specific surface area.[4,7,24]. This involves use of nitrogen as an adsorbate at 77 K. Dehydrated sample is weighed automatically and the samples are then evacuated to 10^{-2} Torr and immersed in liquid nitrogen. Data is recorded and calculated from nitrogen adsorption data with the linear part of BET plot to get BET surface area of samples[7].The surface area of coal fly ash is usually very lower compared to that of zeolite. Surface areas of zeolites show great variations from one method and source of raw materials to the other as demonstrated by various researches.The values of the surface areas for the zeolitic material prepared from the co-disposal precipitates range from 91 to 245 $\text{m}^2 \text{g}^{-1}$ [28], 300-900 $\text{m}^2 \text{g}^{-1}$ as determined by the same method [14].

4. Conclusion and future perspectives

The composition of fly ash, the raw material for zeolite formation depends on the source of coal used during combustion, combustion conditions and variation in particle size. Direct hydrothermal process and alkali fusion followed by hydrothermal treatment can both be used to produce zeolites whose nature or type depends on conditions of zeolitisation. Zeolites have a better exchange capacity for

heavy metal and therefore are important removers of heavy metals from water. It is therefore important to study synthesis of zeolites from coal fly ash of different origin so that almost all the types of coal fly ashes have been utilised and studied. Varying conditions like temperature, time of incubation, concentration of alkaline produce different types of zeolites worth studying in that particular respect. In view of environmental and economic aspects, production of zeolite from CFA may provide cost-effective alternative to commercial zeolites in many applications like heavy metals removal and nuisance organics such as dyes and petrochemical by-products. Future studies may also focus on developing kinetics for zeolite formation so as to fully understand the zeolitisation process, the thermodynamics of zeolite synthesis and investigate the rheology effect of synthesis products and use of zeolite in heavy metal sorption studies.

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