Research Article

Synthesis of Valuable Transition Metal Incorporated Framework Aluminosilicates Using Waste Material Fly Ash

Arun Kant, M. Ramananda Singh, Sudipta Ghosh and Panmei Gaijon*

Department of Chemistry, Kirori Mal College, University of Delhi, Delhi 110007, India

Abstract

The aim of this research was to investigate the possibility of generation of valuable material using considerable waste material like fly ash. Transition metal (zinc and cobalt) and tetrapropylammonium bromide (organic templates) incorporated framework aluminosilicates (zeolites) has been successfully synthesis by the addition of transition metal into the reaction mixture of fly ash in NaOH solution at mild temperature. Generally fly ash contains silica, alumina, mullite, quartz and trace of heavy metals, which is a by-product generated from the thermal power plant based on coal. These three types of synthesized product were characterized using appropriate analytical techniques like Fourier Transform Infrared Spectroscopic studies, X-ray diffraction and Transmission Electron Microscopic. The obtained result show the products synthesized from open hydrothermal method demonstrated the characteristics of zeolite.

Keywords: Aluminosilicates, thermal power plant waste fly ash and transition metal

***Correspondence**

Author: Panmei Gaijon

Email: panmei@kmc.du.ac.in

Introduction

Fly ash is one of the main solid waste by-product of burning pulverized coal generated from the coal based thermal power plants [1, 2] which develop the most advance electrical device which reduces human labours are functioning with the help of electricity [3, 4]. Leading to more combustion of coal in the thermal based power plants and worldwide population relied totally on the use of coal as primary energy source for the production of electricity resulted enormous quantities of fly ash are generated per year [5, 6]. Generally this is residue which is unburned and release away from the burning zone, then collected either by electrostatic or mechanical separators. The particle size of fly ash varies from depending on the combustion method and coal sources which have ranging from 1um to 200 um but the irregularly unburned carbon contents have larger size [7, 8]. Fly ash mainly composed silica (30-40%), alumina (20-30%), quartz, mullite, some metal oxides and trace amount of heavy metals. Several approaches have been made for the proper utilization of fly ash, either minimized the cost disposal or reduce the environmental impact [9]. About 20-30% of fly ash has been used in cement industries [10], remaining fly ash has been disposed in free land, dams and pond. During this process large amount of useable land had become filler site for fly ash. Thus leading the heavy metals and toxic metals to leach through and polluting environment as well as ground water [11] and also more significant worldwide problem for both human health and aquatic ecosystems, due to their bio magnification of the food chain and continued accumulated in the environment and ecosystem [12, 13].

Due to hazardous effect of fly ash many scientific advances innovative technologies have been made which in turn significantly promote the value added applications of fly ash, such as fly ash based geopolymer, zeolite and zeolite-like materials synthesis and other application cases include embankment, road base, blasting grit, catalysis, waste stabilization and agriculture [14]. A variety of zeolites like zeolite P, X, A, Y and ZSM-5 should be synthesized from fly ash, bottom ash and combustion ash which have similar properties with natural zeolite [15]. Metakaolin and kaolin have been used as an aluminium and silicon sources for synthesis of different variety of zeolites like X, A and NaA, Hydroxysodalite, cancrinite, phillipsite, sodalite and other types of zeolite [16-18]. Physical properties of zeolites are crystalline micro and meso porous and have three dimensional open framework structural units of tetrahedral giving a series of pores and cavities having different molecular dimensions [19]. Zeolites are made by silicon and AlO_4^{5-} unit which are bridged through oxygen atoms [20]. Most of the aluminosilicates (zeolites) have uni-valent and di-valent compensating cations and their combinations [21].

Zeolite and zeolite like molecules have a broad spectrum of application like ion exchange, advanced functional material, have significant micro-pores and meso-pores with good thermal stability due to its large surface area [22]. Zeolite have high tendency to absorb water and other polar compounds like ammonia, sulphur dioxide, hydrogen sulphide, carbon dioxide and a good capacity at low temperature as compared with other adsorbents [23]. For several decades zeolites have an important application as catalytic in oil refining and petrochemical industries due to amorphous equivalents. The continuing initiative for higher quality chemical, chemical products and fuels in addition to increase industrial catalytic applications of zeolite have high prospects for further improvement of their significance role in laboratory as well as in industries. Zeolitic catalysts can address many of the issues outlined above and have been used commercially in the process industry for several decades. In oil refining the impact of zeolitic catalysts, notably in fluid catalytic cracking is substantial.

The present study is concerned with the synthesis of framework aluminosilicates (zeolites) using open hydrothermal method from fly ash. As silica (45-65%) and alumina (25-40%) are the main constituents of fly ash therefore can be use the raw material for the synthesis of zeolites. In this paper, we have incorporate transition metal (zinc and cobalt) to enhance our results on converting fly ash into porous aluminosilicates. Due to their unchanging molecular pore sizes and large surface area, porous materials will be very useful for a wide range of applications in various fields such as adsorbents and catalysts. In this work, we have managed to incorporated tetrapropylammonium bromide solution into the reacting medium in order to form a large pore size aluminosilicate structure agreement with experimental data. Therefore the conversion of fly ash into porous materials not only recover the disposal problem but also recover soil and water pollution problem so its consumption as waste material onto useful product.

Materials and analytical techniques

Fly ash obtained from coal based thermal power plant (National Thermal Power Plant NTPC, India), sodium hydroxide, AR grade was purchases from Merck and tetrapropylammonium bromide (Organic template) from spectrochem Pvt. Ltd. Other all the chemicals and reagent used throughout the study were of analytical grade.

The synthesized Aluminosilicate (zeolite like) material were characterized by using various analytical techniques such as X-ray diffraction patterns using Philips X Pert-PRO PMRD (D8 Discover Bruker AXS, Germany), Fourier-Transform Infrared Spectroscopy (Spectrum RXI Mid IR Perkin Elmer), Transmission Electron Microscopy TECNAI G2T30 FEI.

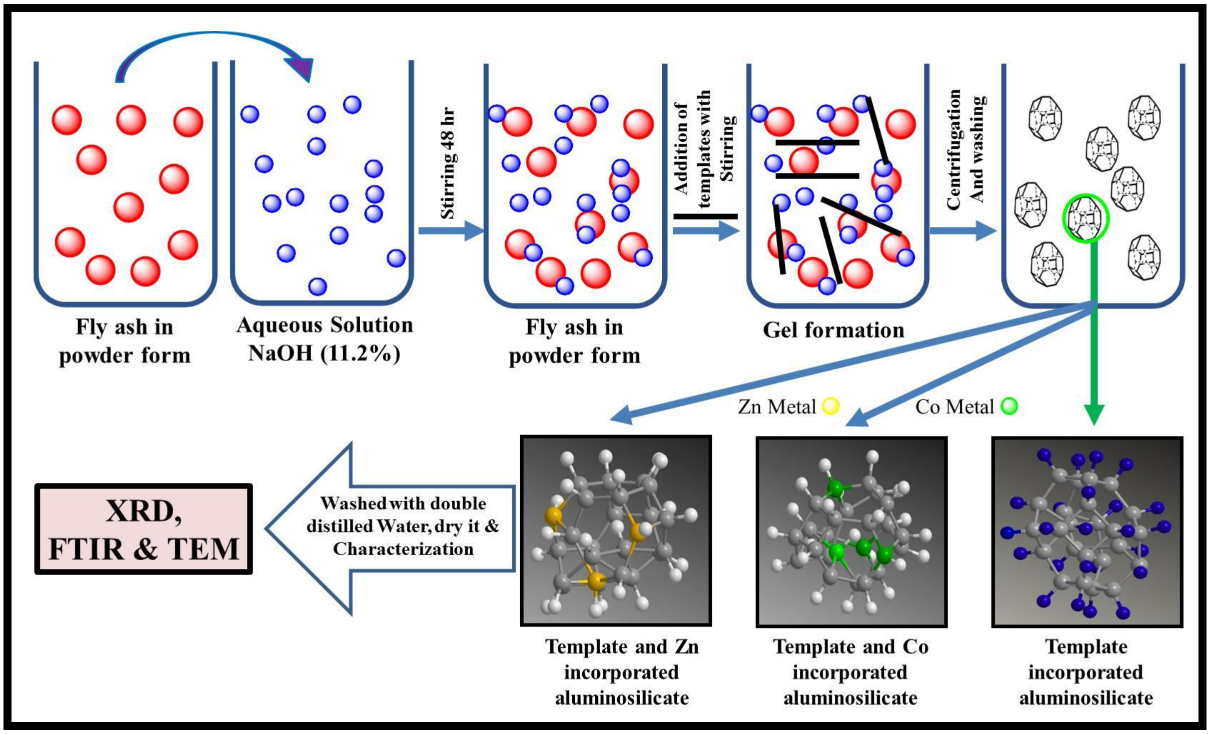
Synthesis of frame work aluminosilicate

Synthesis of frame work aluminosilicate involve in different steps shown in **scheme 1**. Initial 11.2% NaOH was prepared in double distilled water then treated with 5% weight ratio of fly ash was added into it with constant stirring for the gel formation. The above reaction mixture was heated in a conical flask with constant stirring at mild temperature for 48 hr under open hydrothermal process for the gel formation. During this process tetrapropylammonium bromide solution was added drop wise into the reacting mixture medium in order to form a larger pore size aluminosilicate structure. To the above reacting mixture transition metal solutions (1%) were added in the aim that transition metal atom becomes a part of framework structure by substituting aluminium atoms, which will render the effective catalytic property to the synthesized product. The above reaction mixture was kept for curing various temperatures for different time interval followed by room temperature. The basic supernatant solution was decant and stored separately and the residue was washed with double distilled H_2O until the pH of the filtrate was neutral. The final product thus obtained was dried in an oven to constant weight. To confirm the product of synthesized aluminosilicates were characterized by various analytical techniques such as X-ray diffraction patterns, Fourier-Transform Infrared Spectroscopy and Transmission Electron Microscopy.

Result and Discussion

FT-IR analysis of synthesized aluminosilicates

FT-IR spectrometry was found to be most reliable technique for predicting the possible Si-O-Si bonding vibration frequencies in synthesized products. The FT-IR spectra of templates incorporated aluminosilicates; Template with zinc incorporated aluminosilicates and template with cobalt incorporated aluminosilicates were studied using KBr disc method. FT-IR spectra were recorded in the wavenumber region 400-4000 cm^{-1} shown in **Figure 1**. FT-IR analysis of the synthesized products shows adsorption bands in the region 900-1200, 550-800, 540-640, 400-500 cm^{-1} in which 720-780 cm^{-1} belonging to S4R (single four member ring) group of zeolite [24]. The vibration band at 1095cm^{-1} and 905 cm^{-1} shows the presence of quartz and mullite in fly ash [25, 26]. The adsorption band at 561cm^{-1} and 468 cm^{-1} predicts Si/Al ratio and the tetrahedral unit (TO_4^{4-}) present in the fly ash. The synthesized aluminosilicates shows adsorption band at 429 and 460 cm^{-1} corresponds to the adsorption of the S4R and the bending vibration band of O-T-O of the tetrahedral units (TO_4^{4-}). The adsorption band at 562 cm^{-1} corresponds to crystalline nature and Si/Al ratio in the synthesized product [27].



Scheme 1 Schematic representing of synthesizing template incorporated aluminosilicates, template with Co incorporated aluminosilicates and template with Zn incorporated aluminosilicates

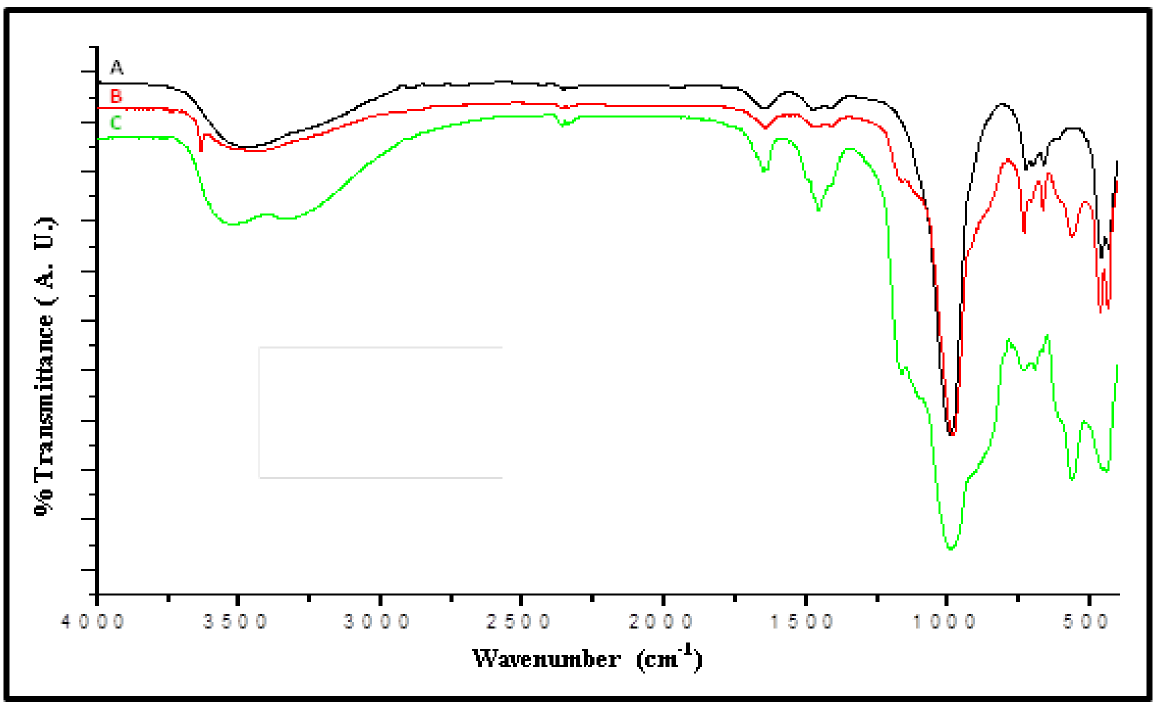


Figure 1 FT-IR spectra of synthesized product, (a) Template added framework, (c) Template with Zn metal added framework and (b) Template with Co added framework

The loss of vibration peak at 562 cm^{-1} in case of organic template added product whereas in other two cases adsorption at that particular peak were observed. The decrease in peak sharpness of the synthesized product compare to the fly ash at 562 cm^{-1} indicates that some amount of silica from the fly ash had been dissolved during the gel formation and has been decant out during the process of washing of the synthesized product to reduced pH of the product. The adsorption bands at 659, 702, 722 and 1007 cm^{-1} corresponds to the symmetric stretching and asymmetric stretching vibration bands of T-O-T bond [28, 29]. The synthesized compounds consist of additional adsorption band at 1411 and 1480 cm^{-1} corresponds to CO_3^{2-} molecules trap in the cavity of the synthesized product [30, 31].

The adsorption band at 1661 cm^{-1} and 3280 cm^{-1} correspond to the bending and stretching vibration band of the zeolitic H_2O molecules of the synthesized aluminosilicates and the adsorption band at 3533 cm^{-1} correspond to the Al-OH stretching band of the aluminosilicates. The vibration frequencies of the synthesized product show similar behaviour to that of the naturally occurring hydroxysodalite. The above FT-IR result indicate that there is no major difference in synthesis aluminosilicates of all three product (template incorporated aluminosilicate, Figure 1a; template with zinc incorporated aluminosilicate, Figure 1c and template with cobalt incorporated aluminosilicate, Figure 1b) are almost similar in properties.

XRD analysis of synthesized aluminosilicates

X-Ray diffraction (XRD) patterns of template incorporated aluminosilicates; template with zinc incorporated aluminosilicate and template with cobalt incorporated aluminosilicate were recorded using Cu Kα radiation (n = 1A^o) operating at 2θ values range 5^o to 70^o shown in **Figure 2**.

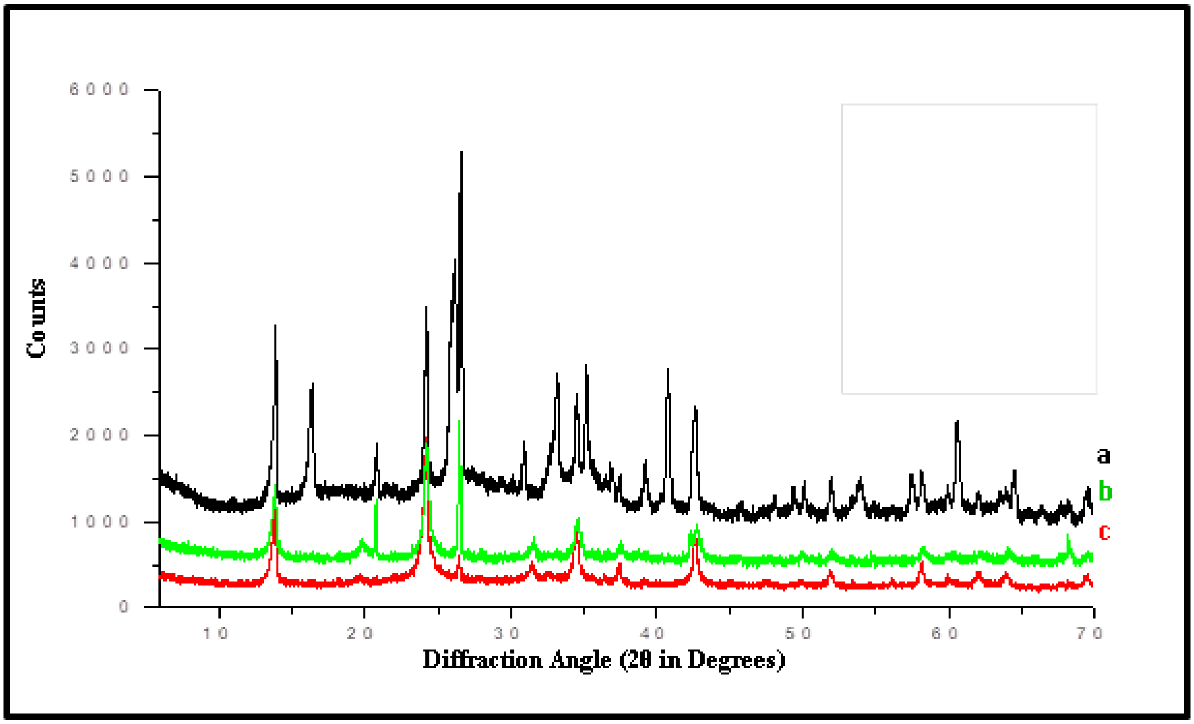


Figure 2 XRD pattern of synthesized product (a) Zn metal Template added framework (c) Co metal Template added framework (b) Template added framework

XRD analysis of organic template incorporated aluminosilicate show less sharp, broad and smooth peeks with some additional peak of hydroxysodalite suggesting that the size of the synthesized product are small in size with 2θ values 20.89, 13.80, 24.31, 26.43, 31.63, 42.73 which indicate less crystalline compare to transition metal incorporated aluminosilicates, Figure 2b. Template with cobalt incorporated aluminosilicate has 2θ values 13.80, 24.31, 26.43, 31.63 and 42.73 which indicate crystalline in nature Figure 2c. In this case products formed by the addition of organic templates with cobalt metal into the reaction medium during gel formation. The product obtained some extra peak and more intense suggesting that the metal has taken part in the product formation whether in the framework or in the cavity of the product. This suggested that the synthesized compound has more than single phase. Template with zinc incorporated aluminosilicate has 2θ values 13.92, 16.29, 20.89, 24.31, 26.43, 31.04, 33.17, 34.58, 35.29, 40.84 and 60.56 indicates more crystalline in nature of products Figure 2a. In this case, the addition of organic template and zinc metal during the process of gel formation to form the product. XRD pattern indicates, this product has been retained fly ash suggesting that NaOH in the reaction medium was insufficient to digest the fly ash for the gel formation.

Transmission electron microscopic with EDX analysis

Surface morphology of organic template incorporated aluminosilicate **Figure 3A- C**; template with zinc incorporated aluminosilicate Figure 3 D-F and template with cobalt incorporated aluminosilicate Figure 3 G-I were analysed by transmission electron microscopic study with EDX analysis.

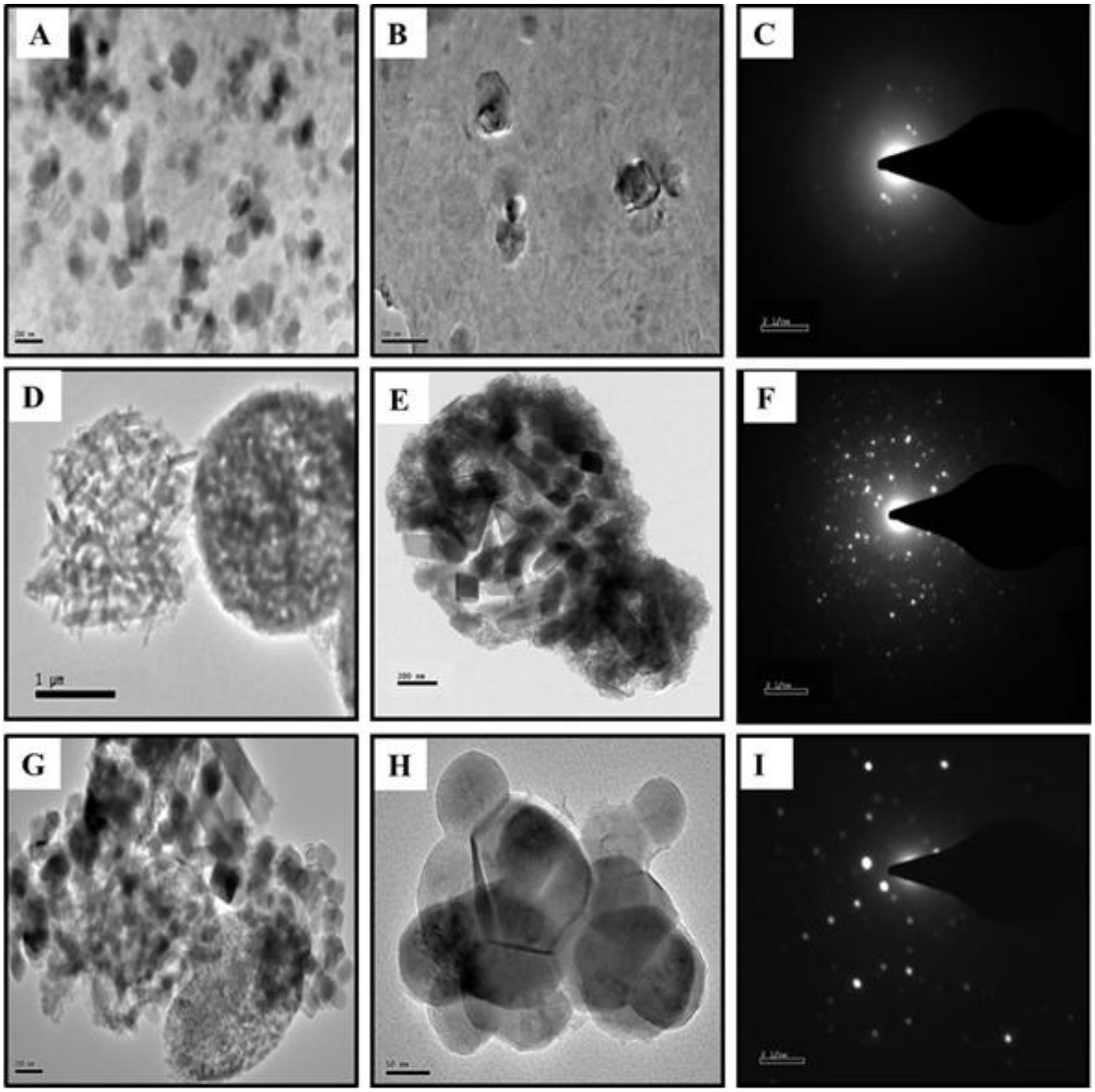


Figure 3 TEM images and EDX pattern of the synthesized product, Template incarporated product (A, B & C), Template with zinc added product (D, E & F) and Template with Cobalt added product (G, H & I)

TEM images of organic template added product show the particles aggregates together to form a cluster which is unable us to isolate single particle and cubic like shape observed, its EDX analysis shows less number of bright spots which are randomly arranged with bright circular ring like image, indicating the product is slightly amorphous in nature as compared to other products, particle size of this product is lies between 50 to 100 nm in range. TEM images of organic template with cobalt added product shows randomly arranged cubic, rectangular and hexagonal structure. EDX analysis of organic template with cobalt incorporated aluminosilicate show large number of bright which are randomly arranged, indicating the product is crystalline in nature these bright spots can also predict the planes in the unit cell crystal. Particle size of this product is lies between 20 to 50 nm in range.

TEM images of organic template with zinc metal incorporated aluminosilicate shows randomly arranged rectangular, hexagonal and rod like structure from a fixed point. EDX analysis shows large number of bright spots which are randomly arranged, indicating the product is crystalline in nature and these bright spots can also predict the planes in the unit cell crystal. The particle size of this product is lies between 75 to 200 nm.

Conclusion

This study has suggested that successfully synthesis of framework aluminosilicate by open thermal method for three valuable products, organic template incorporated framework aluminosilicate, organic template with cobalt incorporated framework aluminosilicate and organic template with zinc incorporated framework aluminosilicate using considerable waste like fly ash. Addition of transition metals with organic template into the reaction mixture was done during gel formation of fly ash with NaOH at mild temperature. Particle size of organic template added aluminosilicate, organic template with cobalt metal incorporated aluminosilicate and organic template with zinc incorporated aluminosilicate was lies between 50 to 100 nm, 20 to 50 nm and 75 to 200 nm respectively. In case of organic template with zinc incorporate aluminosilicate intensity of peaks increases and some extra peaks suggested that the synthesized aluminosilicate have more than one phase. The intensity of extra peak increases in both cases of organic template with cobalt incorporated aluminosilicate and organic template with zinc incorporated aluminosilicate, suggesting that both cobalt and zinc have been placed in the cavity of the framework structure as well as become the member of the framework structure by isomorphs substitution of aluminium and Silicon atom.

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Reference

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