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Hydrothermal Synthesis and Characterization of Zeolite: Effect of Crystallization Temperature

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Abstract

The synthesis and characterization of zeolites designed for the removal of pesticide, radioactive waste and as slow release fertilizer is described. The zeolites were hydro thermally synthesized by varying the concentrations of Si and Al at different crystallization temperature between 75°C to 150°C. Different instrumental techniques viz. X-ray diffraction, FTIR, SEM, EDS, TEM and TGA were used to characterize the product obtained at different synthesis parameters. The broad and sharp peaks obtained in diffractogram shows the amorphous and crystalline nature of the materials respectively. The composition of SZM was found approximately close to the concentrations of the precursors taken during synthesis. The FTIR spectra of these zeolites in framework vibration region also shows sharp feature for zeolites in the 500-650cm^{-1}. High crystalline nature of the material is reveals by the absorption bands at 520-570 cm^{-1}. The synthesized zeolites were used for the sorption studies for malathion, Pd(II), Ru(III) and plant nutrient Nitrate.

Keywords: Zeolites, hydrothermal synthesis, sorption.

Introduction

Zeolites are inorganic crysttaline materials with a framework of tetrahedral TO_4 building units (T=Si, Al, etc.). The three-dimensional crystalline porous skeletons of zeolite is form by tetrahedral TO_4 units linked by sharing of oxygen atoms. The T-O-T links which forms a variety of rings, are responsible for zeolites cages and channels of different window sizes. The negative framework charge which is generated by the presence of the $A1^{3+}$ atom at the center of an AlO_4 tetrahedron connected to a neighboring SiO_4 tetrahedron by sharing an O atom is balanced by exchangeable cations, such as an alkaline or alkaline-earth cation and thus, the property of ion exchange is provided[1]. The large number of active sites at the edges and on the external surface is found on Nano-crystal catalysts. Chemical environmental synthesis conditions such as stirring rate, seeding, crystallization temperature, gel composition, alkalinity, Si/Al ratio and template concentration etc. are well known factors to control the crystal size. Among these factors, Si/Al ratio and crystallization temperatures are most important for crystal size control.

Material and Methods

For the proposed work zeolite named SZM has been synthesized by hydrothermal method. The reaction mixture is transferred in to a Teflon lined stainless steel pressure vessel and placed in preheated (75°C, 100°C, 125°C and 150°C) oven at autogeneous pressure and static conditions for 72 hrs. Tetraethoxy silane $(C_2H_5O)_4Si$, Aluminium nitrate $[Al(NO_3)_3]$, Potassium nitrate (KNO_3) are used as starting materials for the synthesis of zeolites. The sodium hydroxide (NaOH) solution is used as template and alkali source. SZM had been synthesized by hydrothermal treatment at various crystallization temperatures of 75°C, 100°C, 125°C and 150°C. The molar compositions of the precursor gels as obtained by EDX analysis are: $Na_{10.50}Al_{19.09}Si_{14.44}O_{55.98}$. The materials thus synthesized were thoroughly characterized by instrumental techniques viz. X-ray diffraction (XRD), Fourier transform infra red spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and thermo gravimetric analysis (TGA).

Results and Discussion

Powder X-Ray Diffraction (XRD): The powder diffraction pattern explores the different features to characterize the crystalline materials. Powder diffractogram data is most commonly used as a "fingerprint" in the identification of a material. Bruker Axs D8 Advance X-Ray Diffractometer was used to recorded the Powder X-Ray diffraction pattern of all the materials. Samples were scanned in the 2θ range between 0° - 60° at the scanning speed of 1 step/second using Cu-Kα radiation source of wave length 1.54056A°. The samples synthesized at temperatures lower than 125°C indicate the amorphous phase material as indicated by XRD patterns (figure 1). The material synthesized at 150°C shows the most prominent reflection peak at 26.0° indicating highly crystalline

nature of the material. At lower synthesis temperatures i.e. 75°C, 100°C and 125°C the materials exhibited the surface area typical to the amorphous materials. Crystals obtained at 150°C and above have much higher surface area figure 2. It has to be pointed out that the resolution of XRD patterns improves as the Si/Al ratio increases. This is due to Al incorporation in the framework which reduces the degree of order[2].

FTIR Study of Synthesized Materials: Zeolites are found to exhibit typical infrared spectroscopic patterns which can group in two classes. The first is due to internal vibration of primary unit of structure ($TO_{4/2}$ tetrahedron) which is not sensitive to other structural vibration. This vibration is found in the range 950-1250cm^{-1} and 420–500cm^{-1}. These Strongest vibration at 950-1250cm^{-1} and 420–500cm^{-1} are assigned to T-O stretching and T-O bending mode (T = Si or Al) respectively. The stretching modes are sensitive to the Si–Al composition of the framework and may shift to a lower frequency, while the bending mode may be related to the linkages between tetrahedral.

The vibration which are sensitive to the overall structure and the joining of the individual tetrahedral in secondary structural unit as well as their existence in the large pore openings are of second types of vibrations.

The bimodal absorbance in spectra is indicated by the hydroxyl bond (– OH stretch) near 3550cm^{-1} in the spectra. The band at 3440cm^{-1} indicates the loosely bound water molecules. A strong characteristic structure sensitive bands due to the presence of attached water molecule indicates a water (H_2O) bending vibration at 1630cm^{-1}. Thereby sorption and desorption of water (hydration and dehydration) may be easily monitored by IR, observing the change occurred in these vibration bands.

The band at 550–580cm^{-1} can be associated with ring of tetrahedral and / or octahedral[3]. Absorption bands at 520 – 570cm^{-1} indicates the high crystalline nature of material. These bands indicate pronounced crystallization and thus confirm the XRD investigations described earlier [4]. Specially, this assigned peak is characteristic peak of stretching frequencies of six-coordinated aluminum[5-7]. Four member ring deformation mode of the network is observed around 730 cm^{-1} along with other modes[8,9]. The peaks below 550cm^{-1} is generally due to δ (O-T-O) bending and rotation mode. The peaks between 700-850cm^{-1} and 1000 to 1150cm^{-1} are assigned to symmetric and anti symmetric T-O-T stretching vibration. The IR peaks observed for SZM (150°C) is presented as transmittance spectra and given in figure-3.

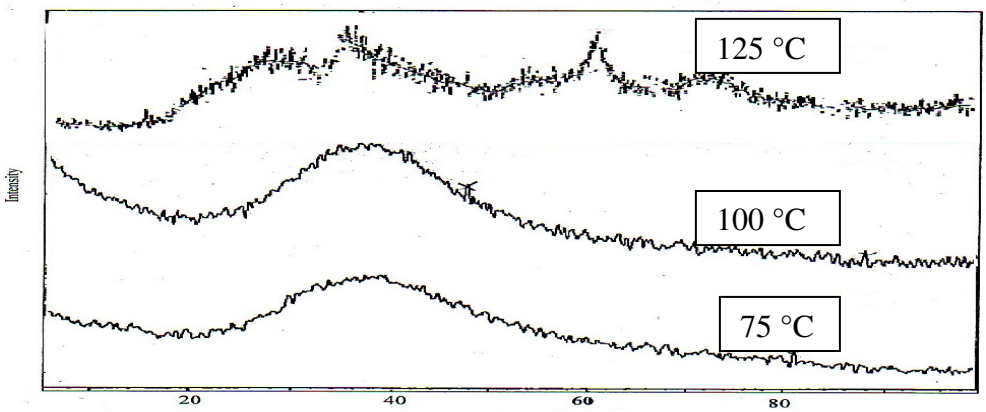

Figure-1
XRD patterns of SZM at Crystallization Temperature of 75°C to100°C.

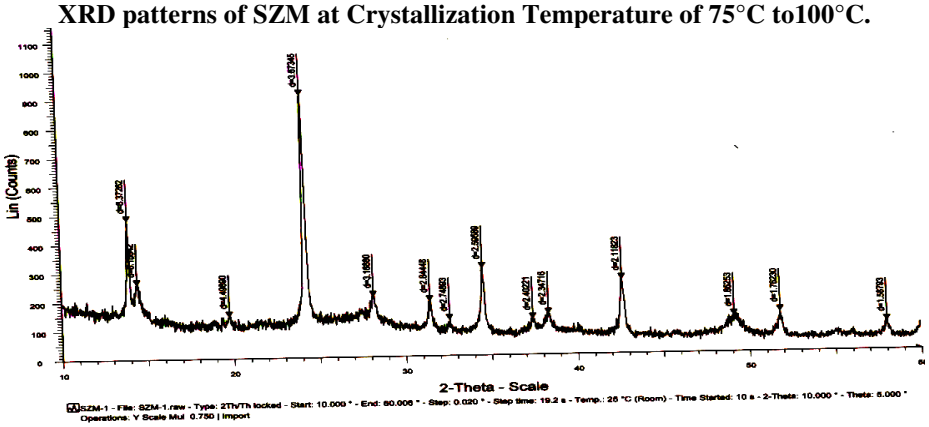

Figure-2
XRD patterns of SZM at Crystallization Temperature of 150°C

DTA/TGA Study of Synthesized Zeolites: The number of water molecules attached with the hydrothermally synthesized zeolite SZM and its thermal stability was investigated using DTA/TGA. Upon heating the sample from room temperature to 200°C a continuous weight loss of 7.99% and 15.2% is clearly observed in DTA/TGA thermo-grams obtained for SZM (150°C). This weight loss is may be due to the dehydration of physically adsorbed water. When the sample is further heated in the temperature range of 200 to 700°C the weight loss observed is attributed to desorption of remaining water enclosed in the material matrix. Reduced weight loss in this region was observed with increase in crystallization temperature as well as Si/Al ratio of the sample which is consistent with the fact that zeolite becomes more hydrophobic as the Al content decreases[2].

TEM Study of Synthesized Materials: The very small size of synthesized material can accurately be determined by TEM rather than SEM. TEM have the ability to resolve and show individual particles clearly in an aggregation of particle mass. TEM observation shows that the nano size crystals can be obtained from hydrothermal synthesis method. SEM and TEM images of SZM shows a nano particles of size 15-20 nm.

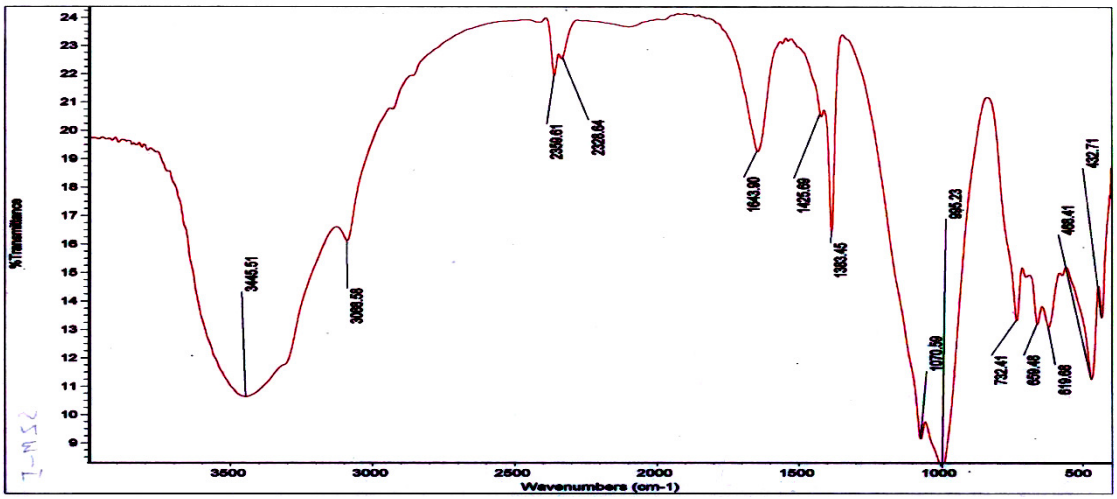

Figure-3
FTIR Spectrograph of SZ at Crystallization Temperature of 200°C

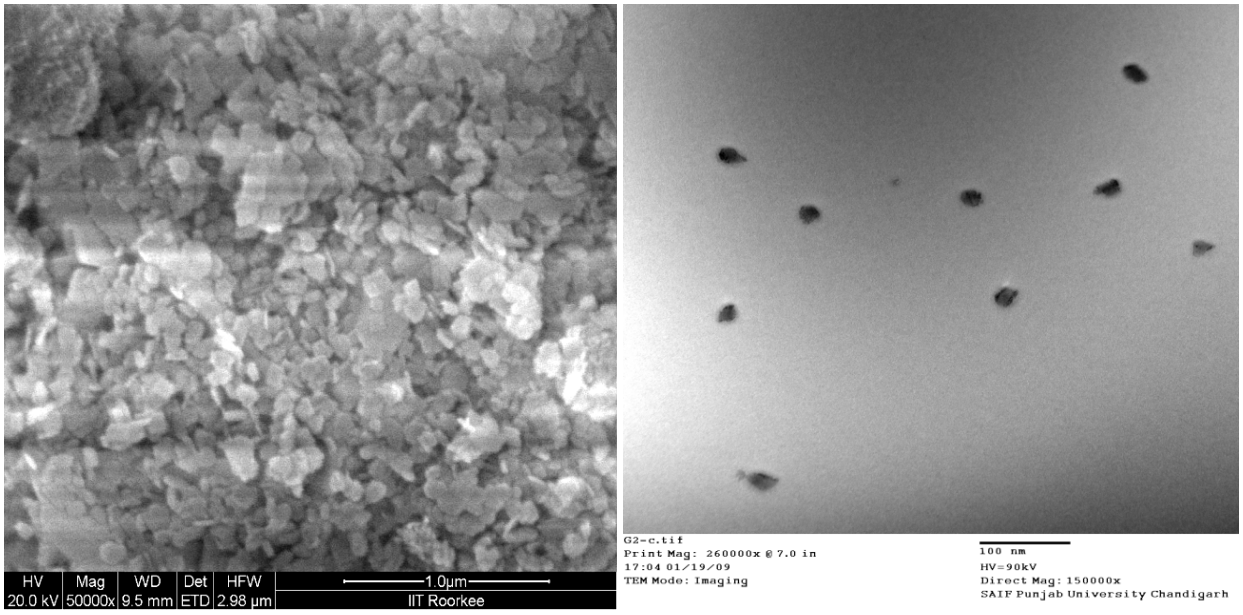

Figure-4
SEM and TEM micrograph of SZM at Crystallization Temperature of 150°C

Conclusion

From the above study it can be concluded that the crystallization temperature has a pronounced effect on crystal size and morphology. For a given Si/Al ratio, at synthesis temperature of above 150°C the smallest crystals were obtained whereas at crystallization temperatures lower than 150°C, amorphous phase was observed. Zeolite named SZM with Na, Al and Si in the molar ratio of 1 : 3 : 2 was synthesized at crystallization temperatures 75°C to 150°C and characterized by various techniques. The results indicate that the morphology of crystals is also affected by crystallization temperature it can be concluded that crystallization temperature of 150°C is appropriate for the synthesis of crystalline materials.

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