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Isomorphous Substitution of Zn^{2+} in aluminosilicate framework creates two types of mesopores without templates

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Abstract : Mesoporous materials have significant applications in catalysis, adsorption and separation techniques. The material containing pore size between 2 to 50 nm is called as mesoporsous material. The studies on catalysis by solid acids are vast. Aluminosilicates are well known solid acid catalysts. Isomorphous substitution into the framework may enhance the physico-chemical properties of the material. In the present work, the zinc metal ion is introduced into the tetrahedral aluminosilicate framework increases its bronsted acid sites and also creates two types of mesopores. The material activity is maximum at 370 ^{o}C. The adsorption application of organic dyes has been carried out to test the activity of the material. The material is effectively adsorbs the congo red and methylene blue dyes from aqueous solution.
Key words: Isomorphous substitution, Zn^{2+}, Porous materials, No template, Surfaces, Adsorption.

1. Introduction

Solid acid catalysts such as MCM-41, MCM-48, ZSM-5, SBA-15 and 16 exhibits high activity and adaptability in all fields like alkylation, adsorption and catalysis however, these are pure silica based materials and they do not have enough acidity for catalytic reactions [1-2]. Inclusion of aluminium [3] and other metal ions [4-5] into their tetrahedral framework may increase their acidity and catalytic function. Mesoporous materials have good surface area, high thermal stability, good acid sites and uniform pore size [6]. Aluminium incorporated mesoporous materials were initially reported by Corma et al. [3]. Introducing of zinc into the framework leads to replace the aluminium and producing two negative charges into the tetrahedral framework and these ions are connected with the bronsted acid sites. As a result, the numbers of Bronsted and Lewis acid sites in Zn incorporated material are the same, but the number of acid sites is higher than that the normal aluminosilicate material [7].

In the present study, Zn incorporated aluminosilicate catalyst is synthesized and characterized by XRD, FT-IR, BET and TPD.

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2. Materials and methods

Aluminium Chloride (98% Merck), Sodium silicate (Meta) (Loba Chemie) and Zinc chloride is used in the mesoporous material preparation.

In a typical synthesis, 13.5g of aluminium chloride is dissolved in water with vigorous stirring. Then 28.5g of sodium silicate powder is added and 2.725 g of $ZnCl_2$ is added. The obtained resultant mixture is stirred on a magnetic stirrer for half an hour and kept for one day to attain complete precipitation. The gel molar composition is $AlCl_3$: Na_2O_3Si: 0.2 $ZnCl_2$: 300 H_2O. The final product is washed with distilled water and dried at the 120 ^oC for 3h in hot air oven.

This as synthesized sample is calcinated at 600 ^oC in the presence of air until all the impurities are completely removed from the pores of the material.

2.1 Characterization Techniques

The resultant material is characterized by different spectroscopic techniques such as XRD, FT-IR, BET and TPD. Structure and crystallinity of the material is determined by Low – angle X – Ray Diffraction (XRD) patterns on a Bruker D8 advance using Cu – α radiation (λ = 1.5418Å). FT – IR spectrum of the sample is recorded by JASCO – 410, FT – IR model spectrophotometer using a KBr pellet method. The TPD – NH_3 desorption curve is recorded in chemisoft TPx V1.02. Nitrogen adsorption – desorption measurement is carried out on Micrometrics, ASAP 2020 V3.00H for pore size analysis.

3. Results and Discussion

The material is characterized by following techniques such as, XRD, FT-IR, BET and TPD.

3.1.1 XRD measurements

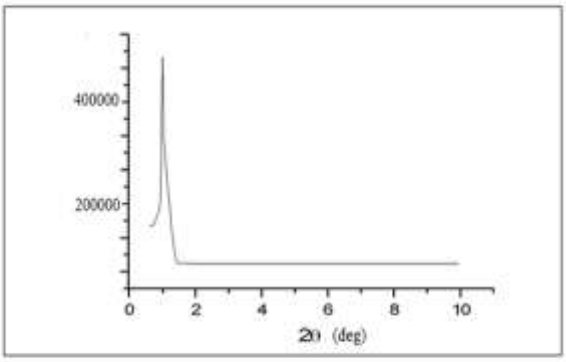

Figure 1: XRD pattern of nanoporous Zn-$AlSiO_4$ material

The XRD pattern (Figure 1) shows the crystalline nature of the material. This sharp low angle peak at 1.1 degree confirms the formation of mesoporous material and the characteristic peak of hexagonal symmetry with a d_{100} of 86.07 Å [8].

3.1.2 FT-IR spectrum

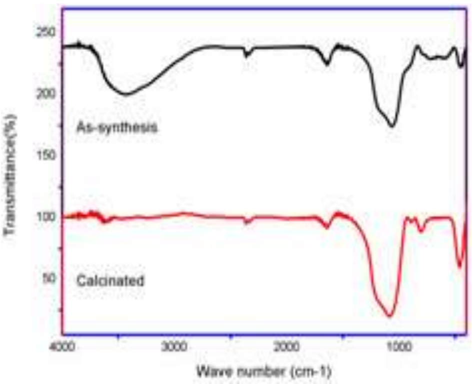

Figure 2: FT-IR spectrum of nanoporous Zn-AlSiO$_4$ material

FT-IR spectrum is used to confirm the tetrahedral framework formation and the spectrum of Zn-AlSiO$_4$ material is shown in figure 2. The stretching vibration at 3500 is due to surface silanols and adsorbed water molecules in the framework while deformational vibrations of adsorbed molecules cause the adsorption bands at 1635-1656 cm^{-1} it confirms the presence of water molecule in the as-synthesized material after the calcinations the peak is disappeared. The absorption bands at 1075 and 1228 cm^{-1} are due to asymmetric stretching vibrations of Si-O-Si framework, while the 1000-1075 cm^{-1} band are due to Si-O-M+ ((M) Al and Zn) vibrations in metal-incorporated silanols. Zinc metal ion incorporated tetrahedral framework is observed in 1000 to 1200 cm^{-1} region. Symmetric and asymmetric stretching vibrations are appeared at 781 cm^{-1} and 1075 cm^{-1} region. These stretching vibrations confirm the fundamental vibrations of tetrahedral formation and the bending mode of vibration is observed near 453cm^{-1} region. The characteristic peak at 1075 cm^{-1} confirms the Zn-O-Si and Al - O - Si vibration. The hydroxyl group exhibits the excellent evident for the presence of catalytic active sites [7,9,10].

3.1.3 Nitrogen adsorption – desorption measurement

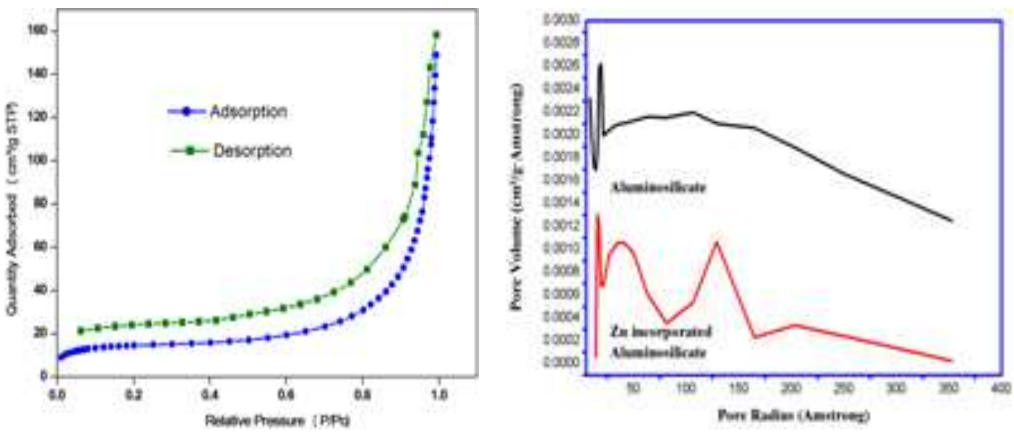

Figure 3: Figure A (A) N$_2$ sorption isotherm for nanoporous Zn-AlSiO$_4$ and

Figure B (B) pore size distribution of AlSiO$_4$ & Zn-AlSiO$_4$

Porosity and surface area of the material is analyzed by nitrogen adsorption–desorption method and it is given in Figure (3). The metal ion incorporated material has 52.2393 m²/g BET surface area with the pore sizes of 12 and 34 nm and plain aluminosilicate material has 57.9020 m²/g BET surface area and the average pore size is 16.3 nm. Type IV isotherm hysteresis loop confirms the mesopores of the material, the capillary condensation of nitrogen in the mesopores is shifted to lower relative pressure, which recommends that the pore size is narrowed and distributed [11,12].

3.1.4 Temperature Programmed desorption

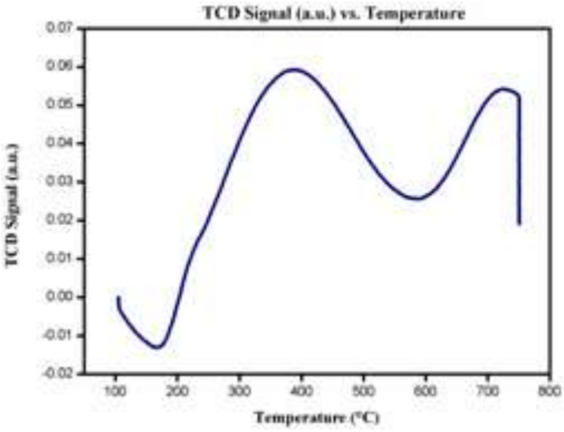

Figure 4:NH_3 TPD for nanoporous Zn-$AlSiO_4$

Acidic nature of the material is determined by Temperature Programmed Desorption (Fig. 4). From TPD, the material has two types of acid sites such as bronsted and lewis acid sites, it has 10.18357 mL/g STP of acidity and the material is highly active at 370 ^oC. This low temperature active site is more useful to carry out the reaction continuously without any coke depositation [13].

Adsorption capacity of the material is tested by adsorption of congo red and methylene blue from aqueous solution and it is highly effective for dye removal from the aqueous solution.

4. Adsorption application

Adsorption of congo red and methylene blue dyes are studied up to 15 mins and it is shown in Table 1. Rapid adsorption takes place within 10 mins. This adsorption study proved that the material has high efficiency even though it has less surface area. This highly active nature of the material may be due to the strong bronsted and lewis acid sites are created by the Zn^{2+} incorporation in the tetrahedral framework. These strong acid sites enhance the multilayer adsorption. Hence, the material has strong affinity towards dye adsorption on lower surface area.

Table 1

Adsorption application of nanoporous Zn-$AlSiO_4$ material

Dye	Initial dye concentration (ppm)	Contact Time (min)	Adsorption (%)
Congo red	100	5	55
	100	10	98
	100	15	98
Methylene blue	100	5	75
	100	10	99
	100	15	99

5. Conclusion

Introducing of Zn^{2+} ion into the framework leads to replace the Al^{3+} and producing two negative charges into the tetrahedral framework and creating more bronsted acid sites. That is the reason the Zn^{2+} incorporated materials have high acidity and the introduction of metal ion into the framework also creates two types of mesopores in the tetrahedral framework. Physicochemical properties of the Zn^{2+} incorporated material is analyzed by XRD, FT-IR, BET and TPD. Zn^{2+} incorporated material contains higher number of bronsted acid sites (10.18357 mL/g STP of acidity) so it is more effective for adsorption on lower surface area leads to increase the multilayer adsorption.

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