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ESTERIFICATION OF BENZOIC ACID OVER ZINC INCORPORATED SOLID ACID CATALYST

J. Clara Jeya Geetha[a], M.Balavinoth[a], M.R. Devi[b] and J. Ilavarasi Jeyamalar[a]*

[a]Department of Chemistry and Research Centre, Pope's College (Autonomous), Sawyerpuram-628 251, Tamil Nadu, India
(Affiliated to Manonmaniam Sundaranar University, Tirunelveli-627012, Tamil Nadu, India)
[b]Department of Chemistry, Sree Devi Kumari Womens College, Kuzhithurai, 629163, Tamilnadu, India
**Corresponding author Email: ilavarasichem@gmail.com*

ABSTRACT:
The discovery of mesoporous materials by Mobil Oil Company raises the researcher's interest in mesoporous materials. The zinc-incorporated mesoporous silica material (Zn-MSI) was synthesized using a simple sol-gel approach from the silica source of sodium silicate and template cyclohexanone. The synthesized material was studied by using several spectroscopic techniques such as FT-IR, XRD, SEM, TEM and BET analysis. The results indicated the formation of a mesoporous material with good substantial porosity. The material showed good catalytic activity for the esterification of benzoic acid with ethanol. The experimental conditions such as contact time, temperature, mole ratio, and catalyst dosage were further studied for maximal conversion.

KEY WORDS: Mesoporous, Catalytic activity,Esterification, Benzoic acid

INTRODUCTION

Porous silicate materials have found great utility and have been playing a dominant role in recent years in heterogeneous catalytic reactions owing to their large accessible surface area which allows high catalyst loading. Porosity increases the surface area and also enhances the number of active sites on the catalyst [i-iii]. In the porous structure, chemical reactions may take place on the surface inside the pores. This involves diffusion in and out of the pores and able to interact with atoms, ions, and molecules not only at their surfaces but also throughout the bulk of the material [iv-vi]. Porous materials have important uses in the area of optics, catalysis, gas separation, drug delivery, membranes, energy, and health [vii-ix]. Application heavily depends on material composition and structure; particularly pore size, shape, distribution, and connectivity [x-xi]. Mesoporous silica frameworks like MCM-41 and FSM have received attention because of their useful applications and potential values in the area of catalysis, sensing, and adsorption by reason of their large internal and external surface areas and huge well-organized pores [xii]. The $ZnAlPO_4$ material prepared by Da-Lei Sun *et.al.*,and found that,

as a heterogeneous catalyst, ZnAlPO4 exhibits very high activity and selectivity under mild reaction conditions for the methoxycarbonylation of HDA with DMC to form dimethylhexane-1,6-dicarbamate.[xiii].Sharad V. Lande *et al.,* prepared Zn-modified MCM-22 catalysts has excellent stability and the reaction is highly selective towards diphenyl methane[xiv]. The esterification reaction is conventionally carried out by homogeneous catalysis under acidic conditions. Sulfuric acid is the most widely used homogenous acid catalyst for fatty acids esterification[xv] . Zn-based catalysts are very important material for many organic reactions dealing with carbonyl species [xvi].Ali Moaddeli et.al, was prepared nanodesigned mesoporous zinc-combined copper oxide (NMZI-CuO) as a resourceful and recyclable heterogeneous nano catalyst. The results obtained from the characterization of the recovered catalyst, indicate that the structure of the catalyst was maintained after 4 cycles of reuse.[xvii].Youming Ni*et al.,*have prepared mesoporous Zn/ZSM-5 zeolite catalyst and revealed that the Zn impregnated catalyst Zn/HZ5/0.3AT exhibited dramatic improvements in catalytic lifetime and liquid hydrocarbons yield.[xviii].The current study describes the Sol-Gel fabrication and characterization of Zn-incorporated mesoporous silica molecular sieves (Zn-MSI). The synthesized material's catalytic activity was tested by esterification reaction of benzoic acid with ethanol. Nearly 50% conversion occurred around 100°C.

2. EXPERIMENTAL

MATERIALS

Sodium meta silicate (purity wt.99%) as the silica source, cyclohexanone (purity wt.98%) as a template, benzoic acid and ethanol (96%)) in the present study were purchased from Merck Company, zinc sulphate (99.5wt. %) was purchased from Sigma and Aldrich.

Synthesis Of Mesoporous Solid Acid Catalyst

The Zn-MSI was synthesized from sodium meta silicate. The molar composition of the gel subjected to the sol-gel method is 0.05 Na_2SiO_3: 0.02 $ZnSO_4.4H_2O$:0.01 $(CH_2)_5CO$. The silica source sodium silicate (6.103 g) was dissolved in deionized water (60 mL). Then the template$(CH_2)_5CO$(0.01 moles) was added to Na_2SiO_3 solution. The resultant mixture was stirred for 2 hrs at room temperature.Then 50 mL of zinc sulfate (3.23 g) solution was slowly added and stirred continuously. The pH was raised to 10 by adding dilute sulphuric acid. The gel obtained was aged for 48 hours at 30^0C. After aging, the product was heated to evaporate water on a hot plate at 110^0C. The synthesized material was washed, dehydrated, and calcined in open air at 300^0C. During calcination, impurities and organic cyclohexanone molecules were completely removed from the molecular sieves, which also created mesopores on the surface.

2.1. CHARACTERIZATION:

The synthesized sample was characterized by FT-IR, XRD, BET analysis, SEM and TEM for verifying the structure, framework vibration, surface area, pore size and morphology respectively. The Fourier Transform infrared (FT-IR) sample was recorded by the measurement of JASCO FT-IR model Spectrophotometer. X-ray powder diffraction pattern was recorded on a shimadzu 6000 diffractiometer using Cu-Kα radiation n (λ=1.5418 Å) at room temperature with the scanning rate of 5 degrees per minute. The SEM analysis was performed on a JEOL JSM 6360 scanning electron microscope. The BET surface area and pore size were measured on micromeritics, ASAP 2020 V3.00H.Transmission electron micrograph (TEM) image was recorded by JEOL 2011 microscope operated at 200 kV.Nitrogen adsorption-desorption measurement was made using on micromeritics, ASAP 2020 V3.00 H at 77 K.

2.2. Catalytic run:

Esterification reactions were carried out in a batch reactor fitted with a reflux condenser and a thermometer. In a typical reaction, the desired amount of ethanol, benzoic acid and 0.1 g of calcined mesoporous catalyst were added and allowed to stirrer for 2 hrs. Temperature of the reaction mixture was slowly raised up to 200°C and reflux for 6 hrs. The products were separated out from the reaction mixture by filtering.

2.3. Calculation of maximum percentage of conversion:

The Ethylbenzoate products and the benzoic acid are separated by distillation method. The conversion of the reaction is calculated as,

Conversion (%) =Total no of moles of reactants -Unreacted moles of reactant ×100
Total no of moles of reactants

3. RESULTS AND DISCUSSION

3.1. Characterisation of Zn-MSI:

Figures 1a and 1b show the FT-IR spectra of the synthesised and calcined sample.The synthesized sample has peaks that appear in distinct, strong bands at 2933 cm^{-1}, which corresponds to the organic template's C-H stretching modes.The bending vibrations of template molecules are measured in the 1500-1600cm^{-1} range. The corresponding bending vibration mode is observed at 1636 cm^{-1}. These vibrations disappear in calcined samples. The absorption peak at 1088 cm^{-1} corresponds to the stretching of asymmetric and symmetric Si-O-Si group[xv]. The IR frequency responsible for tetrahedral framework of incorporated mesoporous material is around 500 to 420 cm^{-1}.The low angle XRD pattern of (Zn-MSI) is shown in Fig 1c. The diffraction peak obtained at a very low angle of 0.6 degrees, indexed as (1 0 0), implies that the material has short range mesostructure. The calcined (Zn-MSI) sample of wide angle powder XRD is shown in e Fig 1d.The absence of a ZnO signal in the wide angle XRD indicates that the zinc has been integrated into the tetrahedral skeleton. This XRD pattern shows that, the existence of anamorphous pore wall, as observed by the broad peak appeared at around 20–25°2θ[xix].

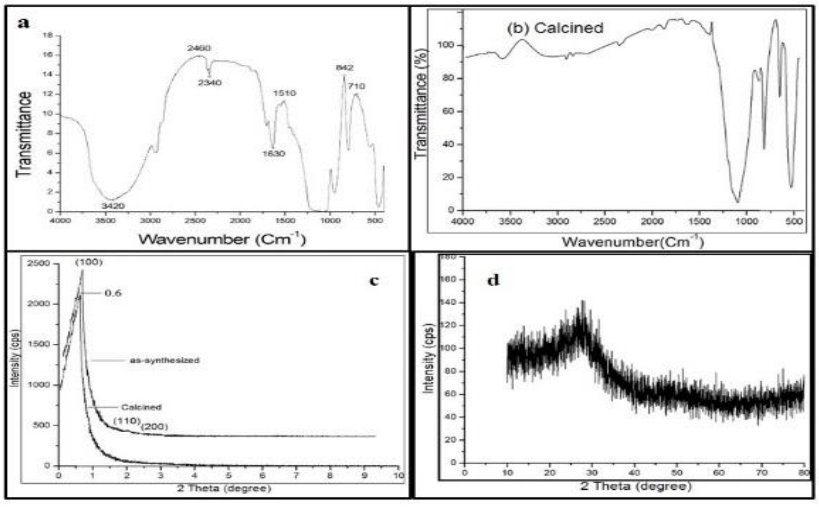

Fig 1. Synthesized Zn-MSI (a) FT-IR spectrum of as-synthesized
(b) FT-IR spectrum of calcined (c) low angle PXRD (d) wide angle PXRD

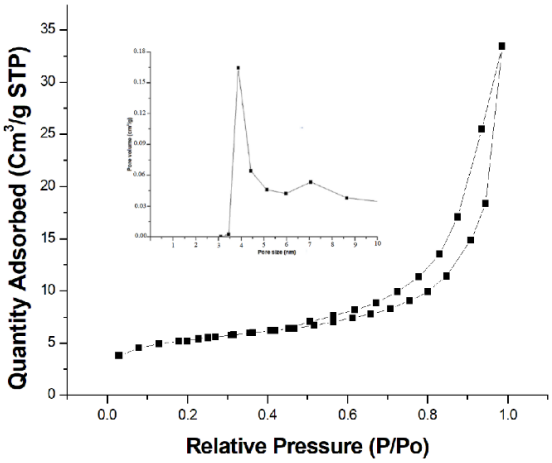

Fig 2.N_2 sorption isothermof Calcined Zn-MSI

Figure 2 displays the calcined (Zn-MSI) nitrogen adsorption desorption isotherm. The isotherm can be categorised as a type IV isotherm using IUPAC nomenclature. When the relative pressure P/P0 was less than 0.3, the mesopores of Zn-MSI underwent monolayer adsorption and capillary condensation. The material has a BET surface area of 45 m^2/g and a specific pore volume of 0.17 cm^3/g.

SEM was applied to determine the morphology, size, as well as size distribution of the Zn-MSI particles. SEM images of calcined Zn-MSI, are shown in Fig 3a, 3b, and 3c and it shows a sheet-like morphology with disordered mesopores[xx].The elements that were present in the zinc-incorporated mesoporous silicates were determined using energy dispersive X-ray spectroscopy (EDX) analysis. Figure 3d illustrates an EDX spectrum. The mesoporous catalyst's elemental analysis revealed that it contains zinc, silica, and oxygen.

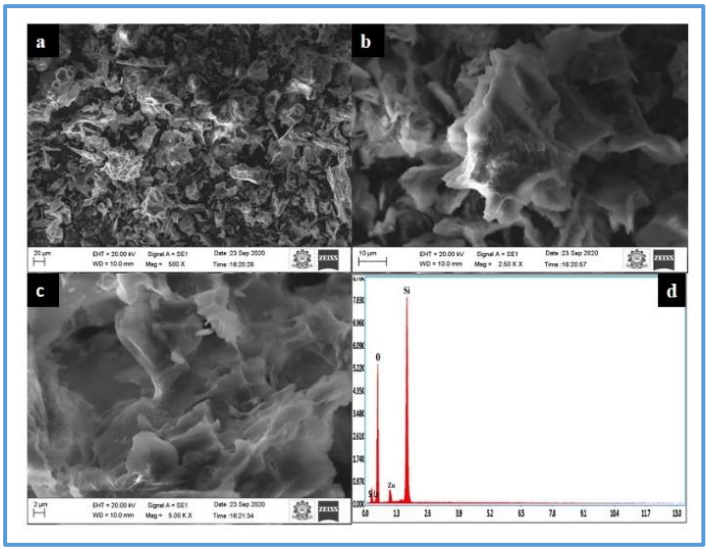

Fig 3. Synthesized and calcined Zn-MSI (a,b & c) SEM micrograph and d) EDAX image

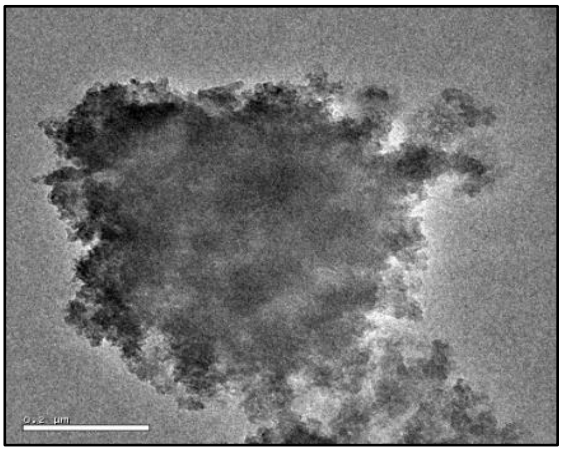

Fig 4.Synthesized and calcined Zn-MSI TEM image

Figure 4 depicts the TEM image of calcined Zn-MSI. In the TEM image of Zn-MSI, the network of disordered mesoporous molecular sieves is visible. Generally speaking, the material's image displays a crystalline structure with short-range order.

3.2 Catalytic activity

The esterification reactions took place in a batch reactor with a reflux condenser. Acid and alcohol (1:3 mol ratios) were heated to 80 °C with accuracy while being stirred continuously with a magnetic stirrer. The calcined sample was dried for 1 hour at 100 °C before being used in the reaction[xxi].

The products were filtered from the reaction mixture and separated using a simple distillation process. The experimental settings such as the result of contact time, temperature, catalyst dosage, and the molar proportion of the reactants were optimized for maximum conversion

Fig 5a.shows the esterification of benzoic acid with ethanol carried out at different temperatures from 50 to 300^{o}C with the acid : alcohol mole ratio of 1:3 and appropriate contact time. The conversion of acid slowly increases up to 200^{o} C. Then, when the temperature rises, the conversion rate decreases.

In fig 5b. the effect of reaction time on the esterification of benzoicacid with ethanol studied on zinc incorporated mesoporous catalyst is shown. The esterification reactions were carried out for 3 to 15 hrs. The conversion percentage increases significantly within the first three hours and gradually increases as time passed. There was no appreciable conversion appeared after 15 hrs.

The esterification of benzoic acid with ethanol in pursuance of mesoporous silica catalyst was studied from 0.02 g to 0.1 g and the results are plotted in a graph (fig 5c).Increase of catalyst loading increases the percentage of conversion. The products and the reactants were separated by distillation method. In this study, acid : alcohol mole ratio of 1:3, temperature at 200^{o}C and 3 hours duration was maintained throughout the reaction.

The effect of mole ratio of benzoic acid with ethanol on esterification reaction has been studied over mesoporous zinc incorporated silica catalyst and is plotted in fig.5d. The conversion is gradually increased as the amount of alcohol is increased to a maximum. The remarkable conversion yielded 1: 3 mole ratios.

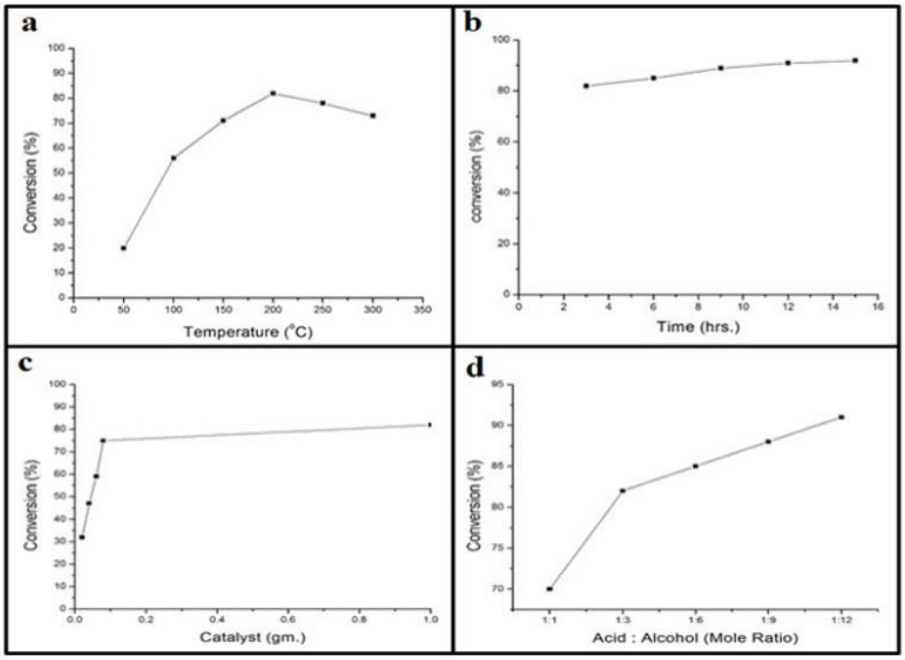

Fig 5. Esterification of benzoic acid with ethanol over Zn-MSIa) temperature, b) contact time , c) catalyst dosage, and d) mole ratio

4. CONCLUSION

A simple technique based on a sol-gel method was used to synthesize a silica-based mesoporous Zn-MSI catalyst with tetrahedral framework. To prove the activity of the synthesized catalyst, the esterification of benzoic acid with ethanol in liquid phase has been performed. The experimental conditions like effect of contact time, temperature, catalyst dosage and molar ratio of the reactants were optimized in liquid phase for maximum conversion of products. The appreciable conversion and selectivity for the synthesized catalyst was found around 200^{o}C. On further increase of temperature the conversion of the product was gradually decreased. Increase of catalyst loading increases the percentage of conversion. The maximum of conversion approximately 82% has been observed over the zinc incorporated mesoporous silica catalyst. The synthesized Zn-MSI catalyst has shown a good stability and reusability and has been easily removed from the reaction mixture by simple filtration process.

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