



# Highly ordered Zn-doped mesoporous silica: An efficient catalyst for transesterification reaction

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## ABSTRACT

Designing highly ordered material with nanoscale periodicity is of great significance in the field of solid state chemistry. Herein, we report the synthesis of highly ordered 2D-hexagonal mesoporous zinc-doped silica using a mixture of anionic and cationic surfactants under hydrothermal conditions. Powder XRD,  $N_2$  sorption, TEM analysis revealed highly ordered 2D-hexagonal arrangements of the pores with very good surface area ( $762 \text{ m}^2 \text{ g}^{-1}$ ) in this Zn-rich mesoporous material. Chemical analysis shows very high loading of zinc (ca. 12.0 wt%) in the material together with retention of hexagonal pore structure. Interestingly, high temperature calcination resulted into zinc silicate phase, unlike any ZnO phase, which otherwise is expected under heat treatments. High surface area together with Zn loading in this mesoporous material has been found useful for the catalytic activity of the materials in the acid-catalyzed transesterification reactions of various esters under mild liquid phase conditions.

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## 1. Introduction

Doping of Zn in various inorganic framework structures is one of the frontier areas of research in solid state chemistry as the resulting materials find wide application in optoelectronics [1], sensing [2], biology [3], catalysis [4], photocatalysis [5] and so on. Zinc oxide nanostructures are extensively studied in the literature for its interesting photoconducting [6], electrical [7] and optical properties [8]. In addition, crucial role played by Zn(II) in pure ZnO and its mixed oxides in heterogeneous catalysis makes many organic reactions feasible. Industrial methanol synthesis [9], chemo-selective hydrogenation of aldehydes [10], transesterification reactions [11], etc. are the most common of them. Transesterification reaction of esters is an important organic transformation useful for synthesis of a large variety of esters, especially in the production of biodiesel and many synthetic materials [12,13]. This reaction may proceed in presence of either basic or acidic catalyst. ZnO and other zinc complexes have surface Lewis acidic property and thus catalyze few transesterification reactions [14]. However, Zn-doped ordered mesoporous material has not been synthesized and employed in the transesterification reactions.

Since its discovery, M41S family of ordered mesoporous materials [15,16] have attracted wide interest in the field of catalysis due to their exceptional surface area and tunable pores of

nanoscale dimensions. But pure silica materials like MCM-41 or SBA-15 found limited application in heterogeneous catalysis due to the absence of acidic or redox species in the materials. The substitution of Si atom by other active metal ions of similar atomic size could modify the structural properties of the resulting metal-doped silica and thus leads to great improvement in catalytic performances [17–19]. In this context incorporation of transition metal ions to the silica framework has been widely investigated in last few decades due to their application in eco-friendly, industrially important catalytic reactions [20–22]. Like other elements Zn metal incorporated silica materials show crucial role in heterogeneous catalysis. Previously, Silvestre-Albero et al. [4] reported Zn containing MCM-41 and studied its catalytic behavior. However, the amount of Zn loading in the siliceous framework was quite low and this could be attributed to its limited catalytic activity. Hence, synthesis of ordered mesoporous silica with high Zn content is quite challenging task, which is not reported till date. We have synthesized Zn-rich silica material via a simple co-condensation method of Zn(II) and silicate precursors in the presence of a mixture of surfactants CTAB and SDS. In this context it is pertinent to mention that the imperative role of tartaric acid in the synthesis of metallosilicate has been proved before [23,24]. We have used tartaric acid to increase the Zn loading in the silica framework and build a stable mesoporous Zn-doped matrix.

Furthermore, the stoichiometric compound zinc silicate ( $\text{Zn}_2\text{SiO}_4$ ) with  $\alpha$ -willemit structure is of significant importance for its various commercial applications [25]. A variety of methods have been reported related to the synthesis of  $\text{Zn}_2\text{SiO}_4$  nanostructure [26]. But to the best of our knowledge, no attempt has

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been made to obtain  $\alpha$ -willemitite  $Zn_2SiO_4$  nanostructured material via Zn-doped ordered mesoporous silica. Our present study deals with the conversion of amorphous Zn containing silica material to crystalline zinc silicate on high temperature calcination. Herein, we report the synthesis of Zn-rich highly ordered mesoporous silica, its detailed characterizations and catalytic application in the transesterification reaction.

## 2. Experimental section

### 2.1. Materials used

Tetraethyl orthosilicate (TEOS, Sigma-Aldrich) and Zn(II) chloride (E-Merck) were used as silica and zinc sources, respectively. Surfactants cetyltrimethylammonium bromide (CTAB, Loba Chemie) and sodium dodecylsulphate (SDS, Loba Chemie) were used as templates. DL-Tartaric acid (TA, E-Merck) was used to stabilize Zn(II) through complex formation and thus to have better interaction with the silicate species during hydrothermal synthesis. For pH adjustment tetramethylammonium hydroxide (TMAOH, 25% aqueous solution, Sigma-Aldrich) solution was used.

### 2.2. Procedure

We prepared three samples by co-condensation method with different Zn:Si molar ratios varying from (2–10):50. In a typical synthesis, SDS (0.47 g) was mixed with tartaric acid (TA, 1.31 g) in a plastic beaker containing about 60 g distilled water. After few minutes CTAB (3.00 g) was added to the above solution under vigorous stirring at room temperature. Immediately the mixture became viscous and this was kept under stirring for about 30 min. Next, TEOS (3.5 g) was added to this suspension under continuous stirring. The suspension was vigorously stirred for about 2–3 h, which enhances the miscibility of the organic phase with aqueous phase along with the hydrolysis of the silicate species. Then 0.50 g  $ZnCl_2$  (for samples ZS-5/5A) dissolved in 2 g  $H_2O$  was added slowly to the resulting mixture followed by constant stirring for another 4 h. After that TMAOH solution was added dropwise to this mixture and a heavy white precipitate appeared gradually. The pH was maintained strictly to *ca.* 11.0. The resultant mixture was aged overnight under stirring at room temperature and finally transferred to a polypropylene bottle for hydrothermal treatment at 353 K during 72 h. Finally the solid product was recovered by filtration, washed thoroughly with water so that the surface of the sample was totally free from adhered loosely bound Zn(II) ions. White product was dried at room temperature and calcined at 703 K temperature to take out the organic templates from the material. Calcined sample was designated as ZS-5. For other two batches the resulting calcined powder samples were synthesized following the same procedure and named as ZS-10 (Si/Zn molar ratio=10:1) and ZS-25 (Si/Zn molar ratio=25:1). The molar ratios of various constituents for all the above samples were (2–10)  $ZnCl_2$ :50.0 TEOS:25.0 CTAB:5.0 SDS:50.0 TA:9860  $H_2O$ . The sample

ZS-5 was further heated at temperature 1173 K for 2 h to enhance the crystallinity of the pore-wall.

### 2.3. Characterizations

Powder X-ray diffraction (XRD) patterns of the materials were recorded on a Bruker AXS D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered  $CuK\alpha$  ( $\lambda=0.15406$  nm) radiation. Nitrogen and adsorption/desorption isotherms were obtained using a Beckmann Coulter SA 3100 surface area analyzer at 77 K. Prior to the measurement, all the samples were degassed at 453 K. JEOL JEM 6700F field emission scanning electron microscope (FE SEM) with an energy dispersive X-ray spectroscopic (EDS) attachment was used to record the morphology of the sample and its surface chemical composition. Transmission electron microscopy (TEM) images were recorded in a JEOL JEM 2010 transmission electron microscope. Fourier transform infrared (FT IR) spectra of these samples were recorded on KBr pellets by using a Shimadzu FT IR 8300 spectrophotometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a TA instrument Q600 DSC/TGA thermal analyzer. UV-visible diffuse reflectance spectra were recorded by using a Shimadzu UV 2401PC spectrophotometer with an integrating sphere attachment and  $BaSO_4$  pellet was used as background standard. The Zn content of the samples was measured using Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) by dissolving the solid powder in aqueous solution containing minimum amount HF/HCl.

### 2.4. Procedure for the catalytic transesterification reactions

The transesterification reactions of different ethyl esters were carried out in a 50 ml capacity round bottom flask fitted with a water condenser and placed in a temperature controlled oil bath under constant stirring at a fixed temperature. Methanol, 1-butanol, 2-propanol or benzyl alcohols (all procured from Merck, India) were used as transesterification reagents and required amount of solid catalyst was added. The reactions were carried out with or without solvent. At different interval of time reaction mixture was monitored by thin layer chromatography (TLC) using 10% ethyl acetate-pet ether solution. After the reaction was completed, solid catalyst was filtered and the alcohol was evaporated by using a rotary evaporator. The products were identified by  $^1H$  NMR spectroscopy and percentage of conversion was measured by capillary Gas Chromatography (GC, Agilent 4890D, with FID detector).

## 3. Results and discussions

### 3.1. Synthesis conditions

The physico-chemical characterizations of all zinc-doped mesoporous silica materials are enlisted in Table 1. In order to synthesize 2D hexagonally ordered mesophase we have employed mixture of surfactants, cationic CTAB and anionic SDS in the

**Table 1**  
Physico-chemical properties of all mesoporous zinc-doped silica samples.

Sample name	Zn:Si ratio synthesis mixture	Zn:Si ratio product		BET surface area ( $m^2 g^{-1}$ )	Pore volume ( $cc g^{-1}$ )	Pore diameter (nm)	d spacing XRD (nm)	Wall thickness (nm)
		EDS	AAS					
ZS-5	1:5	1:7	1:8	762	0.87	2.98	3.68	0.70
ZS-10	1:10	1:10	1:9	765	0.87	3.05	3.72	0.67
ZS-25	1:25	1:15	1:14	799	0.90	2.58	3.54	0.96

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