



Controllable synthesis of niobium doped mesoporous silica materials with various morphologies and its activity for oxidative catalysis



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ABSTRACT

Nb doped HMS-X (Nb-HMS-X) was synthesized by sol–gel/emulsion method using non-ionic tri-block copolymer surfactant PEO₁₄₀PPG₃₉PEO₁₄₀ (P123) as a structure directing agent. The effect of synthesis condition on the pore morphology and nature of pore ordering was investigated. Small-angle X-ray Scattering (SAXS) revealed highly ordered pore structure in Nb-HMS-X. It is demonstrated by Field Emission Scanning Electron Microscopy (FESEM) that the materials possessed various morphologies such as, regular spheres, disordered and tube-spheres depending on synthesis conditions. The solid state ²⁹Si nuclear magnetic resonance measurements showed that chemical environment of silicon atoms get modified significantly with synthesis condition. Furthermore, the synthesized niobium doped hollow mesoporous silica (Nb-HMS-X) was effective to catalyze ethyl benzene oxidation reaction where activation of C–H bond took place.

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1. Introduction

Since the discovery of ordered mesoporous silica materials, there has been a tremendous effort devoted to the control of their nanostructure, texture and macroscopic morphology. In recent years, ordered mesoporous materials have aroused interest not only for their synthetic features, but also due to the possibility of tailoring the pore structure, framework composition and morphologies over a wide range. Many research groups have investigated different surfactant-silica chemistry systems that yield various shapes including spherical beads, gyroids, ropes, toroids, ellipsoids, shells, helical structures, as well as thin films, fibers and monoliths, depending on the synthesis conditions [1–7]. The progress of this field is reflected in searches for a variety of well-organized and structured materials, characterizing a relevant class of mesoporous compounds, embracing a series of silicas that are classically named as MCM-41 [8], SBA-15 [9] and SBA-16 [10]. Thus, many potential applications arise from the promising properties related to the high surface areas of these materials, including

catalysis, catalytic supports, sorption, sensors, in medicine and nanotechnology [11–16].

The morphology of mesoporous silicates is important for industrial applications, for example, films in catalysis and separation, monoliths in optics, and uniformly sized spheres in chromatography. Controllable synthesis on both the mesoscale (mesostructure) and macroscale (morphology) is therefore crucial but possible. Mesostructure assembly and morphology growth influences each other. It has been found that several factors can affect the morphology of the final materials [17,18]. Among the numerous synthesis parameters which determine the morphology and texture of the resulting mesoporous materials, one can mention the synthesis temperature, hydrothermal treatment conditions (hydrothermal treatment time and hydrothermal treatment temperature) of the reactants in the aqueous medium [19]. It also includes the presence of a co-surfactant and/or co-solvent, temperature, stirring, as well as the procedure used for the mixing of the reactants or for the heating stage (i.e. in one or two steps). According to the nature of the surfactant and pH of the synthesis media, three main types of interactions are involved. In alkaline media, where the siliceous species bear negative charges (I⁻), the interactions with cationic surfactant S⁺ are electrostatic (S⁺I⁻) [20]. Non-ionic

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surfactants (S^0) used in neutral media favors hydrogen bonds and Van der Waals interactions (S^0I^0) in the reaction medium [5]. In acidic media, the interaction between the silica and the surfactant is mediated by X^- anions as described by $S^+X^-I^+$ [21], whereas the surfactant S is a cationic surfactant (S^+) or a non-ionic polyethylene oxide based surfactant $S^0(H_3O^+)$ with ethoxy oxygen atoms bound to H_3O^+ [22]. The different structures which are formed depend on the molecular geometry of the surfactant modulated by the concentration, temperature, pH (g factor), presence of co-surfactant as well as other chemicals like salts or organic molecules known as organogelator [23(a,b)].

For transition-metal substituted mesoporous silicas, it is apparent that the transition metal center and the porous structure both play important roles in obtaining desirable properties. Attributed to the development in the material science, the silicas with different morphology and mesostructure have been successfully synthesized [24,25]. However, only limited attention has been paid to the structure and morphology control of the transition-metal substituted mesoporous silicas, partly due to the mismatch for the incorporation of transition metal ions and the formation of silicas with controlled morphology and mesostructure. For example, the nonionic-surfactants (such as P123, F127) have been widely used as templates for the fabrication of mesostructured silicas normally in strongly acidic conditions [26]. However, the highly acidic media are not ideal for incorporation of transition metal ions due to the larger solubility of the $Si-O-M$ species. The previous studies showed that the mild reaction media may solve this problem [27–29], but the structural and morphological control of silicas in mild reaction medium is not well developed yet. Apart from these it is still a challenge to synthesize transition-metal functionalized mesoporous silicas with desirable active metal centers for different reaction.

Oxidation catalysis constitutes an important research area because it represents the core of a variety of chemical processes for producing bulk and fine chemicals. Therefore, the design of active, selective, and recyclable heterogeneous catalysts is a challenging goal in the field of oxidation catalysis [30,31]. Allylic oxidation of alkyl aromatics (like ethylbenzene) is an important transformation in organic synthesis [32,33]. Classically, stoichiometric amount of oxidant such as manganese dioxide, selenium dioxide were employed for allylic oxidation [34]. Nowadays, the development of catalysts to get the desired product seeks for high atom efficiencies of chemical reactions to reduce manufacturing costs and to minimize burdens to the environment. In a constant search for cleaner (“greener”) technologies [35], there is a definite need for catalytic oxidations that use dioxygen (O_2) or hydrogen peroxide as the stoichiometric oxidant [36]. Acetophenone can also be produced by the liquid-phase oxidation of ethylbenzene by oxygen or air using homogeneous transition metal compounds as catalyst [37].

Recently we have prepared a new class of mesoporous material, named as HMS-X catalyst in which different metal doping resulted interesting catalyst for several reactions e.g. Beckmann rearrangement, Styrene epoxidation, Bayer-villiger epoxidation etc [38–41]. In this work it has been shown about the change of mesostructure, pore size, and accessibility of the internal mesopores by adjusting several processing variables. More specifically, the aim consists in describing the different silica particles morphologies in light of the formation mechanism and in understanding the exact role of the synthesis condition on the control of the macroscopic morphology. Furthermore the catalyst is prepared with two more loadings and its activity was checked for ethylbenzene oxidation reaction using TBHP as an oxidant. All the materials have been thoroughly characterized by different instrumental techniques like BET surface area

and porosity measurement, SAXS, FESEM, HRTEM, UV–Vis spectra, FTIR and ^{29}Si NMR techniques.

2. Experimental

2.1. Materials and catalyst preparation

Hexagonally ordered periodic mesoporous silica Nb-HMS-X was synthesized by using triblock copolymer as a template under acidic condition by the hydrothermal sol–gel procedure as per literature [35,36]. In a typical synthesis Pluronic P123 (Aldrich, MW = 5800) (4 g) was dissolved in 144 mL distilled water followed by addition of 7.4 g 35% HCl (Merck) in continuous stirring. After stirring for 4 h a clear solution was obtained and then 4 g n-butanol (>99%, Merck) was added to this solution and stirred for another 1 hour. Then tetraethyl orthosilicate (8.4 g) (99%, TEOS, Acros) and lastly $NbCl_5$ (0.81 g) (99%, Aldrich) dissolved in ethanol were added to this solution and stirred for 24 h at 35 °C temperature. The synthesis mixture had the molar ratios P123: H_2O : HCl: n-Butanol: TEOS: $NbCl_5$: 0.017: 200: 5.4: 1.325: 1: 0.075 (molar ratio). After stirring, the mixture was taken in a closed polypropylene bottle and aged at 100 °C temperature for 24 h under static hydrothermal condition. Subsequently the material was filtered in hot condition without washing and then dried at 100 °C for 12 h in air. Finally the as synthesized materials were calcined at 540 °C for 24 h with a temperature increasing rate of 1 °C min^{-1} in a muffle furnace (Thermcraft, USA). The material obtained after calcination was the desired material i.e. Nb-HMS-X (Si/Nb = 13). The labels of material prepared at different conditions are listed in Table 1.

2.2. Catalyst characterization

The nitrogen adsorption–desorption isotherm of the sample were measured at liquid nitrogen temperature –196 °C with a surface area analyzer (NovaWin-3200, Quantachrome Instruments, USA) instrument. Pre-treatment of the samples were carried out at 250 °C for 5 h under high vacuum. Pore size distributions were calculated from the desorption branch of isotherms using Barrett–Joyner–Halenda (BJH) method and NLDFT (Non-linear Density Functional Theory) model with cylindrical pore approximation [42]. Small-angle x-ray scattering (SAXS) measurements were performed using a laboratory based SAXS instrument with $Cu K_{\alpha}$ X-ray source. The scattered intensities $I(q)$ were recorded as a function of scattering vector q ($=4\pi \sin \theta/\lambda$, where 2θ is the scattering angle, and λ is the X-ray wavelength). Field emission scanning electron microscope (FESEM) was carried out using Supra 55, Carl (Zeiss, Germany) microscope. Sample was supported on lacey carbon and then coated with platinum prior to measurement. The HRTEM investigation was done on JEOL JEM 2100 (USA) microscope

Table 1
Nb-HMS-X (Si/Nb = 13) catalyst synthesized at different condition.

Code	Synthesis temperature	Hydrothermal treatment time	Hydrothermal treatment temperature	Calcination temperature
S-1	35 °C	24 h	100 °C	540 °C
S-2	35 °C	24 h	100 °C	As-synthesized
S-3	Room temperature	24 h	100 °C	540 °C
S-4	50 °C	24 h	100 °C	540 °C
S-5	35 °C	12 h	100 °C	540 °C
S-6	35 °C	18 h	100 °C	540 °C
S-7	35 °C	24 h	80 °C	540 °C
S-8	35 °C	24 h	120 °C	540 °C

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