Microporous and Mesoporous Materials 223 (2016) 46–52

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Evaporation-induced self-assembly of mesoporous zirconium silicates with tunable acidity and facile catalytic dehydration activity

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ARTICLE INFO

Article history:
Received 8 August 2015
Received in revised form
3 October 2015
Accepted 20 October 2015
Available online 28 October 2015

Keywords:
Zirconium
Evaporation-induced self-assembly
Lewis acid
Dehydration
Isopropanol

ABSTRACT

Zirconium ions were incorporated into mesostructured silicate by evaporation-induced self-assembly (EISA) method without the addition of a mineral acid. Zr loadings up to 26.5 wt% were achieved. The BET surface area and the pore volume of the Zr-EISA samples are in the range of 818–614 m^2/g and 1.2–1.01 cm^3/g, respectively. Amorphous ordered pore structure was evident from HR-TEM images. Diffuse reflectance UV–Vis spectra reveal that a majority of the Zr exists as isolated framework species and impart Lewis acidity. Pyridine FTIR analysis revealed the presence of both Lewis and Brønsted acid sites in the Zr-EISA samples. The Zr-EISA materials exhibit excellent isopropanol dehydration activity with nearly total olefin selectivity characterized by a moderate activation energy (approximately 86 ± 1 kJ/mol).

1. Introduction

Surfactant aided synthesis of ordered mesostructured silicate materials with controlled pore size and morphology has drawn considerable attention in recent years. Examples include non-ionic triblock copolymer assisted synthesis of ordered large-pore mesoporous silicas such as SBA-15 (space group *p6mm*) [1], SBA-16 (space group *Im3m*) [2], FDU-12 (*Fm3m* symmetry) [3,4], KIT-5 (space group *Fm3m*) [3] and KIT-6 (space group *Ia3d*) [5]. The synthesis of these mesoporous silicates is usually performed under strongly acidic condition that (a) often limits framework incorporation of active metal ion species, and (b) forms metal oxide aggregates on the surface. We show in this work that evaporation-induced self-assembly (EISA) technique helps overcome this limitation and allows significantly greater metal incorporation into mesoporous structures compared to conventional techniques.

Solvent evaporation techniques have previously been demonstrated for the formation of mesostructured silicates from amphiphilic templates [6]. For instance, Nagamine et al. [7] prepared hexagonal mesostructures using solvent evaporation employing cetyltrimethylammonium chloride and tetraethoxysilane (TEOS) in ethanol at a relatively low HCl concentration. Spray drying [8] and aerosol evaporation techniques [9,10] have also been shown to form mesoporous materials, employing either ionic, amphoteric or non-ionic surfactants as templates. In another example, using room temperature drying for approximately two days, Liu et al. [11] prepared three-dimensional bicontinuous mesoporous silica with *Ia3d* symmetry, FDU-5, using P123 triblock copolymer as template. There are relatively few reports on the preparation of metal-incorporated mesoporous silicate via the EISA method [12,13].

Recently, we reported the synthesis and characterization of mesoporous Zr-incorporated silicate catalyst Zr-KIT-6 [14]. The Zr-KIT-6 material was found to be predominantly Lewis acidic, and shown to be active for both isopropanol and ethanol dehydrations, producing propylene and ethylene respectively with high selectivity [15,16]. Similarly, we prepared Zr-KIT-5 materials and showed them to be effective catalysts for the Friedel–Crafts alkylation reaction [17]. However, using the conventional hydrothermal synthesis technique, the maximum Zr loading achievable without

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http://dx.doi.org/10.1016/j.micromeso.2015.10.026
1387-1811/

losing structural integrity is limited to approximately 6 wt% (Si/Zr = 20). Higher Zr loadings (Si/Zr ≤ 10, approximately 13 wt% Zr) lead to a disordered heterogeneous sample in the case of Zr-KIT-5 and a phase transformation to either an amorphous or SBA-15 type material for Zr-KIT-6. In an attempt to obtain increased Zr loadings without losing structural integrity, we report here for the first time the preparation of Zr incorporated mesoporous material with higher Zr loadings (Si/Zr = 40 to 5, 3.2–26.5 wt% Zr) without the addition of mineral acid and using only the template material and metal source dissolved in a suitable solvent. The prepared catalysts are characterized in detail using standard techniques and successfully tested in the dehydration of isopropanol, yielding high activity and nearly total olefin selectivity at moderate activation energy.

2. Materials and methods

2.1. Materials

Triblock copolymer Pluronic P123 (EO_{20}–PO_{70}–EO_{20}), ethanol (200 proof, HPLC grade) and zirconium(IV) oxychloride octahydrate (reagent grade) were purchased from Sigma–Aldrich. TEOS and $ZrOCl_2 \cdot 8H_2O$ (98%) were purchased from Acros Organics and Alfa Aesar, respectively. Isopropanol (99.9%) and acetonitrile (99.9%) were purchased from Fisher Scientific. Zirconia nanopowder (ultrapure) was purchased from Sigma–Aldrich. Helium (HP) and nitrogen (HP) were purchased from Matheson. All solvents and reagents were used as received without any further purification.

2.2. Catalyst preparation and characterization

First, 4.5 g of triblock copolymer P123 were dissolved in 75 mL of ethanol. Subsequently, 10 g of TEOS were added and the mixture was stirred for 30 min. Finally, a solution containing appropriate amounts of $ZrOCl_2 \cdot 8H_2O$ (0.39 g–3.06 g) dissolved in 15 mL of ethanol and deionized water (0.5–2.5 mL) was added and the stirring was continued for another 2–6 h. The resulting mixture was then transferred to a porcelain evaporating dish (125 mm dia × 250 mL) and kept aside for 2–4 days for solvent evaporation. The resulting rigid solid is then recovered and heated in a 50 mL Parr autoclave at 100 °C for 24 h. The solid was then calcined in air at 550 °C for 6 h at a heating rate of 1.5 °C/min. The synthesized samples are named as Zr-EISA (Si/Zr). Techniques including SAXS, XRD, diffuse reflectance UV–Vis, FTIR, N_2 sorption, HR-TEM and SEM used to characterize the Zr-incorporated materials are explained elsewhere [14,17].

2.3. Isopropanol dehydration studies

Intrinsic kinetic study of the Zr-EISA catalyst samples for isopropanol (IPA) dehydration was performed with a stainless steel fixed-bed reactor. The reactor outlet is connected to a HP 5890 GC configured for online analysis and equipped with a ZB-WAX column and flame ionization detector. The catalyst samples were loaded and pretreated for 5 h at 500 °C in flowing air (Matheson) prior to reaction. A pre-mixed solution of isopropanol (99.9%, Fisher) and acetonitrile (internal standard, Sigma–Aldrich) was introduced with an ISCO syringe pump to a heated line where it is vaporized and then mixed with flowing nitrogen (High Purity, Matheson). The gas mixture is then preheated to the reaction temperature and passed through the fixed catalyst bed containing the Zr-EISA materials and exits to the sample loop in the GC for analysis. A schematic representation of the experimental unit for dehydration is given in Fig. S1. More details of the reactor setup and operation are provided elsewhere [16].

3. Results and discussion

3.1. Characterization of Zr-EISA

The elemental compositions of the Zr-EISA samples, as determined by ICP-OES, are listed in Table 1. The silicon to zirconium ratios in the Zr-EISA samples were confirmed to be in close agreement with those in the synthesis mixture.

The mesoporous character of the Zr-EISA samples is evident from the nitrogen adsorption–desorption isotherms (Fig. 1a). All Zr-EISA samples exhibit type IV adsorption isotherm with a sharp adsorption increase in the relative pressure (P/P_0) range of 0.6–0.8, attributed to capillary condensation within the mesopores. Furthermore, a H1-type hysteresis loop characteristic of mesoporous materials having a narrow pore size distribution is also evident. The textural properties of Zr-EISA samples, derived from N_2 physisorption measurements, are summarized in Table 1. As the Zr content is increased from 3.2 to 26.5 wt%, the BET specific surface area and the pore volume of Zr-EISA samples decreased from 818 to 614 m^2/g and from 1.2 to 1.01 cm^3/g, respectively. The pore size distributions of the Zr-EISA samples are shown in Fig. 1b. A narrow pore size distribution centered around a mean pore size of 7.1 nm was seen for the 3.2 wt% Zr sample (Si/Zr = 40). The mean pore size increased slightly to 8.1 nm with an increase in Zr content (to 15.3 and 26.5 wt%). This is attributed to the presence of occluded water inside the mesopore network of Zr-EISA samples at higher Zr loadings that may cause pore expansion during thermal treatment.

Wide angle XRD diffractograms of the Zr-EISA samples (Fig. 2) between 2θ values of 10° and 80° show no reflections due to ZrO_2 up to a Zr loading of 15.3 wt% (Si/Zr = 10). Reflections characteristic of ZrO_2 are observed at a higher Zr loading (26.5 wt%, Si/Zr = 5). The large hump observed between 15 and 25° is due to the amorphous nature of mesoporous silica.

Fig. 3 shows the small-angle X-ray scattering patterns of Zr-EISA samples. All samples show an intense peak around 0.88–1.05° (2θ), attributed to the (100) reflection of the hexagonal structure. The intensity of this peak decreases with an increase in Zr loading. For Zr-EISA containing 3.2 wt% Zr (Si/Zr = 40), an additional unresolved hump between 1.7° and 1.9° 2θ was noticed. These secondary reflections disappear with increasing Zr content suggesting the progressive loss of ordered structure at higher Zr loadings. Interestingly, even at very high Zr loading (26.5 wt% Zr, Si/Zr = 5), a weak diffraction of the main (110) peak exists indicating the presence of ordered channels albeit without any long-range ordering.

A representative TEM image of Zr-EISA with a Zr loading of 3.2 wt% (Si/Zr = 40) clearly shows ordered hexagonal arrays of mesopores in the direction parallel to the pore axis (Fig. 4A). However, at higher Zr loadings, ordered pore structure that is

Table 1
Physical properties of Zr-EISA catalysts.

Zr-EISA (Si/Zr)[a]	Si/Zr[b]	Zr wt%[b]	S_{BET}[c] m^2/g	V_{tp}[d] cm^3/g	$d_{P,\ BJH}$[e] nm
40	46	3.2	818	1.20	7.1
20	23	6.2	758	1.09	7.1
10	9	15.3	641	1.10	8.1
5	4	26.5	614	1.01	8.1

[a] Molar ratio in the synthesis gel.

[b] Actual molar ratio and Zr wt% in sample determined by ICP-OES.

[c] S_{BET} = BET Specific Surface Area from adsorption isotherm at P/P_0 between 0.05 and 0.30.

[d] V_{tP} = Total pore volume at 0.99 P/P_0.

[e] $d_{P,BJH}$ = pore diameter calculated from N_2 adsorption isotherms using the BJH model.