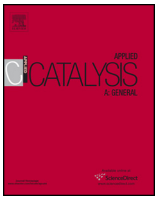
Applied Catalysis A: General 475 (2014) 469–476

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Enhanced metal loading in SBA-15-type catalysts facilitated by salt addition: Synthesis, characterization and catalytic epoxide alcoholysis activity of molybdenum incorporated porous silica

Sridhar Budhi[a,b], Chorthip Peeraphatdit[a], Svitlana Pylypenko[c], Vy H.T. Nguyen[a,d], Emily A. Smith[a,d], Brian G. Trewyn[a,b,*]

[a] *Department of Chemistry, Iowa State University, Ames, IA 50011, United States*
[b] *Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, United States*
[c] *Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, United States*
[d] *U.S. Department of Energy, Ames Laboratory, Ames, Iowa 50011, United States*

ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form 23 January 2014
Accepted 30 January 2014
Available online 7 February 2014

Keywords:
SBA-15
Alcoholysis
Epoxide
Molybdenum
Salt effect

ABSTRACT

We report a novel method to increase the metal loading in SBA-15 silica matrix via direct synthesis. It was demonstrated through the synthesis and characterization of a series of molybdenum containing SBA-15 mesoporous silica catalysts prepared with and without diammonium hydrogen phosphate (DHP) as an additive. Catalysts prepared with DHP show a 2–3 times increase in incorporation of molybdenum in the silica matrix and pore size enlargement. The synthesized catalysts were characterized using nitrogen sorption, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma–optical emission spectroscopy (ICP–OES). The catalytic activity of catalysts prepared with DHP for alcoholysis of epoxides was superior than the catalyst prepared without DHP. Alcoholysis of epoxides was demonstrated for a range of alcohols and epoxides under ambient conditions in as little as 30 min with high selectivity.

1. Introduction

Mesoporous materials have gained momentum after the discovery of ordered mesoporous silicates (M41S) by scientists at Mobil Corporation [1] two decades ago. Since then it has gained global interest by addressing pressing problems of society such as energy and environment. Metal incorporated porous silica materials have been tested in applications such as catalysis [2], hydrogen energy [3], etc. as efficient and reusable catalysts. The most comprehensively studied porous silica material for various applications (catalysis, host–guest chemistry, chromatographic separation) is MCM-41 since it has high specific surface area with uniform mesoporous channels [4]. However, small pore size and limited hydrothermal stability has limited its applications.

Stucky and coworkers [5] developed a new class of mesoporous silica called SBA-15 containing uniform cylindrical pores with tunable pore size (5–30 nm) and thick pore walls using environmentally benign non-ionic block copolymers as structure-forming templates under strong acidic conditions. However, unlike MCM-41-type synthesis, incorporation of metal ions in the framework of this mesoporous silica support for downstream applications is challenging because of strong acidic synthetic conditions. The highly acidic synthetic conditions of SBA-15 are detrimental for incorporation of metal ions through co-condensation [6] as it breaks the Si–O–metal bond. Additionally, under SBA-15 synthetic conditions, highly solubilized metal ions fail to precipitate and incorporation in the silica framework is not effective. Thus, post-synthetic grafting [7] is the widely used technique for doping metal ions in SBA-15 framework. Owing to these difficulties there have only been a few reports in the literature for direct incorporation of metal ions in SBA-15 framework. Vinu and coworkers [8] have optimized the synthetic conditions to synthesize SBA-15 under relatively low acidic conditions for improved incorporation of metal ions. It was later determined that metal incorporation efficiency was better under these less acidic conditions [9].

Improvements and tailoring of mesoporous silica for specific applications are often done by adding additives to the reaction mixture. Hydrocarbons added during the synthesis of mesoporous materials influences average pore size, crystallinity and pore size distribution [10]. Addition of inorganic salts is another approach to modify the textural properties of mesoporous silica. Addition of salts such as $MgCl_2$, $Ni(CH_3COO)_2$, and $Mg(CH_3COO)_2$ increased

---

[*] Corresponding author at: Colorado School of Mines, Department of Chemistry and Geochemistry, 152 Coolbaugh Hall, 1500 Illinois St, Golden, CO 80401, United States. Tel.: +1 11 303 384 2224.
E-mail address: btrewyn@mines.edu (B.G. Trewyn).

0926-860X/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2014.01.055

the periodicity of mesophase structure as demonstrated by Wang et al. [11]. Enlargement of the average pore size was observed when NaCl was added to reaction mixture when Krämer et al. [12] synthesized cubic *Ia3d* mesoporous silica. Tunable morphologies were reported by employment of K_2SO_4 and Na_2SO_4 by the Stucky and Zhao research groups [13,14]. Despite these advancements, to the best of our knowledge, there are no literature reports for the role of salts in dictating the incorporation of metals in a silica matrix.

Epoxidation, one of the most studied reactions in the literature, is of academic and industrial importance. It is a valuable intermediate to yield a range of products with applications in the pharmaceutical, polymer and agrochemical industries through regioselective ring opening. Nucleophiles such as alcohols, amines, cyanides, hydroxides, halides to name a few, can open epoxides. Ring opening of epoxides by alcohols (alcoholysis) yields β-alkoxyalcohols, which are precursors for mandelic acid and antibacterial agents including β-lactam antibiotics. Ring opening of epoxides are chemically cleaved by acid or base catalysts under elevated temperatures. In addition to acids and bases, several metal ions such as Al(III), Sn(II), Sn(IV), Co(III), triflates, Cr(III), and Lewis acid supported metal–organic frameworks were recently reported as catalysts for ring opening of epoxides [15]. However, these catalysts are either toxic, less abundant in nature, involve complex preparatory procedures for synthesis, energy-intensive or require prolonged reaction times.

Next to titanium, molybdenum is the most studied transition metal through incorporation into silica matrix due to its wide catalytic applications. Molybdenum is widely studied in oxidation reactions, petroleum chemistry [16] and recently in the conversion of biomass into renewable energy [17]. A few examples of reactions catalyzed by molybdenum are epoxidation of olefins [18], decomposition of NO_x [19], hydrodeoxygenation, hydrodenitrogenation, hydrodesulfurization, alkane oxidation [20], oxidative dehydrogenation [21], metathesis [22] and transesterification [23]. To the best of our knowledge, there have been only two reports where Mo was used to study the ring opening of epoxides on alumina support [24,25]. However, their studies failed to distinguish whether the catalytic activity was due to Mo or Al(III) ions on the support. Graham et al. [26] demonstrated ring opening of epoxides using aluminosilicates where Al(III) was the active catalyst. Thus, the reports of catalytic activity by molybdenum on alumina for ring opening of epoxides could potentially be due to the presence of both molybdenum and alumina. These reports clearly indicate that participation of supports on catalytic activity cannot be ignored.

Mo incorporated SBA-15 is often prepared by post-synthesis impregnation and grafting rather than direct synthesis due to poor metal incorporation. Apart from highly acidic conditions, the oxidation state of molybdenum ions (+6) make isomorphic substitution by Si (+4) challenging. Thus, we need a comprehensive preparatory procedure for direct synthesis of metal incorporated SBA-15. Herein, for the first time, we report the synthesis of Mo-SBA-15 through co-condensation using DHP as an additive added in the reaction mixture. Addition of DHP was found to influence the incorporation of molybdenum along with other textural properties. These catalysts were successfully tested for alcoholysis under ambient conditions for a wide range of alcohols.

2. Experimental

2.1. Materials

Ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ and diammonium hydrogen phosphate $[(NH_4)_2HPO_4$, DHP] were purchased from Fisher Chemicals, and were used as the molybdenum precursor and additive, respectively. Triblock copolymer poly(ethylene glycol)-block-poly(propyleneglycol)-block-poly(ethylene glycol) (Pluronic P123, MW = 5800, $EO_{20}PO_{70}EO_{20}$, Aldrich) was used as the structure-directing template. Tetraethylorthosilicate (Aldrich) was used as the silica source for the synthesis of SBA-15. HCl (2 M) solution was prepared from 37 wt% HCl purchased from Fisher Chemical. All epoxides and alcohols tested for catalytic activity were purchased from Fisher and Aldrich. All reagents were used as received without further purification.

Synthesis of Molybdenum incorporated SBA-15 catalyst: In a typical synthesis, 4 g of pluronic P123 was added to 30 mL nanopure water in a polypropylene bottle at 313 K and stirred at 600 rpm for 3 h. A solution of previously mixed HCl (2 M, 10 mL) in 60 mL of water was also added to the dissolved template solution and stirred for another 1 h. TEOS (9 g, 4.3 mmol) was added drop wise to the reaction mixture, followed by quick addition of the required amount of ammonium heptamolybdate tetrahydrate. The samples were labeled as Xg-Mo-SBA-15-TTT. *X*g denotes amount of molybdenum precursor added and TTT represents the hydrothermal treatment temperature in degrees Celsius. For the syntheses that involved addition of the additive, diammonium hydrogen phosphate, labels were Xg-MoP-SBA-15-TTT, where *X*g is the amount in grams of molybdenum and DHP added and TTT as defined above. In cases where different amounts of molybdenum precursor and DHP were added it was denoted by *X*gP-*Y*gMo-SBA-15-TTT where *X*g and *Y*g is amount of DHP and molybdenum precursor in grams, respectively. Whenever the additive was included, it was added along with the molybdenum precursor. After addition of all components, the reaction mixture was stirred for another 24 h at 313 K and then subjected to hydrothermal treatment at the desired temperature for an additional 48 h. The reaction mixture was cooled, filtered and washed with methanol and water. The resulting sample was oven dried overnight at 373 K and then followed by calcination at 550 °C for 8 h to remove the template in presence of flowing air.

2.2. Characterization

X-ray diffractograms (XRD) of synthesized samples were recorded utilizing a Rigaku Ultima (IV) diffractometer using Cu $K\alpha$ radiation source. The diffractograms were recorded from 0.5° to 10° with a step size of 0.02°. Wide angle XRD was recorded for certain samples from 20° to 80° at a rate of $1^\circ\ \mathrm{min}^{-1}$. Surface analyses of samples to determine surface area and pore sizes were measured utilizing nitrogen sorption analysis in a Micromeritcs ASAP 2020 analyzer. The samples were degassed for 6 h at 373 K prior to measurements. The Brunauer–Emmett–Teller (BET) and the Barrett–Joyner Halenda (BJH) equations were used to calculate specific surface area and pore size distributions, respectively. Transmission electron microscopy (TEM) imaging was done using a Tecnai F^2 microscope. Particle morphology was determined by scanning electron microscopy (SEM) using a Hitachi S4700 FE-SEM system with 10 kV accelerating voltage. Raman spectra were collected using a previously described instrument with 785 nm excitation and a 10×, 0.3 numerical aperture objective to collect the Raman scatter [27]. The laser power at the sample was 6 mW. Spectra were collected with a 30-s acquisition, and were background subtracted using a spectrum collected with no sample in the sample holder. XPS was used to characterize the oxidation states of Mo in the catalysts on a Kratos Nova X-ray photoelectron spectrometer supplied with a monochromatic Al $K\alpha$ source operating at 300 W. Casa XPS was used for analysis and quantification of spectra, sensitivity factors were supplied by manufacturer. A linear background was applied to C 1s, O 1s, and Si 2p regions, and a Shirley background was applied to Mo 3d region. Analysis