



Novel tungsten-incorporated mesoporous silicates synthesized via evaporation-induced self-assembly: Enhanced metathesis performance



Jian-Feng Wu^{a,1}, Anand Ramanathan^{a,1}, Bala Subramaniam^{a,b,*}

^a Center for Environmentally Beneficial Catalysis, The University of Kansas, Lawrence, KS 66047, USA

^b Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66045, USA

ARTICLE INFO

Article history:

Received 29 December 2016

Revised 12 February 2017

Accepted 14 February 2017

Keywords:

Tungsten

Evaporation-induced self-assembly

Metathesis

Ethylene

2-Butene

ABSTRACT

Tungsten-incorporated mesostructured silicates were successfully synthesized by evaporation-induced self-assembly (EISA) method. Tungsten loadings from 2.9 to 22.2 wt% were achievable, with the corresponding BET surface areas decreasing from 520 to 284 m²/g at increased W loading. The W-EISA samples displayed amorphous ordered pore structure with an average pore size distribution of 2.3–3.3 nm. Hydrated isolated tetrahedral [WO₄]²⁻ species and hydrated octahedral polytungstate species were identified from diffuse reflectance UV/Vis spectra under ambient conditions. Uniform distribution of W species, mostly located near the surface, was evident from XPS W 4f photoelectron image. At 450 °C and 1 atm, for the reaction of ethylene + 2-butene metathesis to form propene, the W-EISA catalysts outperform either impregnated catalysts (WO₃/SiO₂ and WO₃/KIT-6) or one-pot synthesized W-KIT-6 catalyst, implying better W utilization in the W-EISA catalyst.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Alternative propylene routes are being sought by chemical companies in order to make up the shortages in naphtha-based propylene [1]. In this context, on-purpose propylene technologies such as olefin metathesis and methanol-to-olefins technologies have attracted considerable attention [2,3]. For the heterogeneous ethylene + butene metathesis reaction, the most frequently reported catalysts contain W, Mo or Re as the active species [4–15].

The traditional industrial catalyst WO₃/SiO₂, prepared by the wet impregnation method [16–22], suffers from the limitations including low dispersion of the active W species and the formation of inactive crystalline WO₃ species, even at low W loading [16,23,24]. It is widely accepted that good dispersion of the active species is critical to superior catalytic performance [16,25]. To address this challenge, several novel synthesis techniques for metathesis catalysts have been reported, such as grafting [8,26–31], sol-gel method [32–39], non-hydrolytic sol-gel method [40–44], thermal spreading [45,46], flame-spray pyrolysis [47], and aerosol method [48–50]. However, some of these synthesis methods have shortcomings. For example, the grafting method requires expensive substrates. The sol gel method requires filtration as an

additional step and also suffers from the leaching of metal ion during synthesis. The non-hydrolytic sol-gel method involves operation under an inert atmosphere in a glove box. The thermal spreading method allows only limited control over the physico-chemical properties of the catalyst. The flame-spray pyrolysis and one-pot aerosol methods require special instrumentation. Hence, a relatively simple synthesis method that provides a high dispersion of accessible active sites and is easily scalable continues to be of interest.

An attractive way for synthesizing metathesis catalysts is by evaporation-induced self-assembly (EISA). The EISA method has been successfully applied to synthesize various oxides and mixed oxides possessing ordered mesopores with enhanced thermal stability [51–53]. Recently, we employed a modified EISA method to prepare Zr silicates (Zr-EISA) and achieved a high dispersion of Zr species (up to ~15 wt% Zr loading) without any detectable formation of bulk ZrO₂ species [54]. In the current work, we extended this approach to prepare W-EISA metathesis catalysts with enhanced W loading as well as dispersion of active W species compared to reported methods. The surface composition of the synthesized W-EISA catalysts was characterized by XPS, and their TOFs were assessed for the cross-metathesis reaction of ethylene and 2-butene to yield propene. Our results show that the W-EISA catalysts in general show better propene yield and TOFs than reported W-based metathesis catalysts.

* Corresponding author at: Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66045, USA. Fax: +1 785 864 6051.

E-mail address: bsubramaniam@ku.edu (B. Subramaniam).

¹ Contributed equally.

2. Experimental

2.1. Chemicals

Triblock copolymer Pluronic P123 (EO₂₀-PO₇₀-EO₂₀, average MW = 5800), and tetraethyl orthosilicate (TEOS, 98%) were purchased from Sigma–Aldrich. 2-Butene (≥ 95 wt%, 39% *cis*-2-butene and 61% *trans*-2-butene) and ethylene ($\geq 99.5\%$) were purchased from Matheson Tri-Gas Inc. Tungsten (VI) chloride (99.9%-W) was purchased from Strem Chemicals. All the reagents were used as received without further purification.

2.2. Catalyst preparation

First, 4.5 g of triblock copolymer P123 were dissolved in 40 mL of ethanol. Subsequently, 10 g of TEOS were added and the mixture was stirred for 30 min. Then a solution containing appropriate amounts of WCl₆ (0.19 g–1.89 g) dissolved in 35 mL of ethanol was added and the stirring was continued for another 30 min. The resulting mixture was then transferred into a borosilicate petri dish (100 mm diameter \times 20 mm height) and kept in a fumehood for 2–4 days for solvent evaporation. The resulting solid flakes (“as-synthesized catalyst”) were then calcined in air at 500 °C for 5 h at a heating rate of 1.5 °C/min. The synthesized samples are designated as W-EISA (X) where X represents W wt%. A schematic of this procedure is shown in the [Supplementary Materials \(Fig. S1\)](#).

2.3. Catalyst characterization

Small angle X-ray scattering and wide angle XRD patterns of W-EISA samples were obtained in a PANalytical Empyrean instrument, operating at 45 kV and 40 mA. The samples prepared for TEM analysis were suspended in ethanol solution and ultrasonically treated for 15 min. Approximately 10 μ L of this mixture were deposited onto the copper grid, which was then transferred into the TEM chamber for analysis after drying in air. The catalyst morphology and particle size were analyzed by bright-field and dark-field transmission electron microscopy (TEM) using an FEI Technai G2 transmission electron microscope, operating at an electron acceleration voltage of 200 kV.

The tungsten and silicon contents of the catalysts were obtained from inductively coupled plasma optical emission spectrometry (ICP-OES) analysis using a Horiba Jobin Yvon JY 2000 instrument. The nitrogen adsorption-desorption isotherms were measured on a Quantachrome NOVA 2000 instrument. The total acidity of the catalysts was obtained from temperature-programmed desorption of ammonia (NH₃-TPD) analysis using a Micromeritics Autochem 2910 instrument. The structure of the surface species was measured by diffuse reflectance UV/Vis (DR UV/Vis) spectra with a PerkinElmer Lambda 850 spectrometer, using Spectralon as the reference. Detailed procedures for the various techniques (ICP-OES analysis, N₂ adsorption-desorption isotherms, NH₃-TPD and UV/Vis) are described elsewhere [38]. The XRD and UV/Vis measurements were performed under ambient conditions.

A dual-beam charge neutralizer was employed to compensate the charging effect. The spherical capacitance analyzer was operated with a pass energy of 46.95 eV for surface W/Si ratio analysis and 117.4 eV for secondary-electron X-ray induced image (SXI). To maximize information from the catalyst surface, the sample stage was tilted to 20° [38]. Prior to the analysis, the surface of the catalyst sample was sputtered with Ar⁺ ions (2.0 keV) for 5 min. The following spectra were recorded: survey spectrum, Si 2p and W 4f. The resulting spectral data were processed with MultiPak software. All XPS peaks were referenced to the Si_{2p} peak at 103.3 eV.

The chemical nature of the carbon deposits on the used catalyst was studied by solid state NMR. The used catalyst sample was packed into a 4 mm Bruker rotor in an air atmosphere. Then, the sample was investigated by ¹³C cross-polarization (CP) MAS NMR spectroscopy on a Bruker Avance III WB 400 MHz NMR instrument at a spin rate of 10.0 kHz. The ¹³C chemical shifts were referenced to tetramethylsilane (TMS) and the precision of the ¹³C chemical shift is ± 1.0 ppm.

2.4. Metathesis activity

The catalytic activity of W-EISA catalysts for the metathesis of ethylene and 2-butene to propene was evaluated in a stainless steel fixed-bed reactor (i.d. = 9.4 mm) described elsewhere [38]. Briefly, 1 g of catalyst (0.425–0.850 mm mean diameter) was calcined in a muffle furnace at 500 °C for 5 h and then loaded into the reactor. A thermocouple probe was placed in the catalyst bed to measure the catalyst temperature. The catalyst was first treated with air (100 std cm³/min, moisture < 67 ppm) for 5 h, then at 550 °C for 1 h with N₂ (50 std cm³/min), following which the reactor was cooled down to the desired reaction temperature. A mixture of ethylene and 2-butene (ethylene/2-butene molar ratio = 3) was then introduced into the reactor. The reaction studies were performed at 450 °C and 1 atm at a weight hourly space velocity (WHSV) of 2.0 h⁻¹ based on the total ethylene + 2-butene flow rate. An on-line Varian CP-3800 gas chromatograph, equipped with an Agilent GS-gaspro[®] column (30 m \times 0.320 mm) and a flame ionization detector (FID), was used to analyze the reaction products. The line between the reactor and the six-way valve was heated to 160 °C to prevent product condensation. A typical gas chromatograph based on sampling and analysis of the reactor effluent stream is given in the [Supplementary Materials \(Fig. S2\)](#). The various catalyst assessment metrics are as follows [38]:

$$X_{2\text{-butene}} = \frac{[2\text{-butene}]_{\text{in}} - [2\text{-butene}]_{\text{out}}}{[2\text{-butene}]_{\text{in}}} \times 100\%$$

$$S_{\text{propene}} = \frac{[\text{propene}]_{\text{out}}}{[2\text{-butene}]_{\text{in}} - [2\text{-butene}]_{\text{out}}} \times 100\%$$

$$Y_{\text{propene}} = X_{2\text{-butene}} \times S_{\text{propene}} \times 100\%$$

$$\text{Mass balance closure} = \frac{[\text{Total carbon in products}]}{[\text{Total carbon in feed components}]} \times 100\%$$

$$\text{TOF (s}^{-1}\text{)} = \frac{m_{2\text{-butene}}(\text{g} \cdot \text{h}^{-1}) / M_{2\text{-butene}}(\text{g} \cdot \text{mol}^{-1}) \times Y_{\text{propene}}}{3600(\text{s} \cdot \text{h}^{-1})} \bigg/ \frac{m_{\text{catalyst}}(\text{g}) \times W_{\text{wt}\%}}{M_{\text{W}}(\text{g} \cdot \text{mol}^{-1})}$$

X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5000 Versa Probe II instrument. Monochromated Al K α (50 W, 15 kV) X-ray was used with a beam diameter of 200 μ m.

where $X_{2\text{-butene}}$, S_{propene} and Y_{propene} represent the steady state values of 2-butene conversion, propene selectivity and propene yield, respectively; $m_{2\text{-butene}}$, $M_{2\text{-butene}}$ and m_{catalyst} represent mass flow

Download English Version:

<https://daneshyari.com/en/article/4757484>

Download Persian Version:

<https://daneshyari.com/article/4757484>

[Daneshyari.com](https://daneshyari.com)