Novel Tungsten-incorporated Mesoporous Silicates Synthesized via Evaporation-Induced Self-Assembly: Enhanced Metathesis Performance

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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 520-284 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.

Keywords: Tungsten; Evaporation-Induced Self-Assembly; Metathesis; Ethylene; 2-Butene.

1. Introduction

Alternative propylene routes are being sought by chemical companies in order to make up the shortages in naptha-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 physicochemical 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 ZrO_2 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.

2. Experimental

2.1 Chemicals

Triblock copolymer Pluronic P123 ($\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$, 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 WCl_6 (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 show 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 μL 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 2000e 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.

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. 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 ^{13}C 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 ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) and the precision of the ^{13}C 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 cm^3/min , moisture < 67 ppm) for 5 h, then at 550°C for 1 h with N_2 (50 std cm^3/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 x 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]:

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

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

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

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

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

where $X_{2-butene}$, $S_{propene}$ and $Y_{propene}$ represent the steady state values of 2-butene conversion, propene selectivity and propene yield, respectively; $WHSV$, $M_{2-butene}$ and $m_{catalyst}$ represent weight hourly space velocity, molar mass of 2-butene and the mass of catalyst, respectively. The “apparent turnover frequency” (TOF) is based on steady state values of propene yield, obtained in the absence of mass transfer limitations. It is extremely difficult, if not impossible, to quantitatively determine the amount of active W species under reaction conditions. To compare the performance of various W-based catalysts, we use an “apparent TOF value” based on the total W content in the various catalysts. Thus, at either similar W loading or similar W surface density, differences in “apparent TOF” values provide a measure of the differences in accessible active W sites. Such an approach for comparing relative performances of metathesis catalysts has been previously reported by other groups [42, 47] and by us [38].

3. Results

3.1. Structural characterization

The SAXS pattern of W-EISA samples showed a peak centered around $1.18 - 1.23$ (2θ °), whose intensity decreased with an increase in W loading (Fig. 1). No additional peaks were detected at higher 2θ values, indicating a low degree of ordering in the mesoporous structure. In addition, peak broadening was also evident at increased W loadings, implying a decrease of long range ordering in these samples. These trends are also evident from TEM micrographs (Fig. 2) of the W-EISA samples that showed amorphous ordered mesoporous structure for W loadings up to 13.8 wt% (Fig. 2a-c) but a worm-type disordered mesoporous structure at the highest W loading (22.2 wt%, Fig. 2d).

Fig. 1. Small angle XRD patterns of W-EISA catalysts with tungsten loading (wt%) of 2.9, 6.9, 13.8, and 22.2.

Fig. 2. TEM images of W-EISA samples with tungsten loading (wt%) of (a) 2.9, (b) 6.9, (c) 13.8 and (d) 22.2.

3.2 Textural and acidity characterization

N₂ physisorption of W-EISA samples (Fig. S3) displayed type IV isotherm [55]. At 2.9 wt% W loading, a sharp step occurs between 0.37 and 0.55 P/P_0 , signifying capillary condensation of N₂ in the mesopores. At higher W loadings, this step change is not as clearly resolved and the characteristic hysteresis loop was also not observed, similar to MCM-41 type samples. The BET surface area, pore volume, and average pore size of the W-EISA samples are in the range of 284 – 520 m²/g, 0.16 – 0.41 cm³/g and 2.3 – 3.3 nm, respectively (see Table 1). The surface area and

pore volume were found to decrease significantly at the highest W loading (22.2 wt%). NH₃-TPD results (Table 1 and Fig. S4a) for the W-EISA samples revealed a general trend of increasing acidity with W loading, with a nearly linear increase up to 13.8 wt% W (Fig. S4b). The values between the theoretical (Si/W) ratio in the synthesis gel and the measured (Si/W) ratio by ICP-OES are really close, indicating there is no loss of W during the synthesis.

Table 1. Physicochemical properties of W-EISA catalysts

W-EISA			S_{BET} (m ² /g) ^d	V_{tp} (cc/g) ^e	$d_{\text{p, BJH}}$ (mm) ^f	Total acidity (mmol NH ₃ /g) ^g
Theoretical (Si/W) ^a	Measured (Si/W) ^b	W (wt%) ^c				
100	103	2.9	515	0.41	3.3	0.07
40	41	6.9	471	0.31	2.6	0.21
20	18	13.8	520	0.31	2.4	0.39
10	10	22.2	284	0.16	2.3	0.51

^a Molar ratio in the theoretical synthesis gel, ^b Molar ratio in sample determined by ICP-OES, ^c W content in sample determined by ICP-OES, ^d S_{BET} = BET specific surface area, ^e V_{tp} = total pore volume, value at 0.99 P/P_0 , ^f $d_{\text{p, BJH}}$ = pore diameter calculated from N₂ adsorption isotherms using the BJH model, ^g determined from NH₃-TPD profiles.

3.3 Characterization of W species

Wide-angle XRD patterns of the W-EISA samples are provided in Fig. S5. All W-EISA samples exhibit a broad band from $2\theta = 15$ to 35° attributed to amorphous silica. Characteristic diffraction peaks for WO₃ were not detected for W loadings up to 13.8 wt%, suggesting that the W species are well dispersed in these samples. At the highest W loading (22.2 wt%), broad peaks with low intensity were identified at 24° and 33° . These peaks are attributed to crystallites of WO₃.

The DR UV/Vis spectra of W-EISA samples (Fig. 3) were measured at wavelengths ranging from 200 to 800 nm under ambient conditions. The absorption peak around 236 nm is attributed

to hydrated isolated tetrahedral $[\text{WO}_4]^{2-}$ species, similar to those observed in Na_2WO_4 [32, 56, 57]. The peak around 267 nm on W-EISA (2.9 wt% W) sample is assigned to hydrated octahedral polytungstate species [32, 56, 57]. This peak is red-shifted to approximately 282 nm at higher W loadings with increased intensity. This observation suggests an increase in the cluster size of polytungstate species at the higher W loadings. A broad peak observed around 400 nm at the highest W loading (22.2 wt%) is due to WO_3 species [32, 56, 57]. STEM micrographs also show evidence of WO_3 nanocrystals in the W-EISA catalysts (see Fig. S6).

Fig. 3. Diffuse reflectance UV-Vis spectra of W-EISA samples. The UV/Vis measurements were performed at ambient conditions.

3.5 XPS characterization

In order to understand the distribution of the surface W species as well as the interactions between W species and the support, the surface W/Si atomic ratio $(\text{W/Si})_s$, W 4f binding energy and the peak widths of the W-EISA samples were investigated by XPS (Fig. S7). The $(\text{W/Si})_s$ values increase with W loading (Table 2) but are lower than the corresponding (W/Si) values

based on the total W and Si contents in the various samples. As inferred from Fig. 4, the $(\text{W/Si})_s$ values are close enough to the parity line suggesting that the W species are mostly located near the surface. The deviation of the $(\text{W/Si})_s$ values from the parity line increases with W loading till 13.8 wt% W, and then approaches the parity line at the highest W loading (22.2 wt%). This trend is attributed to the formation of nanocrystal WO_3 species (between 1 and 10 nm) on the catalyst surface at the highest W loading, as confirmed by the combination of wide-angle XRD patterns (Fig. S5) and the STEM analysis (Fig. S6). The data corresponding to the control sample W-KIT6 (13.7) is above the parity line, indicating the crystalline WO_3 species are formed on the surface, as also confirmed by wide-angle XRD pattern of W-KIT6 (13.7) catalyst (Fig. S8).

Table 2. Surface characterization of W-EISA samples by XPS: W/Si ratio, W 4f binding energy and W 4f peak width.

Catalyst	Total W/Si values	W_s (at. %)	Si_s (at. %)	$(\text{W/Si})_s$ atomic ratio	W 4f	
					BE (eV)	fwhm (eV)
W-EISA (2.9)	0.0097	0.60	99.40	0.0060	37.0	5.4
W-EISA (6.9)	0.0245	1.57	98.43	0.0160	36.6	5.1
W-EISA (13.8)	0.0547	3.80	96.20	0.0395	36.5	4.2
W-EISA (22.2)	0.1005	8.71	91.29	0.0954	36.3	4.7

Fig. 4. Comparison of total W/Si ratio (ICP analysis results) and surface W/Si ratio (XPS results) of W-EISA samples and W-KIT-6 (13.7) catalyst. The values in parentheses denote the W wt%.

For W loadings between 2.9 and 22.2 wt%, the W-EISA samples show generally decreasing trends in the W 4f binding energy and the peak width values. Among these catalysts, W-EISA (2.9) shows the highest values of W 4f binding energy and the peak width, indicating a stronger interaction between W species and the support. The abrupt increase in peak width observed in W-EISA (22.2) sample may due to the formation of WO_3 species (Figs. 3, S5 and S6).

Fig. 5 compares the XPS W 4f photoelectron images of the W-EISA (13.8) catalyst with that of a W-KIT-6 (13.7) mesoporous silicate with similar W loading. The bright yellow spots on the W-EISA (13.8) samples (Fig. 5a) are smaller and more uniform compared to those on the W-KIT-6 (13.7) sample (Fig. 5b), indicating better dispersion of W species on the W-EISA sample. This conclusion is supported by the fact that the W-EISA (13.8) catalyst shows better metathesis

performance (59.2% propene yield) compared to the W-KIT-6 (13.7) catalyst (36.6% propene yield) [38] at identical reaction conditions (see following section).

Fig. 5. XPS W 4f photoelectron image of (a) W-EISA (13.8 wt% W) sample compared with (b) W-KIT-6 sample (13.7 wt% W). The size of bright yellow spots is indicative of the size of W species on the surface.

3.6. Metathesis activity results

The metathesis activity of the W-EISA catalysts was tested at the following conditions: $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, $\text{WHSV (ethylene and 2-butene)} = 2.0 \text{ h}^{-1}$, $n(\text{ethylene})/n(\text{2-butene}) = 3/1$. Exemplary conversion and selectivity profiles for the W-EISA (13.8) catalyst are shown in Fig. 6. Following the typical break-in period of approximately 2 h, when the tungsten-carbene and tungsten-cyclobutane intermediates are believed to form [19], the 2-butene conversion attains a steady value of $68.1 \pm 0.1\%$. The corresponding selectivity values are $87.0 \pm 0.1\%$ for propene, $11.5 \pm 0.1\%$ for 1-butene (formed from 2-butene isomerization) and 1.5% for pentenes (formed from the secondary cross-metathesis and isomerization [38]). Therefore, 2-butene is mainly converted to propene. The mass balance closure at steady state was $100 \pm 2.5\%$, which is within

experimental error. Similar profiles for 2-butene conversion, propene selectivity and propene yield for all the W-EISA catalysts are provided in the Supplementary Materials (Fig. S9).

Fig. 6. 2-Butene conversion, propene, 1-butene and pentenes selectivity as a function of time on stream of W-EISA (13.8) catalyst at $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, WHSV (ethylene and 2-butene) = 2.0 h^{-1} , $n(\text{ethylene})/n(2\text{-butene}) = 3/1$.

As shown in Fig. 7, the 2-butene conversion increases with W loading reaching a plateau at higher W loading, suggesting the formation of inactive W species beyond a certain W content. The propene selectivity follows an identical trend of 2-butene conversion. In contrast, the selectivity toward the major by-product, 1-butene, follows the opposite trend due to its transformation to 2-butene (the main reactant for the metathesis reaction) [38]. At all W loadings, selectivity towards the pentenes remains low.

Fig. 7. 2-Butene conversion, propene selectivity, 1-butene selectivity and pentenes selectivity as a function of W loading amount at $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, WHSV (ethylene and 2-butene) = 2.0 h^{-1} , $n(\text{ethylene})/n(2\text{-butene}) = 3/1$.

As shown in Fig. 8, the steady state propene yield increases with W loading up to 13.8 wt% and then reaches a plateau at higher W loading. This trend is explained in terms of the increased formation of nanocrystalline WO_3 species at the higher W loadings (see Figs. S5 and S6). While such species contribute to an increase in the total acidity, they possess little or no metathesis activity, as inferred from Fig. 7.

Fig. 8. Propene yield and catalyst total acidity as a function of tungsten loadings on W-EISA catalyst at $T = 450^\circ\text{C}$, $P = 1$ atm, WHSV (ethylene and 2-butene) = 2.0 h^{-1} , $n(\text{ethylene})/n(2\text{-butene}) = 3/1$. The propene yields represent the mean of the steady state values between 4.3-7 h.

As shown in Table 3, the apparent TOFs observed with the W-EISA samples increase significantly at lower W loadings. The W-EISA (2.9) catalyst shows the highest TOF, suggesting that a large fraction of the accessible W species is active. Further, at either similar W loadings or surface density (0.44 and 0.48 W/nm^2), the TOFs of W-EISA catalysts are greater than those observed with either impregnated W catalysts (WO_3/SiO_2 and $\text{WO}_3/\text{KIT-6}$) or W-KIT-6 catalyst [38], indicating better W utilization in the W-EISA catalyst.

Table 3. Comparison of apparent TOFs on various W-based mesoporous silicates at similar operating conditions: $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, WHSV (ethylene and 2-butene) = 2.0 h^{-1} , $n(\text{ethylene})/n(2\text{-butene}) = 3/1$.

Catalyst	W loading (wt%)	W surface density (W/nm^2) ^a	Apparent TOF ($\text{mmol}_{\text{propene}} \text{mol}_\text{W}^{-1} \text{s}^{-1}$)
W-EISA (2.9)	2.9	0.18	8.03 ± 0.14^b
W-EISA (6.9)	6.9	0.48	4.75 ± 0.03^b
W-EISA (13.8)	13.8	0.87	3.13 ± 0.01^b
W-EISA (22.2)	22.2	2.56	1.97 ± 0.05^b
WO ₃ /SiO ₂ (7.4)	7.4	0.94	2.76 ± 0.03^c
WO ₃ /KIT-6 (7.6)	7.6	0.44	3.18 ± 0.03^c
W-KIT-6 (13.7)	13.7	1.44	1.95 ± 0.02^c

^a Values calculated from the nominal W loading and assuming that all W atoms are uniformly dispersed across the catalyst surface.

^b Mean value between 4.3-7 h at steady state.

^c Mean value between 3-7 h at steady state [38].

4. Discussion

All the W-EISA catalysts possess mesoporous structure (pore diameter > 2 nm), as confirmed from SAXS, TEM and N₂ sorption data. At W loadings less than 13.8 wt%, wide angle XRD spectra show no evidence of the presence of WO₃ crystallites (> 3 nm), indicating that the W species are well dispersed within the framework. At higher W loading (22.2 wt% W), however, the long-range order vanishes and nanocrystallites of WO₃ were evident from STEM images (>1 nm, Fig. S6) and wide angle XRD (~10 nm, Fig. S5), respectively.

UV/Vis spectra, acquired at ambient conditions, reveal hydrated forms of isolated tetrahedral [WO₄]²⁻ species and hydrated octahedral polytungstate species at W loadings lower than 13.8 wt%. In addition, WO₃ crystallites are also evident at 22.2 wt% W loading. At the elevated reaction temperatures, these hydrated W species (precursors) typically decompose to form

isolated surface dioxo $(\text{O}=\text{O})_2\text{W}(\text{O})_2$, and mono-oxo $\text{O}=\text{W}(\text{O})_4$ species, while the WO_3 crystallites are unaffected [19]. The dioxo species react with propene to generate the envisioned oxo carbene $(\text{O}=\text{O})(\text{CH}_2=\text{O})\text{W}(\text{O})_2$ species [21].

In the EISA synthesis method, all the Si and W in the source compounds end up in the synthesized catalyst. Hence, the Si/W ratio within the W-EISA catalyst can be accurately adjusted to the desired value (Table 1). Further, the textural properties, the total acidity and the activity of W-EISA catalysts are tuned by the W loading. In contrast, other one-pot methods suffer from varying degrees of metal losses [58, 59]. Analysis of surface W/Si XPS data (Fig. 4) show that the W species within the synthesized W-EISA catalysts are mostly located near the surface and hence easily accessible to the reactants. Comparison of W 4f photoelectron images of W-EISA (13.8) and W-KIT-6 (13.7) catalysts clearly reveals that the W species are more finely dispersed in W-EISA (13.8) compared to W-KIT-6 (13.7) catalyst. This difference is also supported by the XRD data (Figs. S5 and S8).

The activity of the W-EISA catalysts is dependent on the W loading. The 2-butene conversion increases with W loading reaching a plateau at higher W loading, suggesting the formation of inactive W species on the surface beyond a certain W content (~ 13 wt% W). While the propene yields during 7 h continuous runs are stable for W loadings less than 13.8 wt%, it decreases slightly at the higher W loading (22.2 wt%). The attainment of a plateau in propene yield and the slight deactivation trend at 22.2 wt% W loading coincide with the formation of inactive WO_3 nano-crystallites at the higher W loadings (Figs. S5 and S6) [38]. Further, the WO_3 nanoparticles have been reported to favor coke formation [19], which may explain the slight deactivation trend at the higher W loading. The deposits on the used W-EISA (22.2) catalyst are primarily aromatic compounds and oligomers (Fig. S10).

Table 3 compares metathesis activities of the W-EISA catalysts prepared by the EISA method with (a) two impregnated catalysts (WO_3/SiO_2 and $\text{WO}_3/\text{KIT-6}$) [38], and (b) the W-KIT-6 catalyst synthesized by the one-pot method [38]. For at either similar W loading or similar surface density (0.44 and 0.48 W/nm²), W-EISA catalysts outperform the impregnated catalysts WO_3/SiO_2 (7.4) and $\text{WO}_3/\text{KIT-6}$ (7.6) as well as the W-KIT-6 (13.7) catalyst, suggesting better W dispersion and utilization. Interestingly, impregnated WO_3/SiO_2 (7.4) and $\text{WO}_3/\text{KIT-6}$ (7.6) catalysts show evidence of WO_3 crystallite peaks (~40-50 nm) at much lower W loadings (Fig. S8), explaining their inferior metathesis activity compared to W-EISA catalysts.

5. Conclusion

We demonstrated a facile one-step synthesis of W-incorporated mesoporous silicates by the EISA method using WCl_6 as the W source. Highly dispersed W species (isolated tetrahedral $[\text{WO}_4]^{2-}$ species and octahedral polytungsten species) are preferentially generated at W loadings up to 13.8 wt%. XPS W 4f photoelectron image shows direct evidence of the formation of highly dispersed W species on the surface. At the highest loading (22.2 wt% W), WO_3 nanocrystallites are also formed.

The W-EISA catalysts exhibit stable propene yield at 450 °C during a 7 h run in a fixed-bed reactor. The propene yield increases with W loading up to 13.8 wt% and then reaches a plateau (~60%) at higher W loadings, indicating the formation of inactive W species at such W loadings. At 450°C and 1 atm, the W-EISA catalysts outperform either impregnated W catalysts (WO_3/SiO_2 and $\text{WO}_3/\text{KIT-6}$) or the one-pot synthesized W-KIT-6 catalyst, indicating better W utilization by virtue of forming highly dispersed and accessible W species via the EISA method.

Acknowledgments

We acknowledge the support from joint National Science Foundation and Environmental Protection Agency program Networks for Sustainable Material Synthesis and Design (NSF-EPA1339661). The WAXS analysis instrument (XRD) at the University of Kansas was acquired through a NSF Major Research Instrumentation grants CHE-0923449. We thank Dr. Prem Thapa for assistance with TEM and XPS analyses.

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