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Enhanced metathesis of ethylene and 2-butene on tungsten incorporated ordered mesoporous silicates

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ABSTRACT

Tungsten-incorporated 3D mesoporous silicates, W-KIT-6, W-KIT-5, and W-SBA-16 catalysts, outperform supported tungsten oxide catalysts (WO_3/SiO_2 and WO_3/KIT-6) for the metathesis of ethylene and 2-butene to propene at 450 °C. All catalysts exhibit steady activity and stability during 7 h runs in a fixed-bed reactor. Furthermore, on all mesoporous catalysts, a maximum propylene yield was obtained at an optimum W loading at which the catalyst acidity is also maximum. Slightly delayed addition of the W source during the one-pot synthesis protocol markedly improves the propene yield on W-KIT-6 catalyst. XPS results conclusively show that this enhancement is due to preferential enrichment of active W species on the catalyst surface. Extended runs lasting five days reveal very little loss of activity even which is easily recovered by calcination in air.

1. Introduction

In the United States, the supply of natural gas liquids (NGLs) has increased dramatically as a collateral product of shale gas extraction. While this is expected to provide an oversupply of ethylene, a shortage of propene is expected as a result of decreased naphtha availability [1,2]. Hence, the synthesis of propene from ethylene via olefin metathesis [3–9] is receiving renewed interest. Current industrial process for the metathesis of ethylene and 1-butene to propene [the so-called olefin conversion technology or OCT] employs WO_3/SiO_2 catalyst, producing a propene yield of ~54% at approximately 30–35 bar and >260 °C [5]. To develop catalysts that operate at lower pressures and temperatures, a number of experimental [10–30] and theoretical [31,32] investigations have been reported. A majority of the investigated catalysts involve Re, Mo, and W oxides.

Mesoporous silicas possessing high surface area, large pore volume, high thermal stability and low diffusion resistance offer an attractive alternative to amorphous non-ordered silica supports [33,34]. For olefin metathesis, several W-, Mo-, and Re-incorporated mesoporous silicas with different pore structures have been explored. These include WO_3/MTS-9 [26] and MoO_3/HMS [13] catalysts synthesized by the impregnation method, and W-SBA-15 [11], W-MCM-41 [11], W-KIT-6 [27,35], W-FDU-12 [28], Mo-SBA-15 [36], Mo-KIT-5 [25] catalysts synthesized by a one-pot method, SiO_2-Al_2O_3-MoO_3 [37,38], Re-Si-Al mixed oxides [29,39], WSi and WSiAl catalysts [40] synthesized by non-hydrolytic sol-gel method. Although mesoporous silica supports with different pore structures have been reported for olefin metathesis, the influence of structural differences on catalytic performance is unclear. In this work, we compared the performance of three types of W-incorporated ordered mesoporous silicates with different 3D structures for the metathesis of 2-butene and ethylene to propene. These include W-KIT-6 ($Ia3d$) [41], W-KIT-5 ($Fm3m$) [42], and W-SBA-16 ($Im3m$). While W-KIT-6 catalyst had been investigated previously for olefin metathesis involving 1-butene and ethylene [12,30], there are no published reports for the (2-butene + ethylene) metathesis on of W-KIT-6, W-KIT-5 and W-SBA-16 catalysts.

The activity of supported metathesis catalysts depends on the catalyst synthesis procedure. Catalysts prepared using the simple impregnation method typically suffer from low dispersion of the active W precursors and the generation of inactive bulk WO_3 species [10,26,43]. A higher dispersion of W species in the silica framework is achievable by one-pot methods [11,41,44]. However, tungsten accessibility could be a problem if the tungsten species are buried sufficiently deep in the framework. To overcome this prob-

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lem, we investigate herein a modified one-pot synthesis method in which the addition of the tungsten source is delayed until after partial hydrolysis of the silica source, increasing the probability of more active tungsten precursors being deposited on the surface. Appropriate analytical techniques (XRD, UV/Vis and XPS) are employed to gain fresh insights into the relative distributions of W species on the catalysts prepared by various synthesis procedures and to correlate the relative metathesis activity of such catalysts.

2. Experimental

2.1. Chemicals

Triblock copolymer Pluronic P123 (EO_{20}-PO_{70}-EO_{20}, average MW = 5800), Pluronic F127, tetraethyl orthosilicate (TEOS, 98%), fumed silica (particle size: 0.007 μm, surface area: $390 \pm 40\,m^2/g$, batch #: 119k0031), ammonium metatungstate hydrate [$(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$, ≥85% WO_3 basis] and tungsten oxide were purchased form Sigma-Aldrich. Sodium tungstate (99.0-101.0%, $Na_2WO_4\cdot 2H_2O$) was purchased from Alfa Aesar. 1-Butanol (HPLC grade) and hydrochloric acid (certified ACS plus) were purchased from Fisher Scientific. 2-Butene (≥95 wt%, 39% *cis*-2-butene and 61% *trans*-2-butene) and ethylene (≥99.5%) were purchased from Matheson Tri-Gas Inc. All the reagents were used as received without further purification.

2.2. Catalyst preparation

2.2.1. KIT-6 support

KIT-6 support (i.e., without addition of W source solution) was synthesized according to the procedure described elsewhere [45].

2.2.2. WO_3/SiO_2 and WO_3/KIT-6 catalysts

WO_3/SiO_2 and WO_3/KIT-6 catalysts were prepared by wet impregnation of the silica supports (fumed SiO_2 and KIT-6, respectively) with an aqueous solution of ammonium metatungstate, followed by sonication for 0.5 h and stirring for 24 h at room temperature [27,46]. The impregnated samples were first dried in a rotary evaporator at 70 °C for 0.5 h, then dried at 100 °C overnight in an oven. The resulting samples were treated in flowing air from room temperature to 550 °C at a ramp rate of 1 °C/min, followed by calcination at 550 °C for 5 h and natural cooling to room temperature. The resulting solids are denoted as WO_3/SiO_2 (x) and WO_3/KIT-6 (x) where x represents the weight percent of tungsten in these catalysts.

2.2.3. Synthesis of W-KIT-6, W-KIT-5 and W-SBA-16 catalysts

W-KIT-6 [41], W-KIT-5 [42] and W-SBA-16 [47] catalysts were synthesized as described in the cited publications and the resulting catalyst samples are denoted as W-KIT-6 (x), W-KIT-5 (x) and W-SBA-16 (x) where x represents the weight percent of tungsten in the samples.

For preparing W-KIT-6 catalysts, a typical synthesis procedure is as follows. 4.5 g of P123 were dissolved in 160 mL of H_2O and 8.3 g of 37.1 wt% HCl at 38 ± 2 °C. Then, 4.5 g of 1-butanol were added and the system was stirred for 1 h. Following this step, 9.7 g of TEOS and the desired amount of sodium tungstate were added and the stirring continued for 24 h. The resulting mixture was transferred into a Teflon-lined autoclave and heated to 100 °C for 24 h. The solid product was collected and washed by deionized water, then dried at 100 °C overnight. The resulting sample was calcined in flowing air at 550 °C for 10 h at a ramp rate of 1 °C/min.

For preparing W-KIT-5 catalysts, the synthesis procedure is as follows. 2.7 g of F127 were dissolved in 130 mL H_2O and 5.3 g 37.1 wt% HCl at 45 ± 2 °C. Then, 13.0 g of TEOS and the desired amount of sodium tungstate were added and the stirring was continued for 20 h. The crystallization, the product collection and calcination procedures are similar to those for W-KIT-6.

For preparing W-SBA-16 catalysts, the synthesis procedure is as follows. 2.85 g of F127 were dissolved in 135 mL of H_2O and 5.6 g of 37.1 wt% HCl at 45 ± 2 °C. Then, 8.65 g of 1-butanol were added to the above mixture and the stirring was continued for 1 h. Following this step, 13.8 g of TEOS and the desired amount of sodium tungstate were added and the stirring was continued for 20 h. The crystallization, the product collection and calcination procedures are similar to those for W-KIT-6.

2.2.4. Modified W-KIT-6 synthesis

The following modified W-KIT-6 synthesis method was adopted to increase the population of accessible W species on the catalyst surface. The modification involved delaying the addition of the tungsten source. Following the dissolution of P123 triblock copolymer in conc. HCl solution (~0.5 mol/L) and the addition of TEOS, the desired amount of sodium tungstate (dissolved in 5 mL H_2O) was added following a delay of 1, 2, 3, 5 and 8 h. After the addition of the tungsten source, the mixture was stirred for 24 h. The resulting mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 24 h. The solid product was collected and washed with deionized water, then dried overnight at 100 °C and calcined at 550 °C for 5 h. The catalyst samples are denoted as W-KIT-6 (t, x) where t and x represent the delayed addition time of the tungsten source (in h) and the tungsten weight percent, respectively.

2.3. Catalyst characterization

The wide-angle XRD patterns were collected on a Bruker X-ray diffractometer using Mo *Kα* radiation ($\lambda = 0.71073$ Å) operated at 50 kV and 35 mA. The small-angle XRD patterns were collected on a Rigaku system with an S-MAX 3000 instrument operated at 45 kV and 0.66 mA. The tungsten and silicon contents of the catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Horiba Jobin Yvon JY 2000 instrument. The textural properties (BET surface area, pore volume and pore size distribution) of the catalysts were measured on a Quantachrome NOVA 2000e instrument as described elsewhere [41,42,47]. The total acidity of the catalysts was measured by temperature-programmed desorption of ammonia (NH_3-TPD) on a Micromeritics Autochem 2910 instrument equipped with a thermal conductivity detector (TCD) as described elsewhere [41]. The structure of the surface species was analyzed by diffuse reflectance UV/Vis (DR UV–vis) spectra with a PerkinElmer Lambda 850 spectrometer equipped with diffuse reflectance integrating sphere, using Spectralon as the reference.

X-ray photoelectron spectroscopy (XPS) was performed using PHI 5000 Versa Probe II instrument. Monochromated Al *Kα* (50 W, 15 kV) X-ray source was used and the X-ray beam diameter was 200 μm. A dual-beam charge neutralizer was used to compensate for the charging effect. The spherical capacitance analyzer was operated with a pass energy of 46.95 eV. All XPS peaks were referenced to the Si 2p peak at 103.3 eV. To get the information from the outermost layer, the sample stage was tilted to 20°. Prior to the analysis, the surface of the sample was sputtered by Ar^+ ion (2.0 keV) for 5 min [48].

2.4. Evaluation of metathesis activity

The catalytic activity of various W-incorporated catalysts for metathesis of ethylene and 2-butene to propene was evaluated in a continuous flow, stainless steel fixed-bed reactor with i.d. = 9.4 mm. 1.0 g of catalyst (0.425–0.850 mm diameter, precalcined in a muffle furnace at 550 °C for 5 h) was loaded in the central portion of the reactor, held in place by a stainless steel collar and glass wool.