



Metathesis of 2-butene to propylene over W-mesoporous molecular sieves: A comparative study between tungsten containing MCM-41 and SBA-15



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ABSTRACT

Mesoporous silica (MCM-41 and SBA-15) having tungsten oxide in the framework was synthesized by hydrothermal crystallization process using CTAB and P123 as structure directing agents, respectively. Tungsten oxide was supported on the MCM-41 and SBA-15 by wet impregnation method for a comparative study. The synthesized materials were characterized by XRD, N₂ adsorption–desorption, NH₃-TPD, pyridine-FT-IR, UV–vis DRS and Raman spectroscopy techniques. The catalysts were used to perform metathesis reaction of 2-butene in a fixed-bed reactor at different temperatures and under atmospheric pressure. It was observed that catalysts having tungsten oxide in the framework of mesoporous silica exhibited higher activity as compared to tungsten oxide impregnated catalysts. The results revealed that WO₃-MCM-41(30) catalyst has much higher activity at a low temperature (450 °C) as compared to WO₃-SBA-15(30). At 550 °C, WO₃-MCM-41(30) and WO₃-SBA-15(30) showed comparable activity with highest propylene yield of 39 mol% and 37 mol%, respectively. The higher metathesis activity of WO₃-MCM-41 catalysts can be related to the well-dispersed active tetrahedral tungsten oxide species as evidenced from XRD, UV–vis DRS and Raman spectroscopy results.

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1. Introduction

The demand for propylene is increasing for downstream applications such as polypropylene, acrylonitrile, cumene, oxo-alcohols, propylene oxide, acrylic acid and isopropyl alcohol and polygas chemicals [1]. Several on-purpose propylene production technologies are being developed to meet the high demand for propylene which is usually produced from naphtha steam cracking and refinery fluid catalytic cracking (FCC) units [2]. Olefin metathesis is an important organic reaction that transforms less desired olefins to higher desired ones through rearrangement of a pair of C=C bonds and currently it is widely used for the production of propylene from low-value C₄ olefins [3,4]. Currently, the Olefins Conversion Technology (OCT) process licensed by Lummus Technology is the only commercial olefin metathesis technology in the petrochemical industry [5]. The key step in olefin metathesis is the intermediacy of metal carbene active species and consequently the formation of unstable metalocyclobutane. Both homogeneous

and heterogeneous catalysts are used in the metathesis reaction. However, heterogeneous catalysts are widely accepted due to the advantage of higher thermal stability, easy separation from the reaction products and regeneration [6]. The most successful heterogeneous catalysts for olefin metathesis are supported rhenium, molybdenum and tungsten oxides [7].

Rhenium oxide catalysts supported on alumina or silica–alumina are the most active and selective under mild conditions [8]. However, the cost of rhenium compounds are high [5], the catalyst activity with low Re loading (<10 wt%) is poor [9] and the catalysts are easily deactivated [10]. At the same time, molybdenum oxide catalysts supported on alumina [11], siliceous material [12] and silica–alumina [13] have received much attention because of their relatively low price, and their high activity under mild conditions. On the other hand, tungsten oxide supported on SiO₂ [2,14,15], γ-Al₂O₃ [16] and γ-Al₂O₃-HY [1,17,18] require much higher temperature (250–500 °C) to achieve acceptable metathesis activity. Nevertheless, due to long online lifetime, considerable resistance to poisons and continuous regeneration without negative effect on catalyst structure, tungsten based catalysts remain the most attractive for commercial use [19]. Catalytic activity of tungsten oxide catalysts depends on the oxidation

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state of tungsten species [19], the content of tungsten oxide [2,19,20], the properties of support and the pretreatment condition [21].

Mesoporous molecular materials with their large surface area and large void volume, exhibit high catalytic activity after introducing of heteroatoms into the framework [22]. SBA-15 is a mesoporous silica having large pores (5–20 nm), hexagonal structure, large channel diameter and it is thermally, hydro-thermally robust due to its thick framework walls (3–6 nm) [23]. Deposition of tungsten into SBA-15 activated the support which allowed higher diffusion rate [24]. Chen et al. reported that, tungsten oxide was effectively incorporated into the framework of SBA-15 for C₄ olefin metathesis exhibiting 92.6% conversion of 1-butene and 27.0% propylene yield [25]. Direct tungsten incorporation using hydrothermal method has advantages such as high tungsten species dispersibility and strong interaction between tungsten species and silica compared to conventional impregnation method [14,25,26]. Mesoporous silica, MCM-41, shows a highly ordered hexagonal array of one-dimensional channel with a very narrow pore size distribution [5]. To the best of our knowledge, few publications reported tungsten distribution in MCM-41 and none were tested for 2-butene metathesis [27]. MCM-41 has been used as a support for Mo and Ru-based metathesis catalysts for 1-heptene cross metathesis [28].

In this study, we have focused on three main effects on 2-butene metathesis over tungsten supported SBA-15 and MCM-41; (i) the synthesis method and support architecture of tungsten oxide catalyst, (ii) the concentration of active WO₃ species on the support, and (iii) effect of reaction temperature.

2. Experimental

2.1. Materials

Pluronic 123(EO₂₀PO₇₀EO₂₀), tetraethylorthosilicate (98%, TEOS), sodium tungstate (99.99%, NaWO₄·2H₂O), hydrochloric acid (36%), sodium metasilicate (98%, Na₂SiO₃), cetyltrimethylammonium bromide (98%, CTAB), anhydrous ethyl acetate (99.8%) and ammonium metatungstate [99%, (NH₄)₆H₂W₁₂O₄₀·xH₂O] were purchased from Sigma–Aldrich and used without any further purification. 2-Butene with 99.9% purity (50% cis-2-butene and 50% trans-2-butene) was purchased from Saudi Industrial Gas Company, Saudi Arabia.

2.2. Support synthesis

Two types of mesoporous supports, SBA-15 and MCM-41 were synthesized using the hydrothermal method.

2.2.1. Mesoporous SBA-15

Hexagonally ordered mesoporous SBA-15 was synthesized using triblock co-polymer P123 (EO₂₀PO₇₀EO₂₀) as structure directing agent and tetraethylorthosilicate (TEOS) as silica precursor. Synthesis of SBA-15 was performed according to the procedure reported in literature [25]. In a typical synthesis, 6 g of Pluronic 123 was dissolved to 210 ml of 2 M HCl and stirred at 40 °C to achieve a transparent solution. After 3–4 h, 12.8 g TEOS was quickly added into the solution. The solution was stirred at 95 °C for 2 days. The solid products obtained were washed with water and dried at 80 °C overnight. The template was removed by calcination in air at 550 °C for 5 h. The molar ratio of the gel composition is 1 SiO₂:0.0167 P123:5.82 HCl:190 H₂O.

2.2.2. Mesoporous MCM-41

Mesoporous support MCM-41 was synthesized by using the sodium metasilicate (Na₂SiO₃) and cetyltrimethyl-ammonium

bromide (CTAB) as a source of silica and structure directing agent, respectively. Synthesis was performed according to the method described in literature [29]. 9.96 g of sodium metasilicate with 150 ml H₂O was stirred at 85 °C for 30 min. Then, 9.8 g of CTAB was added to the solution and stirred for 10 min. 30 ml ethyl acetate was rapidly added into the solution under vigorous stirring. The stirring was continued for 24 h at 85 °C. The solid products were recovered by filtration. After washing with deionized water several times, the solid was air-dried and then calcined in air at 600 °C for 4 h to remove the template. In this procedure, cheap and convenient sodium silicate was used as an inorganic silica precursor instead of expensive organic TEOS and ethyl acetate was employed as the acid producing precursor instead of a conventional strong acid, such as HCl or H₂SO₄. The synthesis gel molar composition is 1 SiO₂:0.335 CTAB:3.8 EtOAc:120H₂O.

2.3. Catalyst synthesis

Several catalysts were synthesized by supporting tungsten on mesoporous silica SBA-15 & MCM-41 using hydrothermal crystallization and wet impregnation procedures (Table 1). The details of the synthesis procedure are given below.

2.3.1. W containing SBA-15 by direct hydrothermal method (WO₃-SBA-15)

Sodium tungstate (NaWO₄·2H₂O) was used as the source of tungsten ion for the synthesis of WO₃-SBA-15 by direct hydrothermal method. In a typical synthesis of WO₃-SBA-15, tungsten was incorporated into the framework of mesoporous support SBA-15 depending upon the Si/W molar ratio. Pluronic 123 was dissolved in HCl and TEOS was added with vigorous stirring. Then, calculated amount of sodium tungstate solution was added to the solution and stirred at 95 °C for 3 days under hydrothermal conditions. The resultant solid was filtered, dried and calcined at 550 °C for 5 h. The catalysts obtained in this way were identified as WO₃-SBA-15(x), where x represented the molar ratio of silicon to tungsten (Si/W). The molar ratio of the gel composition is 1 SiO₂:0.3–0.6 WO₃:0.0167 P123:5.82 HCl:190 H₂O.

2.3.2. W containing MCM-41 by direct hydrothermal method (WO₃-MCM-41)

In a typical synthesis of WO₃-MCM-41, the solution of sodium tungstate was added into the solution of sodium metasilicate and CTAB, depending upon the Si/W molar ratio. Then ethyl acetate was added as an acid producing precursor and the solution was stirred for 24 h at 85 °C under hydrothermal conditions. After filtration, the solid was air-dried and calcined at 600 °C for 4 h. The catalysts obtained in this way were identified as WO₃-MCM41(x), where x represents the molar ratio of silicon to tungsten (Si/W). The synthesis gel molar composition is 1 SiO₂:0.3–0.6 WO₃:0.335 CTAB:3.8 EtOAc:120 H₂O.

2.3.3. Impregnation method (WO₃/SBA-15 and WO₃/MCM-41)

WO₃/SBA-15 and WO₃/MCM-41 catalysts with different tungsten loading in the range of 5 and 10 wt% of WO₃ were prepared by wet impregnation method. Aqueous solution of ammonium metatungstate [(NH₄)₆H₂W₁₂O₄₀·xH₂O] and the siliceous support SBA-15 or MCM-41 were mixed together and stirred for 3 h. Then the impregnated product was dried in an oven at 80 °C for 12 h and calcined at 550 °C for 5 h. The catalysts obtained in this way were identified as WO₃/SBA-15(x) and WO₃/MCM-41(x) where x is the molar ratio of silicon to tungsten (Si/W).

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