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Molybdenum containing cage like mesoporous KIT-5 for enhanced catalytic conversion of 1-butene and ethylene to propene

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ABSTRACT

Molybdenum containing three-dimensional (3D) cage-like mesoporous KIT-5 (Mo-KIT-5) materials with various Si/Mo ratios was successfully prepared by one-pot hydrothermal synthesis. The obtained materials were characterized by various techniques, such as XRD, N_2 physisorption, TEM, FTIR, UV-DRS, XPS, and NH_3-TPD. Characterization results revealed that molybdenum species could be finely dispersed in the framework of KIT-5 without disturbing long-range ordering at Si/Mo ratios higher than 15, while collapse of mesoporous structure and presence of bulk MoO_3 was observed for Mo-KIT-5-5 sample with a Si/Mo ratio of 5. Mo-contained materials were investigated in catalytic conversion of 1-butene and ethylene to propene. Among all of Mo-KIT-5 materials studied, Mo-KIT-5-40 with Si/Mo ratio of 40 exhibited best catalytic performance caused by the fact that it processed superior textural properties, substantial active Mo species, and appropriate amount of acidic sites. Further decreasing the Si/Mo ratio resulted in declined activity due to the presence of extraframework Mo species. It was found that doped Mo-KIT-5-40 showed better catalytic activity than control supported Mo/KIT-5-40 and Mo/SiO_2-40 catalysts with same Mo loading due to the highly dispersed active Mo species on the mesoporous framework. Moreover, Mo-KIT-5 was also superior to other Mo containing mesoporous materials, such as Mo-SBA-15 with two-dimensional pores and Mo-KIT-6 with three-dimensional cylindrical pores, implying the advantage of this kind of ordered 3D cage-like mesoporous materials in this reaction.

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1. Introduction

Propene is a highly demanded basic building block in petrochemical industry, which is mainly obtained through steam cracking of oil based feedstocks, such as ethane, naphtha and gas oils. Alternatively, methanol to propene (MTP) or methanol to olefins (MTO) producing propene from non-oil resources has attracted great attentions [1]. However, a considerable amount of butene is generated as byproduct. Olefin metathesis, which can convert C4 byproducts into valuable propene, providing an efficient way of utilizing C4 and increasing the yield of propene, is of great importance for industrial application [2]. Since the first report of olefin metathesis in 1964 [3], many supported metathesis catalysts have been developed, including rhenium [4], tungsten [5] and molybdenum [6] based catalysts. Re based catalysts exhibited outstanding catalytic performance for metathesis. But, the high price and limited availability restricts the application of Re. Alternatively, W and Mo with lower cost and compatible catalytic performance were extensively explored for metathesis of olefin.

The performance of supported metathesis catalyst was profoundly influenced by the nature of supports [7,8], such as textural properties and acidity. The most widely used supports were conventional SiO_2 [9], Al_2O_3 [10], zeolite [11] and mixed metal oxide [12]. The rapid development of mesoporous materials during the last decades has stimulated the exploration of mesoporous molecular sieves (MMS) and organized mesoporous alumina (OMA) as metathesis catalysts [13]. Mesoporous materials possessing uniform mesopores, large surface area and pore volume, compared with conventional supports. The large surface area could afford a high amount of active sites and the uniform mesopores facilitate the intra-pore diffusion of reactants and products. To date, many MMS such as MCM-41 [7,14], MCM-48 [7], SBA-15 [7,14–16], HMS [17],

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and KIT-6 [18] have been employed as the supports of metathesis catalysts. In brief, MMS supported W (Mo) catalysts exhibited better catalytic performance than that of conventional silica gels supported catalysts due to the better dispersion of active species on MMS. In addition, the pore size and architecture of MMS also influenced the metathesis activity. Topka et al. [7] systematically studied the metathesis of 1-octene over three typical MMS, i.e. MCM-41, MCM-48, and SBA-15 supported Mo catalysts and the catalytic activity decreased in the order: MCM-41 > MCM-48 > SBA-15. The different dispersion of active species over three supports was responsible for the difference in catalytic performance. Bhuiyan et al. [14] also compared the catalytic property of W-SBA-15 and W-MCM-41 in 2-butene metathesis to propene, and found that W-MCM-41 catalyst showed better activity than that of W-SBA-15. The better activity of W-MCM-41 was attributed to the well-dispersed active tetrahedral tungsten oxide species. Besides mesoporous silica, mesoporous alumina [19] and alumina-silica [20,21] based catalysts also showed promising metathesis activity.

KIT-5, a novel mesoporous silica with ordered 3D cage-like mesopores was first reported by Kleitz et al. [22]. KIT-5 was believed to be superior to 1D mesoporous silicas, because the interconnected 3D large pores were beneficial for mass transportation of reactants and products, and providing more accessible adsorption sites [23]. Therefore, KIT-5 was a desirable catalyst supports for versatile reactions [24–26]. Herein we first report the synthesis of high active mesoporous Mo-KIT-5 catalyst for production of propene from metathesis of 1-butene and ethylene. The catalyst was systematically characterized by multiple characterization techniques. The Mo-KIT-5-40 catalyst exhibited an improved catalytic performance compared with control supported Mo/KIT-5-40 and Mo/SiO_2-40 catalysts with same Mo loading due to high dispersion of active Mo species. The Mo-KIT-5 catalyst was also advantageous to other mesoporous catalysts, such as Mo-SBA-15 and Mo-KIT-6.

2. Experimental

2.1. Chemicals

Pluronic F127 (M_w = 12,500) was purchased from Sigma–Aldrich as the structure directing agent. Tetraethyl orthosilicate (TEOS, AR) and ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., as silicon and Mo sources, respectively. Silica gel (BET surface area, 399 m^2/g) was obtained from Qingdao Haiyang Chemical Co., Ltd. All the reagents were used as received without further purification.

2.2. Catalyst preparation

2.2.1. Synthesis of Mo-KIT-5 catalysts

The Mo-KIT-5 catalysts with various Si/Mo were prepared using Pluronic F127 as the structure directing agent following the procedure described by Kleitz et al. [22]. Typically, 4 g F127 and required amount of ammonium paramolybdate were dissolved in 192 g deionized water and 8.4 g of 35 wt% hydrochloric acid under stirring. To this mixture, 19.2 g of TEOS was dropwise added. The resulting mixture was vigorously stirred at 45 °C for 24 h. Then, the mixture was transferred to a Teflon-lined autoclave, and subject to a hydrothermal treatment at 100 °C for 24 h. The products were collected by filtering without washing, and drying at 100 °C overnight. Finally, the removal of F127 templates was achieved by calcining the sample in a muffle oven at 550 °C for 4 h with a heating rate of 1 °C/min. The catalyst was denoted as Mo-KIT-5-*x*, where the *x* represented the Si/Mo ratio in the synthesis gel.

Pure KIT-5 was prepared using the same procedure as Mo-KIT-5 samples except without adding of ammonium paramolybdate.

2.2.2. Preparation of control Mo/KIT-5-40 and Mo/SiO_2-40 catalysts

For comparison, KIT-5 and SiO_2 supported Mo catalysts were synthesized by wet-impregnation of traditional SiO_2 gel and KIT-5 with 10 ml of ammonium paramolybdate aqueous solution. The impregnated sample was dried at 110 °C overnight and calcined at 550 °C for 4 h with a ramping rate of 1 °C/min. The Mo loading of both catalysts were fixed at 2.5 wt%, which was identical to that of Mo-KIT-5-40, as confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The catalysts were denoted as Mo/KIT-5-40 and Mo/SiO_2-40, respectively, where 40 was the nominal Si/Mo ratio.

2.3. Catalyst characterization

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was employed to determine the real Mo content of sample using PerkinElmer OPTIMA 2100 DV optical emission spectroscopy spectrometer. Small-angle X-ray diffraction (SAXD) and wide-angle X-ray diffraction (WAXD) patterns of samples were collected on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation in the 2θ angle range of 0.5–5° and 20–80°, respectively. N_2 adsorption–desorption isotherm of the sample was measured at 77 K using a Micrometrics ASAP-2020M adsorption apparatus. Before the measurement, the sample was outgassed at 200 °C for 6 h. The specific surface area was determined by the multiple Brunauer–Emmett–Teller (BET) method. The pore volume and pore size distribution were obtained from the adsorption branch of the isotherm using Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images were acquired on a JEOL 2100 transmission electron microscope operated at 200 kV. The Fourier transform infrared spectra (FTIR) were recorded with a Bruker Tensor 27 spectrophotometer. UV–vis diffuse reflectance spectra (UV-DRS) were performed in PE lambda 950 equipment using $BaSO_4$ as reference. X-ray photoelectron spectroscopy (XPS) studies were performed on AXIS ULTRA DLD multifunctional X-ray photoelectron spectroscopy with an Al source. Temperature programmed desorption of ammonia (NH_3-TPD) was carried out in a quartz micro-reactor. 0.1 g catalyst was pretreated at 550 °C for 30 min in He (25 cm^3 min^{-1}) prior to NH_3-TPD measurement before the reactor was cooled down to room temperature, and then the sample was saturated with NH_3. The physically absorbed NH_3 was removed by flushing the sample with He at 120 °C for 2 h. Temperature-programmed desorption of ammonia was carried out from 120 to 650 °C with a ramping rate of 5 °C/min, and the amount of desorbed NH_3 was monitored by a thermal conductivity detector (TCD).

2.4. Metathesis reactions

Catalytic performance of as-synthesized catalysts for metathesis of 1-butene and ethylene to propene was evaluated in a fixed-bed stainless reactor (i.d. 10 mm) under atmospheric pressure. In each test, 1 g of shaped catalyst (20–40 mesh) was placed at the center of the reactor and sandwiched by inert SiO_2 beads. Prior to reaction, the catalysts was in situ activated by high pure N_2 (35 ml/min) at 550 °C for 4 h to remove the moisture, followed by cooling down to reaction temperature. Then, a mixture of ethylene and 1-butene ($nC_2H_4/n1-C_4H_8 = 2$) was introduced and the reaction was started. The metathesis reaction conditions were 450 °C, 0.1 MPa, weight hourly space velocity (WHSV, 1-C_4H_8 + C_2H_4) of 0.8 h^{-1}. The effluent gases released from the reactor were analyzed by an online gas chromatograph (GC) equipped with a flame ionization detector (FID). The calculation of 1-butene conversion and product selectivity has been described elsewhere [15,18].

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