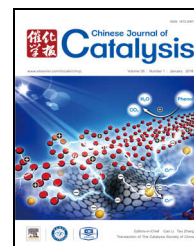


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Article

Self-metathesis of 1-butene to ethene and hexene over molybdenum-based heterogeneous catalysts



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ABSTRACT

A novel route involving self-metathesis of 1-butene under mild conditions that gave high yields of ethene and hexene was proposed. The results of thermodynamic analysis revealed that the Gibbs energy of the target Metathesis I reaction (1-butene → ethene + 3-hexene) was much higher than that of the main side Metathesis II (1-butene + 2-butene → propene + 2-pentene). Suppression of 1-butene double-bond isomerization was the key step to increase the selectivity for the target olefin in the reaction network. The relationship between the catalytic performance and support nature was investigated in detail. On basis of H₂-TPR, UV-Vis spectra and HRTEM results, an alumina (Al₂O₃) support with large surface area was beneficial for the dispersion of molybdenum (Mo) species. Both suitable acidity and sufficient Mo dispersion were important to selectively promote the self-metathesis reaction of 1-butene. On the optimal 6Mo/Al₂O₃ catalyst, 1-butene conversion reached 47% and ethene selectivity was as high as 42% on the premise of good catalytic stability (80 °C, 1.0 MPa, 3 h⁻¹).

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1. Introduction

During the past few years, olefin metathesis reactions have opened up many new industrial routes to important petrochemicals, polymers, and specialty chemicals [1,2]. Olefin metathesis is a powerful carbon-carbon bond rearrangement reaction in which the unsaturated carbon-carbon bonds can be redistributed in the presence of a catalyst. This route has been proved effective to produce value-added olefins according to market demand. Typical examples are the self-metathesis reac-

tion of propene [3] and its reverse reaction (metathesis of ethene and 2-butene to propene) [4–6]. Besides, much attention has been paid to the development of metathesis catalysts from fundamental research to commercial application [7].

The increasing demand for propene has led to propene synthesis routes being focused on during the last few years [8–10]. To date, several olefin metathesis reaction routes using C₄ olefins as raw materials have been developed, including self-metathesis of 1-butene [11–13], cross-metathesis of ethene and 2-butene [14–17] or 1-butene [18], and metathesis of

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2-butene [19]. In the context of declining international oil supply and the emergence of shale gas, the price of propene is volatile and sometimes falls below that of ethene. On basis of surplus C₄ olefins, self-metathesis of 1-butene to ethene and 3-hexene provides a promising route to produce value-added olefins. Here, 3-hexene could be further isomerized to 1-hexene, which is an important comonomer for the production of linear low-density polyethylene and high-density polyethylene. However, few articles on 1-butene self-metathesis have been reported, and only a few patents have been disclosed [20–22].

In this work, we present a novel route to produce ethene and hexene by the self-metathesis reaction of 1-butene. In the complicated reaction network, metathesis of 1-butene and 2-butene to propene is demonstrated to be the main side reaction. Isomerization of the 1-butene double bond is the main step determining target olefin selectivity. Consequently, the major objective of the present study is to find a catalyst suitable for the 1-butene self-metathesis reaction. The factors that influence the product distribution in the metathesis reaction are considered.

2. Experimental

2.1. Catalyst preparation

Na-type mordenite zeolite and Al₂O₃ composite supports were prepared by extruding a mixture of Al₂O₃ (prepared from pseudo-boehmite) and the Na-type mordenite zeolite (Si/Al = 20, Fushun Petroleum Company, China) into strips with a diameter of about 2 mm. The H-type mordenite and Al₂O₃ composite supports were ion-exchanged with 0.8 mol/L NH₄NO₃ solution at 80 °C three times to replace Na⁺ with NH₄⁺, and then washed and dried. The H-type composite supports were obtained by calcination at 520 °C in air for 3 h, ground and then passed through 20–40 mesh filters. The Na-type mordenite and Al₂O₃ composite supports are denoted as NaMOR-*x*Al₂O₃, while the H-type mordenite and Al₂O₃ composite supports are labeled as HMOR-*x*Al₂O₃, where *x* represents the weight percent of alumina. Al₂O₃-*x* and SiO₂ supports were provided by the Aluminum Corporation of China Limited, Shandong Branch. Catalysts labeled as *x*Mo/Al₂O₃-A were prepared by incipient wetness impregnation using an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and left at room temperature for 24 h; here, *x* indicates the weight percent of Mo in the catalysts. The catalysts were dried at 120 °C for 2 h and finally calcined at 600 °C for 2 h.

2.2. Characterization

Nitrogen (N₂) physisorption experiments were performed at -196 °C on a Micromeritics ASAP 2020 instrument. Prior to analysis, samples were outgassed at 350 °C under a vacuum of 10⁻³ Pa for 8 h. Specific surface area was calculated by the standard multipoint Brunauer-Emmett-Teller (BET) method with a *P*/*P*₀ range of 0.05–0.30. Pore volume was determined by N₂ adsorption at *P*/*P*₀ = 0.995.

Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'pert PRO diffractometer using Cu K_α radiation at 40 kV and 40 mA. The chemical composition of samples was determined on a Philips Magix 601X X-ray fluorescence (XRF) spectrometer.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out in a quartz microreactor (i.d. 4 mm), which was connected to an online gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). The TCD response was calibrated by doses containing known amounts of NH₃. Typically, the sample (140 mg) was first pretreated at 605 °C for 0.5 h in helium with a flow rate of 25 mL/min, then cooled to 150 °C and saturated with NH₃. Subsequently, NH₃ was purged in a helium flow for a certain period at 150 °C until a stable baseline was obtained. The reactor temperature was raised from 150 to 605 °C at a heating rate of 19.8 °C/min.

Infrared (IR) spectra were recorded with a Bruker Vertex 70 IR spectrometer at 4-cm⁻¹ optical resolution. Prior to measurements, the samples were pressed into self-supporting wafers with a diameter of 1.3 cm and pre-treated in an IR cell at 450 °C for 1 h under 10⁻² Pa. The cell was cooled to room temperature to record the background spectra. Each sample was saturated with pyridine (Py) and then the excess Py was removed under vacuum at 150 °C for 0.5 h. After cooling to room temperature again, the sample was subjected to IR measurements to quantify the amount of acid sites.

Temperature-programmed reduction of H₂ (H₂-TPR) experiments were carried out using a custom-made setup. Prior to measurements, each sample (100 mg) was pretreated at 550 °C for 1 h under Ar flow to remove water and other contaminants and then cooled to 200 °C. The reduction step was carried out in a mixture flow of 10% H₂/90% Ar from 200 to 900 °C at a heating rate of 15 °C/min. The H₂ signal was monitored online by a TCD detector.

Ultraviolet-visible (UV-Vis) spectra were recorded in a diffuse reflectance mode with a JASCO V-550 spectrometer at room temperature in the range of 200–600 nm at a rate of 40 nm/min.

High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-2100 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV.

2.3. Catalyst evaluation

The self-metathesis of 1-butene was carried out in a fixed bed microreactor with a length of 320 mm and diameter of 7 mm. The catalyst (1 g) was located in the middle part of the fixed-bed reactor. The catalyst was activated in situ at 500 °C for 2 h in N₂ flow before the reaction. The reaction products were analyzed by an online Agilent 7890B gas chromatograph (GC) equipped with a flame ionization detector and Al₂O₃ capillary column.

The GC results indicated that *cis*-, *trans*-2-pentene and *cis*-, *trans*-3-hexene were the major products with C₅ and C₆ structures, respectively. To simplify treatment, we denoted products

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