



Investigations into the C₄ olefin metathesis over Mo/Al₂O₃: Effects of support nature and pretreatment conditions on the product distribution



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ABSTRACT

A series of Mo/Al₂O₃ catalysts were prepared and evaluated in the consecutive metathesis of 1-butene and isobutene. The correlations between the states of Mo species and Metathesis I (2-C₄^m + 1-C₄^m → C₃^m + 2-C₅^m), Metathesis II (2-C₄^m + *i*-C₄^m → C₃^m + *i*-C₅^m) were discussed in detail. It was found that Metathesis I and Metathesis II followed different deactivation rate due to the differences in active sites. Metathesis I was more acidity-sensitive and it was suppressed when alumina was calcined at high temperature due to the decrease of acid sites. Metathesis II kept relative good catalytic stability and high calcination temperature was beneficial to increase the ratio of isopentene in pentene fraction. As revealed by the XPS and reductive pretreatment results, different C₄ olefin molecules on the same Mo-based catalyst exhibited different metathesis activity and partially reduced Mo^V (or Mo^{IV}) species from octahedrally coordinated Mo(O) species contributed to the selective promotion of Metathesis II.

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1. Introduction

Propene and isopentene are two important chemical intermediates which serve as building blocks for petrochemical and plastic products, particularly for the propene. The demand for propene is growing rapidly in the global chemical industry in recent years [1–3]. Several on-purpose propene production technologies, including propane dehydrogenation [3], catalytic cracking of C₄⁺ olefins [4], methanol to olefins [5], and olefin metathesis reactions [6–9], are available. Among them, olefin metathesis could regulate the stocks of light olefins (ethene, propene, butene) upon the market demanding at low energy and environmental cost [10]. And much effort has been devoted to the exploitation of heterogeneous olefin metathesis systems since its discovery in 1964 [11,12].

So far, several olefin metathesis reaction routes have been developed to increase the propene production, including auto-metathesis of 1-butene [13–15], cross-metathesis of ethene and 2-butene [7,8,16], and metathesis of 2-butene [17]. Recently, our laboratory reported a new synthesis route on the basis of C₄ olefin metathesis which could produce propene and isopentene simultaneously [18]. Experimental results revealed that three

interesting reactions occurred on the supported Mo-based catalysts, i.e. 1-C₄^m → 2-C₄^m (Isomerization I), 2-C₄^m + 1-C₄^m → C₃^m + 2-C₅^m (Metathesis I), 2-C₄^m + *i*-C₄^m → C₃^m + *i*-C₅^m (Metathesis II). Mo/Al₂O₃ was proved to be the best catalyst and the selectivity to isopentene and *n*-pentene was closely associated with the acidity and states of Mo species on the catalyst. In other words, the respective activity of Metathesis I and Metathesis II was also closely related to the acidity and distributions of the Mo species. Although propene was the co-product of the two competing metathesis routes, value-added isopentene was obtained only through Metathesis II. Therefore it was meaningful to selectively promote the Metathesis II and increase isopentene selectivity. To the best of our knowledge, few papers systematically dealt with the interrelation between two or more olefin metathesis reactions and Mo species on the same catalyst [19]. Based on the idea that the states of supported Mo species (including the pre-catalyst or reaction intermediates) were strongly affected by the nature (e.g. surface area, OH groups) of the supports [8,20,21], a series of alumina supports with varied textural and surface characteristics were prepared by calcination at different temperatures in this study. Effects of reductive pretreatment conditions on the metathesis activity were investigated. Combining the NH₃-TPD, Raman, H₂-TPR, and XPS characterization results with the catalytic performances, the relationship between Mo species and Metathesis I, II was clarified.

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2. Experimental

2.1. Catalysts preparation

The alumina supports were prepared by extruding the boehmite powder (74 wt% AlOOH, Condea, Germany) with nitric acid solution (12 wt%) into trips, followed by drying at 120 °C for 2 h and then calcination under static air at 200, 400, 500, 600, 700, and 800 °C for 6 h, respectively. The resultant supports were ground into 20–40 mesh for further use. Catalysts containing ca. 6.0 wt% Mo were prepared by incipient wetness impregnation of alumina supports with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and left at room temperature for 24 h. They were then dried at 120 °C for 4 h, and finally calcined at 600 °C for 2 h. The catalysts were denoted as 6Mo/Al-CT where CT stood for the final calcination temperature of the alumina support.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns were collected on a X'Pert PRO diffractometer using Nickel filtered Cu K α radiation. N₂-physisorption experiments were performed at –196 °C on a Micromeritics ASAP 2020 instrument. Prior to analysis, the samples were outgassed at 200 °C under the vacuum of 10^{–3} Pa for 8 h.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out in a quartz micro-reactor (i.d. 4 mm) which was connected to an on line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). In a typical experiment, the sample (100 mg) was firstly pretreated at 600 °C for 0.5 h under continuous He flow (25 ml/min), then cooled to 150 °C and saturated with NH₃. Subsequently, NH₃ was purged in He flow for a certain period at 150 °C until a stable baseline was obtained. NH₃-TPD experiment was then carried out in the range of 150–600 °C at a heating rate of 19.6 °C/min.

Diffuse reflectance infrared Fourier transform spectroscopy (Drifts) experiments were performed on a Bruker VERTEX 70 spectrometer (4 cm^{–1} resolution, 64 scans/spectrum) equipped with a Harrick Praying Mantis optical accessory and a high temperature in situ reaction cell (HVC-DRP) with KBr windows. A liquid nitrogen-cooled MCT detector was used to obtain the spectra in the range of 4000–2000 cm^{–1}. In each experiment, the sample powder (55 mg) was firstly pretreated at 350 °C for 0.5 h under Ar flow (20 mL/min). After the pretreatment, the IR spectrum was acquired when the sample was cooled down to 30 °C. All the resultant spectra were converted into Kubelka–Munk units after subtraction of the background spectrum collected on the dehydrated KBr sample. The apparatus worked in Ar purging mode to minimize the effect of water vapor. For the Al-200 sample, the pretreatment temperature was 200 °C.

Temperature-programmed reduction of H₂ (H₂-TPR) experiments were carried out in a conventional setup similar to NH₃-TPD. Prior to analysis, the sample (100 mg) was pretreated at 550 °C for 1 h under Ar flow (additional reductive pretreatments in 10%H₂–90%Ar at 500 °C were also performed for some samples as discussed in the text). Then the reduction step was carried out in a mixture flow of 10%H₂–90%Ar from 100 °C to 900 °C at a heating rate of 14 °C/min. The H₂ signal was monitored on line by a TCD and the actual H₂ consumption of each catalyst was obtained from the peak area calibrated by the complete reduction of high-purity Ag₂O as standard. The reduction degree was obtained by quantitative analysis of H₂-TPR profiles, which was the ratio of actual H₂ consumption to the hypothetical H₂ consumption (corresponding to the full reduction of the Mo-based, i.e. from Mo⁶⁺ to Mo⁰) [18].

X-ray photoelectron spectra (XPS) were recorded using a VG ESCALAB MK-II spectrometer with a sample transfer system, which allowed samples to be treated at high temperatures and with

different gaseous media. The samples were firstly pretreated in following N₂ at 500 °C for 0.5 h, followed by the reductive treatment in 10%H₂–90%Ar at 500 °C for 1 h. After cooling to 150 °C, the samples were evacuated and then introduced into the analysis chamber without exposure to the air. The Al K α radiation (1486.6 eV) was used as the excitation source. All the binding energies were referenced to the Al 2p line (74.7 eV) for calibration. The surface Mo/Al atomic ratios were calculated using the relative sensitivity factors.

2.3. Catalysts evaluation

The catalytic test was carried out in a fixed bed flow microreactor with an inner diameter of 7 mm. In each experiment, 1 g of the catalyst was charged at the center of the reactor. Conventionally the catalyst was pretreated in situ at 550 °C with inert N₂ (20 ml/min) for 2 h, then the system was cooled down to the desired reaction temperature under the N₂ flow. Afterwards, the olefin mixture flow (the mole ratio of 1-butene to isobutene was 1.5) with the weight hourly space velocity (WHSV) of 1.5 h^{–1} was introduced into the reactor. When the pretreatment included reductive atmosphere, i.e. 10%H₂–90%Ar, the fresh catalyst was first pretreated with inert N₂ at 550 °C for 2 h and then reduced in the flowing 10%H₂–90%Ar at 500 °C for a certain reduction time. After reduction, hydrogen retained on the surface was removed from the catalyst by a thermal treatment in inert N₂. The reaction products were analyzed by an on line Varian CP 3800 gas chromatograph (GC) equipped with a flame ionization detector (FID). The conversion (X) of 1-butene and isobutene and the selectivity (S) to a particular product were calculated according to our earlier report [18]. (This could also be found in the Supporting Information).

3. Results and discussion

3.1. Effects of alumina calcination temperatures

3.1.1. Catalytic performances of the Mo/Al₂O₃ with alumina support calcined at different temperatures

Catalytic performances of the Mo/Al-CT catalysts with time on stream were compared and illustrated in Fig. 1 and Fig. 2. It was obvious that the catalytic activity was closely dependent on the calcination temperature of the alumina support. The Mo/Al-200, with alumina calcined at 200 °C, exhibited the highest 1-butene and isobutene conversions. Both 1-butene and isobutene conversions decreased with the alumina calcination temperatures, and the conversions gradually decreased upon reaction time as shown in Fig. 1A and B. In addition, the Mo/Al-200 sample exhibited the fastest deactivation rate during the first 4.5 h among those catalysts.

The product selectivity to isopentene followed different trends compared with that of feed conversions. As shown in Fig. 1C, Mo/Al-200 exhibited the lowest isopentene selectivity. The highest isopentene selectivity was obtained on the Mo/Al-700 catalyst. In the case of Mo/Al-800, it reached a plateau at about 5.5 h on stream, and the final selectivity at 8 h on stream was lower than that of the aluminas calcined at 600 and 700 °C. Opposite phenomena were observed in terms of *n*-pentene selectivity. As displayed in Fig. 1D, it decreased upon the alumina calcination temperatures, and the *n*-pentene selectivity of Mo/Al-800 at 8 h on stream was only 0.7%. Both ethene and propene selectivities exhibited the same trend, and the lowest values were observed on the Mo/Al-800 (Fig. 1E and F). In addition, each value of propene selectivity kept almost steady during the 2–8 h time on stream.

As shown in Fig. 2A and B, the initial yields of both isopentene and *n*-pentene decreased, and the decreasing trend of the latter was more remarkable upon calcination temperature of alumina support. While at TOS = 8 h, the isopentene yield was significantly

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