Applied Catalysis A: General 517 (2016) 227–235

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Metathesis and isomerization of *n*-butene and ethylene over WO_3/SiO_2 and MgO catalysts: Thermodynamic and experimental analysis

Weili Jiang[a], Ruli Huang[a], Peidong Li[b], Shuo Feng[a], Guanglin Zhou[a], Changchun Yu[a], Hongjun Zhou[a,*], Chunming Xu[a], Quan Xu[a]

[a] State Key Laboratory of Heavy Oil, Institute of New Energy, China University of Petroleum, Beijing 102249, PR China
[b] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

ARTICLE INFO

Article history:
Received 18 November 2015
Received in revised form 6 March 2016
Accepted 8 March 2016
Available online 15 March 2016

Keywords:
Metathesis
Isomerization
Thermodynamic
Propylene
Catalysis
Tungsten oxide

ABSTRACT

The rapid increase in the demand for propylene and its derivatives requires urgently developing propylene-producing technology. To better understand the complicated reactions on W-based metathesis catalyst for propylene production and further to clarify the involved reaction mechanism, thermodynamic calculation was first performed to analyze the gas mixture under different conditions theoretically. The analyzed reaction system is close to the ideal gas under typical reaction conditions. The detailed investigation of reactions under different conditions was then carried out using WO_3/SiO_2 and MgO catalysts in a fixed-bed tubular micro reactor. Experimental results together with calculation demonstrate that temperature plays the most important role in regulating metathesis reaction compared with other factors such as pressure, ethylene content and weight hourly space velocity (WHSV). Also, ethylene content in the feedstock affects a lot on metathesis process. With an optimized ratio of ethylene/*n*-butene, cross-metathesis of 2-butene and ethylene is more likely to take place than that of 1-butene and 2-butene, and *trans*-2-butene has a generally better activity to react with ethylene than *cis*-2-butene due to the steric effect. On the other hand, isomerization is more independent on temperature compared with metathesis reaction. The consumption of 2-butene in metathesis will promote isomerization of 1-butene to 2-butene. Some extreme conditions such as higher pressures, larger ethylene contents and lower temperatures will provide opportunities for polymerization of ethylene. Based on the reaction analysis under different conditions, the reaction routes are summarized and a supposing mechanism for the formation of metallacyclobutane intermediate from *trans*/*cis*-2-butene is proposed.

1. Introduction

Global propylene demand is predicted to reach 110 million tons by 2020, while the production will be only 100 million tons at that time [1]. The rapid increase in the demand for propylene and its derivatives requires urgently developing propylene-producing technology. Currently, propylene is produced mainly from naphtha steam cracking and fluid catalytic cracking (FCC) units, and a small part of propylene is produced from dehydrogenation of propane and metathesis of ethylene and 2-butene units. Because ethane is used as a feedstock in more steam cracking units, which can only produce a small amount of propylene, the shortage of propylene will last for a long time. Therefore, some on-purpose propylene-producing technologies have been developed to solve this issue [2], among which the metathesis process of ethylene and 2-butene to yield propylene attracts significant attention, considering that a large amount of C_4 resource is underutilized.

The ABB Lummus Company firstly reported and commercialized olefin conversion technology (OCT) to produce propylene using WO_3/SiO_2 metathesis catalyst, which is less costly and more anti-poisoning compared with Mo- or Re-based metathesis catalysts [3–5]. However, as the only industrialized catalyst, WO_3/SiO_2 has received so less attention in the laboratory than its Re- or Mo- counterpart, that the nature of the active species as well as the reaction mechanism on WO_3/SiO_2 is still a matter of debate [6,7], and the well-known “carbene mechanism” [8,9] proposed by Hérisson and Chauvin based on metalorganic catalyst still needs additional details in the initiation of active intermediate for hetero-

---

* Corresponding author.
E-mail address: zhouhongjun63@126.com (H. Zhou).

http://dx.doi.org/10.1016/j.apcata.2016.03.009
0926-860X/© 2016 Elsevier B.V. All rights reserved.

Table 1
Composition of mixed C_4.

Component	Propylene	Isobutane	*n*-Butane	*Trans*-2-butene	1-Butene	Isobutene	*Cis*-2-Butene
Content (wt%)	0.42	0.91	28.94	43.54	4.38	2.77	19.04

geneous catalyst [10–13]. This is partly because that the relatively lower activity of WO_3/SiO_2 calls for a higher reaction temperature (573–773 K), at which the surface intermediates should have a very short lifetime and can hardly be characterized and monitored in situ [5]. Thereby some works using first-principle calculation to investigate the mechanism of W-carbene active site formation [12,13]. Another important reason is that WO_3/SiO_2 catalyst exhibits poor metathesis selectivity due to the presence of olefin isomerization [14].

Propylene can be produced from the cross-metathesis reaction of 2-butene and ethylene [15–18], or the cross-metathesis of 1-butene and 2-butene [19]. However, even if pure 1-butene [20,21] or 2-butene [22,23] flows into the reactor, propylene will also be generated owing to the existence of both metathesis and isomerization on the same WO_3/SiO_2 catalyst [6,24]. Bhuiyan et al. investigated the kinetics of the 2-butene metathesis over WO_3-SBA-15 using only 2-butene as a feedstock. They calculated the activation energy of the isomerization from 2-butene to 1-butene, cross-metathesis of 2-butene and 1-butene and the self-metathesis of 1-butene, which is 39.4, 71.3 and 176.9 kJ/mol, respectively [1]. The work of Van Roosmalen et al. showed the rate constant for metathesis is generally lower than that for isomerization on various tungsten-oxide/silica catalysts. After silylation of the weakly Brönsted-acidic silanols with hexamethyldisilazane, all the catalysts exhibited 10- to 100-fold increase in the metathesis rate, with greatly suppressed isomerization rate [25]. A higher rate of metathesis between 1-butene and 2-butene containing *trans*-2-butene was observed than that of 1-butene and 2-butene containing *cis*-2-butene by Engelhardt et al. [26]. Poovarawan et al. found the addition of *cis*-2-butene to *trans*-2-butene will reduce the conversion of 2-butene [15].

In order to reduce the competitive isomerization, small amounts of alkali- or alkali-earth metal ions are usually added into the catalyst to poison the active acid sites [6,27]. On the other hand, however, MgO isomerization catalyst is successfully adopted in OCT to achieve a quickly equilibrated isomerization reaction, in order to supply the 2-butene consumed in the metathesis reaction. Based on this, bifunctional catalysts [28–30] or three-functional catalysts are also reported [31] to obtain an expected propylene yield. A significant enhancement in the metathesis performance of $MoO_x/SiO_2–Al_2O_3$ was also observed when CaO was located upstream [18]. Since the isomers of *n*-butene are easy to convert between each other on either acid or basic catalyst, though based on different mechanisms [6,25,32–34], the reactions on WO_3/SiO_2 mixed with MgO catalyst are generally more complicated, so that the composition of gas mixture is generally poorly controlled.

So far, WO_3/SiO_2 combining with MgO catalyst is the only commercialized metathesis catalyst for propylene production. In order to understand the complicated reactions on the catalysts and further to clarify their reaction mechanism, much effort should also be performed on the reacting process analysis in addition to catalyst compositions [7], preparation methods [35–37], and reaction conditions [15,29]. Herein we used mixed C_4 (mainly *n*-butene) and ethylene as the feedstock to study the metathesis and isomerization on hybrid WO_3/SiO_2 and MgO catalysts. Three main independent reactions were first selected to calculate their thermodynamic properties. With their equilibrium constants determined, the experiments under different conditions were conducted, and products distribution was analyzed in detail to deeply investigate the reaction process.

2. Experimental

2.1. Materials

Silica gel of 10–20 mesh (Qingdao Haiyang Chemical Co., Ltd., China), MgO (AR, Sinopharm Chemical Reagent Co., Ltd.), ammonium metatungstate (AR, Shanghai, China), and ethylene (>99.99 v%, Beijing Haipu Gas Company, Ltd.) were all purchased and used without further purification. The C_4 fraction has been purified strictly in advance, and the total amount of oxygenates is lower than 1 ppm. The hydrocarbon composition of mixed C_4 is shown in Table 1.

2.2. Catalyst preparation

2.2.1. WO_3/SiO_2 catalyst

The WO_3/SiO_2 catalyst with a tungsten oxide loading of 8% was prepared by incipient wetness impregnation of an aqueous solution containing 8.5 wt% ammonium metatungstate onto the SiO_2 support. The samples were dried at 383 K for 12 h, and then calcined in air at 873 K for 8 h.

2.2.2. MgO catalyst

The commercial MgO powder was put into a round-bottom flask with deionized water (mass ratio of $MgO/H_2O = 7:100$). The mixture was heated to reflux under stirring for 20 h. Then the precipitation was filtered and dried at 393 K for 2 h. After calcined in air at 873 K for 8 h, the pretreated MgO powder was shaped with 10–20 mesh as the catalyst.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) pattern of WO_3/SiO_2 catalyst was obtained on a D8 Advance (Bruker) X-ray diffractometer connecting with Ni filtered Cu-Kα ($\lambda = 0.15416$ nm) radiation at 40 kV and 30 mA. The scanning speed was 5 K/min.

N_2 adsorption-desorption isotherms of the catalysts were performed on an ASAP 2020 (Micromerities) instrument to examine the pore properties. The samples were pretreated at 363 K for 1 h and then degassed at 5.7×10^2 Pa, 623 K for 5 h. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method and the pore volume and pore size distribution were derived from the adsorption isotherms using the Barret-Joyner-Halanda (BJH) method.

2.4. Catalyst performance evaluation

The catalyst performance was tested in a fixed-bed tubular micro reactor made of stainless steel tube (length: 320 mm, inner diameter: 16 mm). 2.0 g of WO_3/SiO_2 and 0.85 g of MgO catalysts were mixed and then loaded into the reactor. The catalysts were first pretreated at 823 K under high purity N_2 (0.1 MPa, 120 ml/min) for 8 h. After cooled to the reaction temperature, the continuously flowing N_2 was used to regulate the pressure before the feedstock flowed into the reactor. Ethylene was flowed into the reactor controlled by a mess flowmeter and C_4 was pumped to the reactor. Before entering the reactor, ethylene and C_4 were first flowed into a preheated tube where they were heated to the reaction temperature. The typical reaction conditions were 573 K, 2.0 MPa, E/B (molar ratio of C_2H_4:n-C_4H_8) = 2, WHSV (weight hourly