



Enhanced metathesis activity of low loading $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts for propylene production by using aluminum nitrate as Al_2O_3 precursor



Siriporn Vorakitkanvasin^a, Sirachaya Kunjara Na Ayudhya^b, Kongkiat Suriye^b, Piyasan Praserttham^a, Joongjai Panpranot^{a,*}

^a Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b SCG Chemicals Co., Ltd., 1 Siam-cement Rd, Bang sue, Bangkok 10800, Thailand

ARTICLE INFO

Article history:

Received 30 September 2015

Received in revised form

26 November 2015

Accepted 11 January 2016

Available online 13 January 2016

Keywords:

Metathesis

Propylene production

Rhenium

Aluminium nitrate

2-Pentene

Lewis acidity

ABSTRACT

A series of alumina supported Re_2O_7 catalysts (4 wt% Re loading) were prepared by using aluminium nitrate (ANN) calcined at different temperatures (400, 550, and 750 °C) as the supports and impregnated with ammonium perrhenate solution. Despite their lower pore volume and smaller average pore size, the catalyst performances in the metathesis of ethylene and 2-pentene in terms of 2-pentene conversion and propylene selectivity of all the $\text{Re}_2\text{O}_7/\text{ANN}$ were much improved as compared to the commercial $\gamma\text{-Al}_2\text{O}_3$ supported one ($\text{Re}_2\text{O}_7/\text{Al-com}$) with the $\text{Re}_2\text{O}_7/\text{ANN-550}$ exhibited the best performances. Based on the *in situ* Infrared spectroscopy, the *in situ* Raman spectroscopy, and the *in situ* IR spectroscopy of chemisorbed ammonia and thermodesorption results, the use of ANN as Al_2O_3 precursors provided higher acidic OH group and higher Lewis acid sites, which were necessary for the formation of the 2nd rhenium oxide active species especially for low Re loading. The higher Bronsted acidity on the $\text{Re}_2\text{O}_7/\text{Al-com}$, on the other hand, produced higher amount of coke and C_5+ products. In addition, the acid strength of the Lewis acid sites appeared to be another important factor determining metathesis activity of the supported Re_2O_7 catalysts.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Propylene is one of the most important basic chemicals in petrochemical industry, which is used in the production of polypropylene, acrylonitrile, acrylic acid, acrolein, propylene oxide, glycols, plasticizer oxo alcohols, cumene, isopropyl alcohol, and acetone. The growth in propylene production is primarily driven by the industry demand for polypropylene and is expected to be about 5.7% per year in the near future [1].

The majority of propylene is produced as a byproduct of petroleum refineries and olefin plant steam crackers. Due to the possibility of a supply/demand imbalance, the catalytic, on-purpose technology for propylene production such as metathesis and propane dehydrogenation has gained more interest recently. Supported rhenium oxide-based catalyst is known to be active for olefin metathesis at low temperatures (*i.e.*, 25 °C), whereas, molybdenum oxide- or tungsten oxide-based catalysts require much higher reaction temperatures (100–500 °C) [2–4]. The catalytic performance of

$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ with low rhenium loading can be further improved by addition of the third metal oxides such as MoO_3 , V_2O_5 , or WO_3 . The MoO_3 -, V_2O_5 -, or WO_3 -modified low rhenium loading catalysts were reported to be active and highly selective for the metathesis of methyl oleate. Moreover, their price is lower than the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-SnR}_4$ catalyst for the same reaction [5]. The use of mixed supports such as silica–alumina and alumina–borate also improved the performances of Re-based catalysts in the metathesis reaction because of their high acidity and appropriate amount of Bronsted acidity compared to alumina-supported ones [6]. The alumina–borate-supported rhenium oxide catalysts were tested in both the metathesis of functionalized alkenes [7] and the metathesis of propylene [8]. The $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ catalysts showed high activity and selectivity than the conventional $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst and was attributed to the increase in support acidity and their strong Bronsted acidity. Andreini et al. [9], treated the catalyst based on silica–alumina with hexamethyldisilazane in order to remove surface OH groups and concluded that the acid-base function of these catalysts (mainly their Bronsted acidity) is involved in the reaction. In our recent studies, a relatively high propylene yield (88%) was obtained under mild reaction conditions using the unconventional feed of ethylene and 2-pentene over $\text{SiO}_2\text{-Al}_2\text{O}_3$

* Corresponding author. Fax: +66 2218 6877.

E-mail address: joongjai.p@chula.ac.th (J. Panpranot).

supported Re_2O_7 -based catalysts [4,10–12]. The catalyst performances were found to be influenced by the properties of the SiO_2 - Al_2O_3 supports, which were modified by the SiO_2 - Al_2O_3 compositions [11] and/or the preparation methods [12]. The treating of Al_2O_3 with phosphate also resulted in more acidic surface, belonging to acidic phosphorus-bonded OH groups [13]. At low Re loadings, these supports have also reacted with the ReO_4^- ions resulting in active metathesis sites.

In the present work, the catalytic properties of $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ in the metathesis of ethylene and 2-pentene were enhanced by using aluminium nitrate supports calcined at different calcination temperatures. The catalyst performances were correlated with the formation of well-dispersed active rhenium species. The catalyst properties were further characterized by N_2 physisorption, X-ray diffraction (XRD), inductively-coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), *in situ* Infrared spectroscopy (*in situ* IR), and *in situ* Raman spectroscopy (*in situ* Raman), and *in situ* IR spectroscopy of chemisorbed ammonia and thermodesorption (*in situ* NH_3 -IR)

2. Experimental

2.1. Catalyst preparation

The catalyst supports were prepared by calcination of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ under air at 400, 550, and 750 °C for 4 h and were denoted as ANN-400, ANN-550, and ANN-750, respectively. The supports were impregnated with an aqueous solution of ammonium perrhenate (NH_4ReO_4 , Aldrich) several times to obtain the 4 wt% of rhenium loading. Between impregnation steps the catalyst was held for 2 h at room temperature and then dried at 110 °C for 12 h. After the impregnation step, the catalyst was calcined in dry air at 550 °C for 8 h. For comparison purposes, a commercial $\gamma\text{-Al}_2\text{O}_3$ (Fluka) was also used for preparation of 4 wt% $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ catalyst. The catalyst was denoted as $\text{Re}_2\text{O}_7/\text{Al-com}$.

2.2. Catalyst characterization

The specific surface area, the pore volume, and the pore size of the supports and the catalysts were measured by N_2 physisorption at -196°C using a Micromeritics ASAP 2020 automated system. The specific surface area was calculated according to Brunauer–Emmett–Teller (BET) method and the pore volume and pore size were determined from Barret–Joyner–Halenda (BJH) method. The XRD patterns were collected using a SIEMENS D5000 X-ray diffractometer with $\text{Cu K}\alpha$ radiation and Ni filter. The scans were recorded in the 2θ range of 20 – 80° using a step size of 0.04° . The actual metal loading for each catalyst were measured by ICP-OES on a Perkin Elmer Optima 2100DV instrument. The sample was performed by digestion with a mixture of hydrofluoric and nitric acids at 60°C . The *in situ* IR spectra were acquired with a Thermo Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment for diffuse reflectance spectroscopy. The sample was placed in a Harrick cell, which were cooled by flowing water. Then the sample was heated from room temperature to 500°C at a heating rate $10^\circ\text{C}/\text{min}$ and holding the temperature for 1 h. After that the sample was cooled to 60°C . The spectra were collected using a DTGS detector with a resolution of 4 cm^{-1} and an accumulation of 72 scans. The collection of the initial IR gas phase background was performed by placing a reflective mirror in the laser path. For *in-situ* IR spectroscopy of chemisorbed ammonia and thermodesorption, after pretreatment procedure the sample was saturated with $15\% \text{NH}_3/\text{He}$. After saturation, the physisorbed ammonia was desorbed in a helium gas flow about 1 h. Then the sample was heated from 60°C temperature to 500°C at a heat-

ing rate $10^\circ\text{C}/\text{min}$. The spectra were collected every minute. For *in-situ* Raman spectroscopy, the Raman spectra of catalysts were collected by a high resolution Raman spectrometer system (Horiba-Jobin Yvon Labram-IR) equipped with the visible laser at 532 nm. The LabSpec 5 software was used to operate the experiment and collect the Raman spectra. The laser calibration was performed with a silica slide at 520.7 cm^{-1} . The sample was loaded into the same cell used for IR measurements. The same pretreatment procedure as in the IR experiments was followed. The dehydrated Raman spectra of catalysts were collected at 60°C . The TEM micrographs were obtained using a JEOL JEM-2100 transmission electron microscope with an accelerating voltage of 120 kV. The amount of coke was examined by the temperature programmed oxidation (TPO). The spent catalyst was in a quartz tube under the $1\% \text{O}_2/\text{He}$ flow and heated with the heat rate of $5^\circ\text{C}/\text{min}$ until the temperature reached 900°C , analyzed by GC-8AIT.

2.3. Reaction test

The catalyst performances were tested in the gas-phase metathesis reaction between ethylene and 2-pentene with the molar ratio of ethylene: 2-pentene 3:1, weight hourly space velocity (WHSV) 5.33 h^{-1} , and 1 g catalyst in a fixed-bed reactor (ID tube = 7.5 mm) under atmospheric pressure. In a typical run, the catalyst was pretreated at 500°C for 1 h and then cooled down to reaction temperature at 60°C under nitrogen flow. During the reaction, the products were analyzed by an on-line Agilent 7820A gas chromatograph equipped with a GS-Gaspro 113–4362 capillary column, 0.32 mm diameter and 60 m in length. The GC signals were processed by an EZChrom Elite integrated peak program integrator.

The conversion of the limiting reactant (2-pentene), the selectivity of products, and the yield of products were calculated by the following equations:

2-Penteneconversion (%) =

$$\frac{\text{Amount of 2-pentene in feed} - \text{amount of 2-pentene remained in product}}{\text{Amount of 2-pentene in feed}} \times 100$$

Selectivity of component i (%)

$$= \frac{\text{Amount of component i in products}}{\text{Amount of total products}} \times 100$$

Yield of component i (%) = 2-Pentene

$$\frac{\text{Amount of component i in products}}{\text{Amount of total products}} \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The physical properties of the various Al_2O_3 supported Re_2O_7 catalysts are shown in Table 1. The surface area of the $\text{Re}_2\text{O}_7/\text{Al-com}$ was $136\text{ m}^2/\text{g}$ whereas those of the $\text{Re}_2\text{O}_7/\text{ANN}$ catalysts were ranging between 130 – $170\text{ m}^2/\text{g}$. The pore volume and the average pore size of the $\text{Re}_2\text{O}_7/\text{Al-com}$ were slightly higher than those of the $\text{Re}_2\text{O}_7/\text{ANN}$ catalysts. The actual Re contents were ranged between 3.70 – $3.94\text{ wt}\%$ which were closed to the expected values ($4\text{ wt}\%$). Fig. 1 shows the XRD patterns of all the prepared catalysts. The major XRD peaks at 37° , 39° , 46° , 61° and 67° were attributed to the γ -phase alumina [14]. The characteristic peaks corresponding to Re_2O_7 crystals were absent on all the catalysts because of the low amount of rhenium loading and the Re_2O_7 crystals could be volatile at the calcination temperature above 300°C [3,15,16].

Download English Version:

<https://daneshyari.com/en/article/39089>

Download Persian Version:

<https://daneshyari.com/article/39089>

[Daneshyari.com](https://daneshyari.com)