Olefin conversion on nitrogen-doped carbon-supported cobalt catalyst: Effect of feedstock

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ABSTRACT

A nitrogen-doped carbon-supported cobalt oxide catalyst is able to oligomerize ethylene, propylene, 1-butene and 1-hexene into mixtures of oligomers with above 94.1% dimers. Higher than 72.5% of the dimers produced from 1-butene and 1-hexene are internal linear olefins, while the dimer products from propylene oligomerization are 47.0% linear including 5.9% 1-hexene. Ethylene had the highest oligomerization activity with 56.1–87.0% 1-butene selectivity. The selectivity to linear alpha olefins decreases with an increasing oligomer chain length during ethylene oligomerization. The oligomers formed from ethylene conversion follow a Schulz-Flory distribution. Cossee type mechanism rationalizes the product selectivity from the four olefin feeds, suggesting that a 1,2-2,1 insertion sequence is critical to obtaining linear olefin products. The catalyst was inactive in oligomerizing internal olefins.

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1. Introduction

Light (C2 to C6) linear alpha olefins are important building blocks for the synthesis of fuels and chemicals. The IFP-SABIC Alphabutol technology was implemented to produce 1-butene with the world's largest capacity from ethylene dimerization based on homogeneous catalysis [1]. Chevron Phillips Chemical has announced the start-up of world's largest 1-hexene plant in 2014 [2], which adopts an on purpose route to 1-hexene from ethylene trimerization with a chromium based homogenous catalyst. The light olefins are currently largely produced from steam cracking [3], fluid catalytic cracking (FCC) [4] and Fischer-Tropsch synthesis (FTS) [5]. The shale gas revolution has driven ethylene expansions in the North American market with a 70% collapse in the price of ethane between 2012 and 2013 [6]. The catalytic oligomerization of light olefin can be achieved by heterogeneous acid-catalysis which mainly produces branched oligomers suitable as additives for fuels or synthetic lubricants [7,8], or by homogeneous catalytic systems which mainly produce straight-chain oligomers to make commodity chemicals [9]. Linear oligomers, especially linear alpha

olefins (LAO) have a broad range of applications in the production of performance chemicals and plastics such as polybutylene, co-monomers in PE/PP, polyolefin elastomers, plasticizer and detergent alcohols. Olefin oligomerization to LAOs remains one of the few industrial processes that use homogeneous catalysts [10-14]. The technology uses an expensive and difficult-to-handle co-catalyst activator such as methylaluminoxane (MAO) [15], complex catalyst recovery operations, and a highly purified olefin feed stream [14]. Replacing homogeneous catalysts with an efficient heterogeneous analogue that is potentially regenerable, does not require addition of an activator and is resistant to feed impurities could drastically lower the capital and operating costs, and hence improve the competitiveness of the US chemical industry.

Olefin oligomerization has been proposed to proceed through three different classes of mechanisms: carbocation, metallacycle or Cossee-Arlman. A carbocation mechanism is used to describe olefin oligomerization catalyzed by inorganic solid acid catalysts such as H-zeolites and solid phosphoric acid [8,16,17]. This pathway involves the formation of a secondary or tertiary carbocation over Brønsted acid sites yielding branched oligomers. The formation of highly linear oligomers catalyzed by transition metal complexes is commonly explained by a metallacycle or Cossee-Arlman mechanism. The metallacycle mechanism begins with olefin coordination followed by formation of metallacyclopentane [18]

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in the case of ethylene oligomerization. The product selectivity is frequently determined by the stability of the intermediate metalla-cycles. This mechanism was proposed to rationalize the excess amount of 1-hexene product observed during ethylene oligomerization over chromium-based N-heterocyclic carbene (Cr-NHC) catalysts, through both experimental [18-20] and computational [21] methods. The Cossee-Arlman mechanism involves alkyl migration to a coordinated olefin where the rate constants for chain propagation and chain termination are approximately the same [19]. This mechanism was originally proposed to explain the chain growth for ethylene polymerization over Ziegler-Natta catalysts [22]. It has been lately adopted to explain the product selectivity over transition metal complexes including tridentate cobalt and iron catalysts [19,23], and cobalt metallocene [24] catalyst. A recent theoretical study also provided evidence to describe the oligomer chain growth on the Ni sites within Ni-containing SSZ-24 zeolite during ethylene oligomerization with a Cossee-type mechanism [25].

Schultz and co-workers proposed that olefin oligomerization with CoO_X/N-C catalysts (pretreated at 543 K) occurs by a Cossee-type mechanism, using ethylene, propylene, 1-butene and 1-hexene as feeds [26-28]. However, their experiments were not performed in a continuous flow reactor and they did not analyze the location of the C=C bond making it difficult to probe the chain growth. We reported the use of two-dimensional gas chromatography-mass spectrometry (2D-GC/MS) to accurately identify and quantify most of the octene isomers formed in 1-butene oligomerization [29]. Oligomerization with other olefinic feeds, besides 1-butene, could aid in developing a better understanding of olefin oligomerization over CoO_X/N-C.

We have previously proposed that 1-butene oligomerization follows a metallacycle mechanism on nitrogen-doped carbon-supported cobalt oxide (CoO_X/N-C) catalysts [29]. While this mechanism can explain the product distribution for 1-butene oligomerization at low conversion as we will show in this paper a Cossee-type mechanism better explains the product distribution for different olefins over this catalyst at all conversions. The objective of this paper is to report on the oligomerization of ethylene, propylene, 1-butene, 1-hexene and 1-hexene/internal hexene mixtures with CoO_X/N-C in a continuous flow reactor. This will allow us to develop a more rigorous mechanism for how olefins oligomerize over this catalytic material.

2. Experimental

2.1. Catalyst preparation

A nitrogen-doped carbon-supported cobalt oxide catalyst (CoO_X/N-C) was prepared as described in our earlier work [29]. In a typical synthesis, 5.00 g of sieved activated carbon was treated with 4.55 mL 30% NH_4OH solution and dried on a hot plate in the open air at 403 K for 2 h. A cobalt nitrate solution of 4.66 g Co$(NO_3)_2 \cdot 6H_2O$ in 5.83 mL deionized water was then added onto the treated carbon support to achieve a cobalt loading of 13 wt%. After drying at 403 K overnight, the catalyst was treated with 12.5 mL 30% NH_4OH solution. Finally, the catalyst was dried overnight at 403 K. The carbon-supported cobalt oxide catalyst was pretreated at 503 K for 2 h in helium without air exposure before being exposed to the olefin substrate for oligomerization testing. Catalyst characterization (including elemental analysis, XRD, *in-situ* Raman and XANES) is reported elsewhere [29].

NH_4-ferrierite (NH_4-FER; SiO_2/Al_2O_3 = 20, CP914C) was purchased from Zeolyst. The NH_4-FER catalyst was used directly for terminal/internal hexene mixture synthesis without any pretreatment.

2.2. Catalyst characterization

Powder X-ray diffraction (pXRD) patterns were obtained from Rigaku Rapid II diffractometer with a Mo K_α source with 2θ from $2°$ to $45°$ and a total exposure time of 20 min. Samples were crushed and packed in glass capillaries with a 0.8 mm diameter and 0.01 mm wall thickness.

Thermogravimetric analysis (TGA) was carried out with a TA instruments Q500 system. Approximately 10 mg of sample was used. Measurements were performed in 50 mL/min N_2 flow with 10 K/min ramp rate from room temperature to 1073 K. The catalyst samples were cooled down after reaction in the reactor under 50 mL/min helium flow till room temperature, and remained in the reactor for at least 12 h before exposure to the air prior to the TGA experiments.

Nitrogen Brunauer-Emmett-Teller (BET) surface areas were obtained at 77 K with ASAP 2020 multiple points system (Micromeritics). Before the measurements, the sample was degassed under vacuum at 423 K for 4 h.

2.3. Catalyst activity and selectivity

Measurements of reaction rates and product distributions were performed using a down-flow, fixed-bed stainless steel reactor (9.52 mm outer diameter, 1.24 mm wall thickness) loaded with 500 mg of catalyst, with both ends capped with glass beads (Sigma-Aldrich, 425–600 μm) and quartz wool. All experiments were carried out at 353 K and 31 bar total pressure, which was adjusted with helium (Airgas, UHP) using a back-pressure regulator. After a gas–liquid separator maintained at 268 K and reaction pressure, the gas phase products were analyzed with an online gas chromatograph (GC, Shimadzu) equipped with a Rt®-QS-BOND (Restek) and a flame ionization detector (FID). The liquid products were collected from the separator and analyzed by 2D-GC/MS (Agilent) equipped with both a flame ionization detector (FID) and a mass selective detector (MSD). A more detailed description about the reactor system and the GC operation condition can be found elsewhere [8,29]. The linear alpha olefin feeds in this study include: ethylene (UHP, Airgas), propylene (99.5% polymer grade, Airgas), 1-butene (99.9%, Matheson) and 1-hexene (97%, Sigma-Aldrich). For all the oligomerization experiments, the catalyst was pretreated in 150 mL/min helium flow, ramped to 503 K with 5.5 K/min ramp rate, and held at 503 K for 2 h. The reactor was then cooled to the reaction temperature (353 K) in helium flow. Reactant conversion was calculated based on Eq. (1). Product selectivity, product yield, rate and product distribution were calculated based on Eqs. (2)–(5). Weight hourly space velocity is defined and calculated based on Eq. (6). The overall turnover number (TON) is defined as the moles of carbon in the total observed products per mole of cobalt atom in the catalyst as shown in Eq. (7).

$$\text{Reactant conversion}(\%) = \frac{\text{moles of carbon in the detected products}}{\text{moles of carbon in the feed}} \times 100\%$$

$$(1)$$

Product selectivity (%)

$$= \frac{\text{moles of reactant converted to a specific or a group of product}}{\text{moles of reactant converted}} \times 100\% \quad (2)$$

$$\text{Product yield}(\%) = \text{Product selectivity} \times \text{Reactant conversion}/100 \quad (3)$$