Feature Article

Applications of light olefin oligomerization to the production of fuels and chemicals

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Christopher P. Nicholas

Exploratory Catalysis and Materials Research, Honeywell UOP, 25 East Algonquin Road, Des Plaines, IL 60017, USA

A B S T R A C T

The oligomerization of the light olefins ethene, propene, and butenes into fuels and chemicals has been investigated and commercially practiced for many years. While the area appears on the surface to be mature, many advances have been made in recent years. In this feature article, I discuss the mechanisms of reaction and showcase catalysts and processes useful for oligomerization from both the open and patent literature. Commercially practiced processes are spotlighted. Among the catalysts utilized in the art are acidic catalysts such as solid phosphoric acid and zeolites, as well as metal based catalysts including aluminum alkyls, and nickel and zirconium based complexes and solids. A short section on catalysts and processes which utilize a metalla-cycle mechanism in order to achieve high selectivity to 1-hexene or 1-octene is followed by a discussion of multi-functional materials possessing both acid and metal active sites. Finally, processes where oligomerization is a key step in a multi-step or multi-reaction process are discussed.

1. Introduction

The oligomerization of the light olefins ethene, propene, and butenes into fuels and chemicals has been investigated and commercially practiced for many years [1]. Initially, non-catalytic thermal methods had been utilized to convert light olefins into more useful compounds [2–4], but Ipatieff's discovery of solid phosphoric acid catalyzed oligomerization 80 years ago sparked the first widespread use of oligomerization as a method of synthesizing transportation fuels [5,6]. Mobil then advanced acidic oligomerization technology with commercial application of MFI zeolite in the conversion of light olefins derived from methanol to fuels in their New Zealand refinery from 1985 to 1997. A key step in the overall process is the oligomerization of light olefins to gasoline and distillate [7]. In the meantime, Ziegler had discovered metal catalyzed oligo/polymerization [8], several of which catalyst types have since been commercialized. While thermal methods have been recently investigated again, and radical mediated oligomerization is also feasible, catalytic methods dominate the market due to the control afforded over the product [9,10].

In this feature article, I discuss recent developments in catalytic olefin oligomerization of $C_2–C_5$ olefins, with highlights both from the patent and open literature that have occurred, largely since O'Connor and Kojima's review [11]. To help focus the text, alcohol and other oxygenated molecules are not covered as feedstocks here unless a specific step to produce olefins has been reported, although biomass conversion via oligomerization routes has been successful [12]. The text

is divided according to the mechanism utilized by the catalysts, with acid-catalyzed carbenium chemistry and metal catalyzed 1,2-insertion the two most frequently utilized mechanistic routes for oligomerization. Both types of catalysts are used in currently commercially practiced processes. In these reactions, the relative rates of oligomerization and side reactions such as isomerization (both double bond and skeletal), cracking (mono- and bi-molecular), aromatization, hydride transfer, and coking are a strong function of structure and reaction conditions (e.g. temperature, pressure, contact time) [13,14]. In general, cracking reactions and hydride transfer reactions often leading to aromatics and coke precursors are favored at higher temperatures (> 300 °C) [15], with oligomerization favored at lower temperature (< 200 °C) [16]. Thus, the selectivity to specific products is dependent both on catalyst and process conditions.

Understanding the impact of mechanism on oligomer molecular weight distribution is also important. Two are frequently observed, both of which describe asymmetric oligomer distributions. Because zero insertions is the monomer, negative insertions by definition cannot occur, but production of any length chain is feasible, an asymmetric distribution of oligomers is mathematically necessary.

A long known mathematical function, the Poisson distribution [17], is the less frequently observed and can be utilized to describe distributions of oligomers where production of each oligomer number is independent of others [18]. Acid catalysts need to build a high concentration of dimers before trimers are produced, therefore, acid catalysts should never give a Poisson distribution of oligomers since this key

E-mail address: Christopher.Nicholas@honeywell.com.

condition is not met. Metal based catalysts sometimes give Poisson distributions, but chain termination needs to be independent of monomer insertion as well as chain length independent, and oligomer reinsertion cannot occur.

The Schultz-Flory distribution can be used to describe oligomer distributions where chain termination is kinetically competitive with the rate of propagation and/or reinsertion of oligomers occurs [19,20]. Cracking or other side reactions should not be present at kinetically relevant rates. Most metal catalysts will therefore give Schultz-Flory distributions of oligomers; these tend to be broader than Poisson distributions [21].

Following a discussion of catalysts using acid and insertion mechanisms, I then explore the typically homogeneous catalysts which utilize a metallacycle mechanism to oligomerize ethylene and other light olefins into dimers and trimers. These catalysts are the base of a growing industry to produce C_4-C_8 olefins as comonomers for polyethylene and polypropylene production. After discussing bifunctional catalysts which utilize both metal and acid sites/mechanisms, I finish by looking at several combination processes where oligomerization is one of the key steps.

2. Acid catalyzed oligomerization

While olefin oligomerization is a deactivation or undesired reaction mechanism in many acid catalyzed transformations of olefins [22], it is also a useful method of carbon–carbon bond formation, provided that proper catalyst and conditions are utilized. For over 80 years, C_2-C_5 light olefins have been oligomerized over acidic catalysts to fuels, principally gasoline, but recently to distillates as well. Market sizes are difficult to estimate as the fuels produced via oligomerization are typically not accounted separately from other refinery sources, but an installed base of approximately 60 oligomerization units primarily converting propene, butenes, or combinations thereof with nameplate capacity of about 67.5 M barrels/year of feed remain. Just under 650 oil refineries exist in the world, so 9% of refineries currently practice oligomerization [23].

In addition to fuels, this total capacity includes the primary production of olefin oligomers as precursors to petrochemicals including branched alkylbenzenes (BAB), alkylated phenols, and oxo alcohols. Marketshare of BAB for sulfonation and use as a detergent has been significantly declining in favor of the more readily biodegradable linear alkylbenzenes (LAB, Section 3) [24], but still sees use as oilfield chemicals. The largest alkylated phenol use is in nonylphenolethoxylate non-ionic surfactants, where over 300 million pounds are produced yearly, though market share will decline rapidly in upcoming years [25,26].

Oxo alcohols synthesized from mixed octenes and nonenes see end uses in plasticizers for polyvinylchloride (PVC) including diisononylphthalate (DINP), the hydrogenated non-phthalate version cyclohexane dicarboxylic acid diisononyl diester (DINCH®), diisodecylphthalate (DIDP), trimellitates, and adipates. The use of DINP and DINCH® in particular have been increasing significantly as di-2-ethylhexylphthalate (DEHP) has declined due to environmental concerns. Of the approximately 6 million ton/yr plasticizer market, these molecules had about 33% market share in 2014, with the total share expected to grow in the next several years [27]. Other significant uses for oxo alcohols are in alkylethoxylate non-ionic surfactants whose market share is also increasing [28].

Multiple acidic solids [29] have been utilized as oligomerization catalysts, ranging from the classical silica-supported phosphoric acid, to acidic ion-exchange resins, amorphous silica-aluminas, zeolites and even acidic clays and sulfated metal oxides [30]. The primary mechanism utilized over these materials is a classic carbenium route [31], shown in Fig. 1.

The Brønsted acid site attacks the olefin in reaction 1 leading to the formation of an ion-pair. The carbenium ion formed can react with
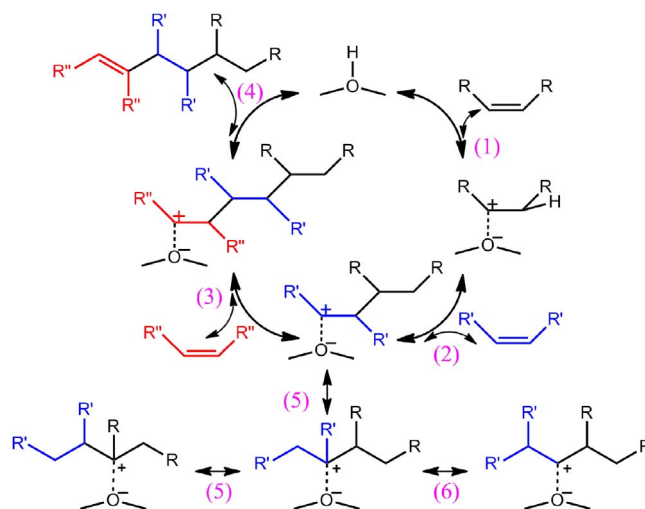

Fig. 1. Carbenium ion mechanism utilized in acid catalyzed oligomerization reactions. The first olefin inserted is black, the second blue, and the third red. Numeration is described in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

another olefin in reaction 2 to give a longer carbon chain. The insertion/chain growth can continue (reaction 3) or terminate (reaction 4) to yield an olefin and the starting acid site. With substitution on the olefin, each olefin addition (dimer, trimer, etc.) yields a branch in the hydrocarbon chain. Isomerization is also quite prevalent in many systems with H-shift (reaction 5) and alkyl shifts (reaction 6) frequently occurring to yield more thermodynamically stable carbenium ions. Thus, true oligomerization products are often not the only products formed. Reaction 1 can be responsible for double bond migration and E to Z transitions. Once the planar carbenium ion is formed, if reversed, the position of the olefin and relative E or Z configuration can change from the initial olefin. The particular acidic solid utilized and confinement effects drive differentials in the relative rates of the multiple reactions as Iglesia and coworkers have shown [32].

2.1. Solid phosphoric acid (SPA)

Phosphoric acid, as a high concentration aqueous solution, had been shown to be catalytically active for the oligomerization of olefins [33,34], with significantly higher yields than thermal polymerization and with activity dependent on the concentration of H_3PO_4 [35,36]. It wasn't until the development of solid phosphoric acid (SPA) that industrial processes for olefin oligomerization were commercialized [37,38]. 80 years after Ipatieff's discovery [5], SPA continues to be utilized commercially due to its high selectivity to gasoline and cost effectiveness.

In addition to UOP's Catalytic Condensation™ process [39], of which more than 250 units have been licensed since 1935 (also called Cat-Poly) [40], and Standard Oil's development of a similar process [41], Sasol have been practicing a SPA based oligomerization process [42] and have published much research in the area. SPA is formed by combining H_3PO_4 with silica sources such as the natural products kieselguhr or diatomite [43], synthetic silicas [44,45], or quartz followed by extrusion [46]. High silica content solids are traditionally utilized, but even low silica content kieselguhr with CaO and MgO contents above 3 wt% (combined) are acceptable as long as the bulk density is less than about 0.3 g/mL [47]. During the reaction between H_3PO_4 and the SiO_2 support, a number of silicon phosphates and hydrogen phosphates including orthophosphate $Si_5O(PO_4)_6$, pyrophosphate SiP_2O_7, hydrogen phosphate $Si(HPO_4)_2 \cdot H_2O$, and tripolyphosphate $SiHP_3O_{10}$ are formed [48]. The orthophosphate is the preferred phase for activity [49], the pyrophosphate for strength [46,50] and the hydrogenphosphate a non-preferred phase. As for many of the other catalyst systems