Fuel Processing Technology 138 (2015) 86–99

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Review

Alkenes oligomerization with resin catalysts

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ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form 25 April 2015
Accepted 27 April 2015
Available online xxxx

Keywords:
Catalysis
Diesel
Fuel
Ion exchange resin
Olefins
Oligomerization

ABSTRACT

The growing interest of chemical and oil refining industries in the catalytic oligomerization of alkenes for the production of synthetic fuels and additives formulated around light gasoline olefins is due to recent environmental restrictions and increasing diesel demand. Furthermore, the drive towards sustainability and the emergent contribution of biorefineries for the manufacture of intermediate and platform chemicals envisages olefins produced from biomass derived alcohols as an important feedstock for subsequent oligomerization.

Over the last years much work has been published on the catalytic oligomerization of propene, butene, isobutene and isoamylene over cation exchange resins, such as Amberlyst and Purolite, and others like Nafion. For instance, isobutene dimers and trimers are accepted additives for gasoline (octane booster) and diesel (cetane booster) while isobutene higher oligomers can be a source for heavier fuels and synthetic lube oils. This paper presents a deep and critical review in the field discussing the influence of the resin (resin-type and their physical and structural properties), the operating conditions and additives used (polar compounds like alcohols), upon oligomerization conversion and selectivity.

Contents

1. Introduction

Ion exchange resins, particularly macroporous resins are versatile catalysts with many industrial applications especially as catalysts for the production of petrochemicals and solvents. For example, the oligomerization of C_4 alkenes with Amberlyst cation exchange resins yields products useful as diesel fuels whereas the oligomerization of higher

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http://dx.doi.org/10.1016/j.fuproc.2015.04.031

olefins with Nafion [1] yields oligomers used as intermediates in the production of lubricants [1].

The first part of this review presents an overview about ion exchange resins and their main characteristics. The second part presents a review on acidic ion exchange resins as catalysts for olefin oligomerization focusing on propene, linear butenes, isobutene and isoamylene. The third part reviews fuel and lube production by path of olefin oligomerization using the same class of catalysts. Finally some conclusions and outlooks are drawn.

2. Resins

The synthesis of organic (polymeric) ion exchangers was first reported in 1935 [2,3]. Over the last decades ion exchange resins have been used in a myriad of industrial applications especially in catalysis where sulfonic acid resins replace conventional mineral acids [4–7]. Those catalysts have been used on a large scale over the last 60 years for example in industrial esterification reactions [4].

Resins are organic polymers whose properties are influenced not only by the nature of the monomer(s), the polymerization and crosslinking degree, but also by specific functional groups incorporated in the polymeric matrix to provide catalytic activity [8]. For example, sulfonic acid groups can be anchored to the resin by sulfonation of the copolymer with concentrated sulfuric acid or chlorosulfonic acid [4] or by copolymerization with aromatic compounds which contain sulfonic acid groups [9,10]. The functional groups can be acidic but also basic, redox or even metallic complexes (transition metals) depending on the envisaged application. Electron withdrawing groups, for example halogens such as bromine and chlorine, can also be incorporated in the polymeric resins to improve their thermal stability [10].

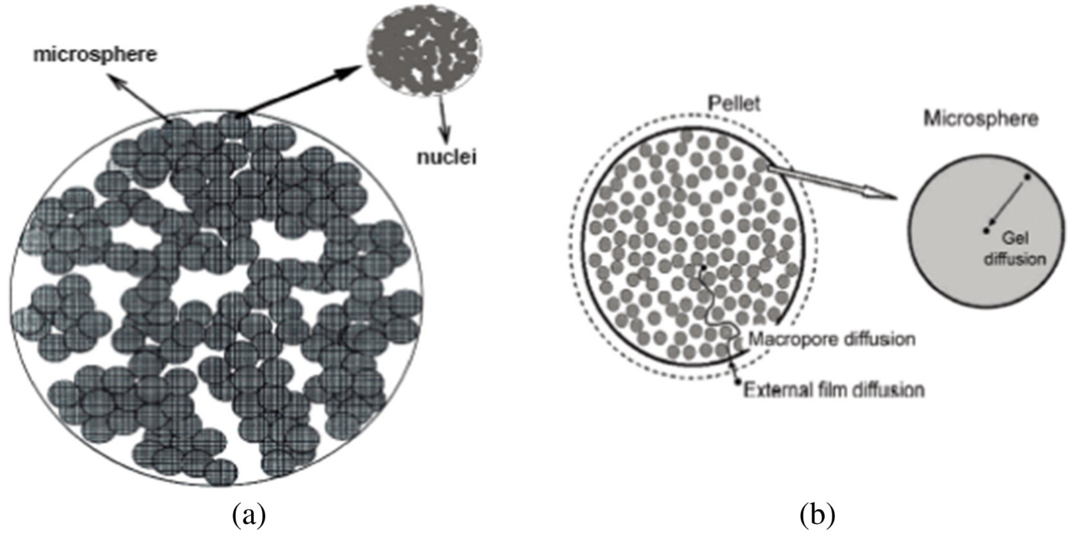
Macroporous ion exchange resins were invented in the 60s [3,11,12]. Compared with the earlier polystyrene resins (gels without true porosity) macroporous resins have a permanent well-developed porous structure whose dimensions can be manipulated by precise polymerization conditions [13]. These resins are usually supplied as spherical beads (pellets) composed of gel microparticle aggregates (Fig. 1(a)) [11,12, 14]. The bidisperse porosity arises from the void spaces between and within the aggregates forming a system of interconnected micro- and macropores. Since most of the catalytic sites (e.g. sulfonic groups) are within the microparticles, the reactants must diffuse through the pellets external film, then through the macropores and finally penetrate in the gel matrix of the microspheres where they react (Fig. 1(b)) [13]. Hence the catalytic performance of macroporous resins is influenced not only by their acidity but also by the specific surface area, porosity, pore size distribution, etc. [15].

The most common macroporous resins are reticular styrene–divinylbenzene co-polymers synthesized in the presence of a phase extender or porogen (for example, a solvent such as heptane), which does not react with the monomers and that is easily removed after the polymerization thus creating a porous polymer matrix [4,11]. Besides, the porous structure is strongly influenced by the type and amount of crosslinking agent (e.g. divinylbenzene, DVB) [11,16]. Higher loads of DVB reduce polymer swelling effects and increase the rigidity of the structure, the total pore volume, the average pore diameter and the specific surface area [17]. For a fixed amount of DVB, increasing the porogen levels (within the macroporous domain in the resin pseudo-phase diagram) also increases the total pore volume and average pore diameter but reduces the specific surface area [18]. Hence, the morphology of the resin particles depends on the nature of the crosslinking agent and the ratio of porogen/crosslinker, among other parameters.

Alternatively to DVB several other aromatic vinyl compounds can be used as co-monomers to prepare functionalized polystyrene based resins, for example, vinyl toluene, vinyl naphthalene, vinyl ethylbenzene, methyl styrene, vinyl chlorobenzene and vinyl xylene [10].

Amberlyst-15 (Fig. 2(a)) is a typical example of a sulfonic polystyrene-co-divinylbenzene macroporous resin whereas Nafion (Fig. 2(b)) is an example of a sulfonic perfluorinated resin, an alternative polymeric backbone structure [4,19]. Nafion has received a considerable amount of attention not only due to its high acidity [20] but also because of its excellent mechanical and thermal stability (i.e. higher maximum operating temperature) [21]. Macroporous resins containing weaker acid groups (for instance, carboxylic, phosphonic, phosphinic and arsonic acids) have been prepared but catalytic industrial applications are scarce in comparison with sulfonic acid resins [4].

Macroporous sulfonic acid resins are the most relevant for industrial catalysis. They are used in processes involving reactions such as etherification, esterification, acetalization, hydration, hydrolysis, alkylation and oligomerization [1,2,22–27]. More specifically, resin catalysts are used for propylene hydration to yield isopropyl alcohol (IPA), to produce methyl isobutyl ketone (MIBK) from acetone, and mainly in the synthesis of methyl t-butylether (MTBE) by etherification of isobutene with methanol (MeOH) [2]. Gelbard [28] provides an interesting review on organic synthesis catalyzed by acid or basic ion exchange resins. Despite the catalytic activity of anionic-resins (i.e. resins containing quaternary ammonium, quaternary phosphonium or pyridinium groups) [4] so far they have no relevant industrial



(a) (b)

Fig. 1. (a) Schematic representation of the bidisperse pore structure of macroporous resin particle beads made from gel-type microspheres [14]; (b) mass transfer mechanisms in the resin pellet [13].