



Effect of macroreticular acidic ion-exchange resins on 2-methyl-1-butene and 2-methyl-2-butene mixture oligomerization

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ABSTRACT

A screening of macroreticular ion exchange resins has been carried out in order to select the most suitable catalysts for liquid-phase oligomerization of an isoamylene mixture. The reaction was performed at mild temperature (343 K) to promote the dimerization and trimerization, and at higher temperature (383 K) to evaluate side reactions like cracking and copolymerization. No compounds higher than trimers were significantly detected at studied conditions. By plotting product yields versus conversion at 343 K, it was showed no significant differences between all catalysts tested. However, at 383 K, the ion exchange resins which mainly work in the external zone were more selective to dimerization and less to cracking and trimerization products, which suggests that trimerization and cracking mainly took place inside the gel-phase of the macroreticular resins.

The most active catalysts were the oversulfonated resins with high cross-linking degree and high acid capacity. A heterogeneous Eley-Rideal kinetic model showed better fitting of dimerization rates than two pseudo-homogeneous models.

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1. Introduction

Environmental concerns associated with safe handling and disposal of corrosive mineral acids have encouraged the development of safer and non-waste producing alternatives for applications in catalysis. Ion exchange resins (IER) are extensively used in many industrial processes. They provide easier separations from the reactive and products by filtration allowing more flexibility than homogeneous catalysts to be loaded, regenerated and reused [1]. Most ion exchange resins are manufactured from spherical polymeric beads synthesized by the procedure of suspension copolymerization [2–7], using styrene (ST) as polymerizing monomer and divinylbenzene (DVB) as cross-linking agent. In the case of macroreticular IER, monomers are diluted with an inert organic liquid called porogen that introduces the mesopores and macropores during the copolymerization process [8]. The porosity is then controlled by the amount and type of porogen and cross-linkage [9–11]. The cross-linking degree determines the flexibility of the matrix, the higher the cross-linking degree is, the less flexibility for the polymer chains. In non polar reaction systems, the cross-linking degree becomes a determinant factor on the behaviour of the catalyst. Microporous ion exchange resins or macroreticular ion exchange resins with low cross-linking degrees remain collapsed in non polar mediums. As there is no liquid that

solvates the polymer matrix, the osmotic pressure is nil, and the elastic forces of the polymer chains constrain the resin matrix, giving a compact structure. Then, the polymer chains will be as close as atomic forces allow. This collapsed structure results in a more hindered accessibility of internal active sites [12]. Consequently, macroreticular resins with permanent meso-macropores are usually more useful than gel form resins for non polar reaction environments [13].

After the matrix formation, the ion-exchangers are obtained by the introduction of $\text{SO}_3^- \text{H}^+$ groups onto benzene rings of ST-DVB [14,15]. The sulfonation degree can be controlled by the time and temperature of the sulfonation reaction [16,17]. Depending on the sulfonation degree the resins can be conventionally sulfonated, oversulfonated and only sulfonated in outer layers of the resin. Conventional sulfonated resins have about one sulfonic group per styrene ring, statistically as para-substitution [18]. It means a maximum of about 5 meq g^{-1} [19]. The oversulfonated resins have a higher concentration of sulfonic groups because they have in some styrene rings more than one sulfonic group. The additional sulfonic groups are predominantly distributed close to the particle surface [20]. In addition to sulfonation it is possible to replace all the hydrogen atoms of the matrix to modify the resin properties. For instance, the chlorination upgrades the thermal stability and the acid strength [21].

The catalytic action of sulfonated resins is different in aqueous or non-aqueous medium. In water solution the catalytic reaction proceeds via hydrated proton named specific catalysis [22], being rather similar to that of homogeneous catalysis. The different

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