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Comparison of ion-exchange resin catalysts in the dimerisation of isobutene

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Abstract

Seven ion-exchange resin catalysts were compared in the dimerisation of isobutene with *tert*-butyl alcohol (TBA) as the selectivity enhancing component. Experiments were also carried out with sodium exchanged resins to study the order of the reaction and the effect of sodium components in the feed. The dimerisation of isobutene was confirmed to be a second-order reaction with respect to the amount of active sites. Ion-exchanged sodium was found to decrease the selectivity for di-isobutenes and thus behave differently than the polar components. The average acidities of the acid groups of the resins treated with various polar components and of the resins ion-exchanged with sodium were obtained by NMR measurements. The results suggested that the effect of TBA and of the ion-exchanged sodium on the acidity is similar. Their different behaviour in the dimerisation of isobutene can be explained by the participation of TBA in the chain scission and by the blocking of the sites by the ion-exchanged sodium. Experiments with the different catalysts showed that the surface sulphonated catalysts are the most active in the dimerisation of isobutene. Furthermore, good selectivities for di-isobutenes are obtained with the medium crosslinked resins (12–20 DVB%).

Keywords: Ion-exchange resins; Isobutene dimerisation; Acid capacity

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1. Introduction

Macroporous ion-exchange resins were invented in the 1960s [1]. These porous materials consist of, for example, polystyrene chains that have been linked with divinylbenzene (DVB). The chains may have SO_3^-groups and thus a negative charge, which is neutralised with positive labile and exchangeable ions such as H^+ [2]. These resins are called cation exchange resins and they are used as catalysts in the production of methyl *tert*-butyl ether (MTBE) and various other oxygenates and lately also in the dimerisation of isobutene (IB) [3].

Macroporous resins consist of gel-type microspheres that form a macroporous polymer structure [1]. The structure of the polymer resin is characterised by the content of the crosslinking component (such as DVB), which determines the surface area and the pore size distribution of the resin [4]. Furthermore, the degree of crosslinking determines the rigidity of the structure and the extent of swelling in the presence of a polar component. Resins with higher crosslinking do not swell as much as the resins with lower crosslinking.

Setínek [5] and Rodriguez and Setínek [6] observed that in liquid phase esterifications on macroporous ion-exchange resins the activity hardly changes as a function of the crosslinking. This was because while high crosslinking decreases the accessibility of the active sites within the resin matrix, the surface area increases and more of the sites are situated on the macropores. Gates et al. [7], on the other hand, observed that in the dehydration of *tert*-butyl alcohol the activity of the resins increases with crosslinking up to 20% DVB.

In non-polar conditions the sulphonic acid sites function as the active sites, but at high water (or alcohol) contents the reactions proceed on the less active solvated protons [8,9]. The sulphonic acid sites are situated not only on the easily accessible macropores, but also inside the gel-type

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Abbreviations: DIB, di-isobutenes (2,4,4-trimethyl pentenes); DVB, divinylbenzene; IB, isobutene (2-methyl propene); IP, isopentane (2-methyl butane); MTBE, methyl *tert*-butyl ether (2-methoxy-2-methyl propane); TAME, *tert*-amyl methyl ether (2-methoxy-2-methyl butane); TBA, *tert*-butyl alcohol (2-methyl-2-propanol); TETRAB, tetraisobutenes; TRIB, tri-isobutenes

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microspheres [10]. Dooley et al. [11] observed that in the reesterification of ethyl acetate with *n*-propanol the active sites inside the micropores are more active than the sites in the macropores. Similar observation was made by Ihm et al. [12] for isobutene hydration.

In the liquid phase esterification of isopropenyl acetate with ethanol it has been observed that the activities depend more on the acid site strength than on the concentration of the acid sites, while in other reactions, such as the etherification of isoamylenes to *tert*-amyl methyl ether (TAME), high concentration of acid sites is more important than the strength of the sites [13].

Impurities such as sodium components may deactivate the acid sites of ion-exchange resins. When the resins have been deactivated by sodium and ammonium hydroxide solutions [14] and with potassium and rubidium ions [7] the conversions have been independent of the type of the ions in the deactivation. Still, the degree of deactivation has affected the conversions but has had no effect on the selectivity [14]. When deactivation by Fe(III) and ammonium ions was compared in the MTBE synthesis [15], lower initial reaction rates were observed with ammonium than with Fe(III) deactivated catalysts. Panneman and Beenackers [16] further observed that the dependence of the activity on the acid capacity is different for different resins.

Uniform deactivation by neutralisation of active sites was observed by Setínek [17], who studied the reesterification of ethyl acetate by 1-propanol with both partially sulphonated and partially neutralised resins. He discovered that the initial rates were the same for all the partially sulphonated resins, but with the partially neutralised resins the initial rates increased with the acid concentration. He concluded that the partial neutralisation proceeds uniformly throughout the resin. In partial sulphonation, in contrast, sulphonic acid groups form a uniform layer and as the sulphonation degree increases the layer grows from the surface to the inner and more difficultly accessible parts of the polymer mass.

The dimerisation of isobutene on cation exchange resins produces 2,4,4-trimethyl pentenes that can be used as high octane gasoline components. Recent studies have shown that using a polar component together with the ion-exchange resin catalyst decreases the activity of the catalyst while the selectivity for di-isobutenes is increased [18]. *tert*-Butyl alcohol (TBA) has been found to be a good polar component as it does not form ethers with isobutene and small amounts are needed to reach good selectivity.

In the etherification of C_4 and C_5 alkenes with alcohols the acid capacity has been found to be the most important property of the resin [13,15] and the activity of the resin to increase with the acid capacity. In the isobutene dimerisation studies, Amberlyst 15 has often been used as catalyst [19,20], although hypersulphonated Amberlyst 35 has been found to be more active [3]. Amberlyst 15 has also been used in the trimerisation of isobutene [21].

The use of different ion-exchange resins in a dimerisation system was studied by Marchionna et al. [22]. They used methanol as the selectivity enhancing component and ion-exchange resins Amberlyst 15, 35, XN1010 and XE586 as catalysts. Isobutene conversion was the highest with the most acidic catalyst Amberlyst 35. The lowest conversion was obtained with the surface sulphonated Amberlyst XE586. This catalyst, however, showed the best selectivity for di-isobutenes.

Hauge et al. [23] compared Amberlyst 15 and Dowex 50 WX8 as well as several zeolites in the dimerisation of isobutene in the absence of a polar component. Amberlyst 15 gave fairly good stability compared to the other catalysts and also good activity. Dowex 50 WX8 showed hardly any activity at all because it is gel-type and needs to swell to allow good accessibility to the active sites.

O'Connor et al. [24] studied C_4 alkene (mainly 1-butene, 7.1 wt.% isobutene) oligomerisation on partially sulphonated ion-exchange resins and observed a non-linear dependence of the conversion on the acid capacity. The product distribution did not depend on the number of acid sites.

In the present study, various ion-exchange resin catalysts were compared in the dimerisation of isobutene with TBA as the selectivity enhancing component. Furthermore, catalyst samples were deactivated with sodium hydroxide solutions and tested in the dimerisation of isobutene to study the order of the reaction and the effect of sodium components in the feed. Experiments were carried out in a continuous stirred tank reactor (CSTR) and from the results the conversion of isobutene, selectivity for di-isobutenes and the di-isobutene formation rates were calculated and compared. The effect of TBA and the ion-exchanged sodium on the catalyst was further clarified by NMR measurements.

2. Experimental

2.1. Reactor

The reactor used in the dimerisation experiments was a CSTR (50 cm^3) that operated in the liquid phase and was stirred with a six-blade mechanical stirrer. The reactor included a mixing baffle and a metal gauze basket in which the catalyst was placed. Two feeding tanks (2 dm^3) were used, one tank containing isobutene as a liquid, and the other a mixture of the polar component (TBA) and the solvent [isopentane (IP)]. The flow through the reactor was achieved with a pressure difference as the pressure in the feeding tanks was 1.8 MPa and in the reactor 1.5 MPa. The tubes in which TBA flowed were heated to 306–308 K to keep TBA in the liquid state (mp 296–298 K). The reactor was heated with hot oil flowing through its jacket.

At the beginning of each experiment the mixed flow containing isobutene, isopentane and TBA was analysed by gas chromatography. After the flow had stabilised and the feed had been accurately analysed, the flow was fed to the reactor. The reaction at each temperature was continued until a steady state was reached. The temperature was then changed while the feed rate and compositions were kept the same.

2.2. Analytical methods in the reactor experiments

The flows to and from the reactor were analysed with an on-line Hewlett-Packard 5890 Series II gas chromatograph (GC). The GC was equipped with an HP-1 capillary column of length 60 m, film thickness 1.00 μm and diameter 0.25 mm. A flame