Trimerization of Isobutene over Solid Acid Catalysts under Wide Reaction Conditions[†]

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Oligomerization of isobutene has been investigated using a few solid acid catalysts in order to produce efficiently triisobutenes that are useful chemical feedstocks for heavy alkylates and neo-acids. Several reaction conditions such as space velocity and isobutene concentration are evaluated, and a few cation exchange resins with various acid capacities were compared in the reaction. High trimers selectivity and high conversion can be obtained over a catalyst containing high acid capacity at low space velocity and relatively low isobutene concentration. The stability of a catalyst for the reaction is high when the acid capacity of the catalyst is high (for example Amberlyst-35).

Key Words : Isobutene, Trimerization, Space velocity, Acid concentration, Cation exchange resin

Introduction

C[4] stream containing butenes is an important raw feedstock in the petrochemical industry which can be further upgraded. Recently, trimerization of light olefins has attracted considerable attention as a method for the production of fuel additives[1] and separating isoolefins from other olefins.[2] Moreover, triisobutenes, for example, are considered to be highly useful for the synthesis of specialty chemicals including neo-acids.[2] Heavy alkylates containing C[9] or higher carbons are used as additives for kerosene and jet fuel[3] and as premium solvents (odorless solvents due to absence of aromatics). Heavy alkylates can be produced by the hydrogenation of olefin oligomers such as triisobutenes.

The blending of MTBE (methyl-*tert*-butyl ether) in gasoline has been banned in California[4] since 2004 because it can give rise to environmental pollution due to the dissolution of MTBE in underground water. The surplus of isobutene is, therefore, expected because it is one of the main raw materials for the synthesis of MTBE.

Hence, the trimerization is a very promising reaction not only for the utilization and separation of isobutene but also for the production of isobutene trimers and heavy alkylates (after hydrogenation of oligomers). Nevertheless, the trimerization of isobutene has not received adequate attention in comparison with the dimerization of olefins.[5-10] Several solid acid catalysts such as sulfated titania,[1,11,12] cation exchange resins (CERs),[2,13] heteropoly acid[14] and zirconia[15] have been suggested for the trimerization. Very recently, ZSM-22 has been used to produce mono-branched trimers of propylene due to shape selective catalysis because of the uniform tubular pore (10-memebered ring) of ZSM-22.[16]

Very recently, we have reported the isobutene trimerization over a few solid acid catalysts such as zeolites beta (BEA)[17] and ferrierite (FER)[18] and cation exchange resins (Amberlyst-35 and Amberlyst-15),[13] and the effect of Lewis acid sites and the porosity was discussed. In this article, we describe the isobutene oligomerization reaction over a few catalysts in more wide reaction conditions in order to produce efficiently isobutene trimers. Especially, the effects of isobutene concentration, space velocity and acid site concentration on the trimerization are described in detail.

Experimental

Trimerization of isobutene (99%, Rigas Korea) was carried out in the liquid-phase using a fixed bed continuous flow reactor (OD 3/8 inch, stainless steel 316) equipped with a back pressure regulator (Tescom). The reaction temperature and pressure used for the reaction were 70 °C and 15 bar, respectively. The reactor temperature was maintained constant by a water jacket in which water, kept at constant temperature, was flowing continuously with the help of a circulator. The reactant (isobutene) and a diluent (*n*-butane, 99%, Rigas Korea) were continuously fed by using liquid mass flow controllers (Bronkhorst HI-TEC). The space velocity of isobutene, WHSV (weight-hourly space velocity, g-isobutene/g-dried catalyst/h) was varied between 2.5-50 h^{-1} by controlling the flow rates of isobutene and n-butane. The feeding rates of the isobutene and the diluent were reported in wt%.

Several commercial solid catalysts including cation exchange resins and a zeolite ferrierite (Zeolyst-914C, ammonium form, SiO_2/Al_2O_3 = 20, surface area = 400 m^2/g) were used in this study. Cation exchange resins, macroporous and containing sulphonic acids, were purchased from Rohm and Haas. The acid capacities of the Amberlyst-15, Amberlyst-35 and Amberlyst-DT are 4.7, 5.2 and 3.1 mequiv. H$^+$/g,[19]

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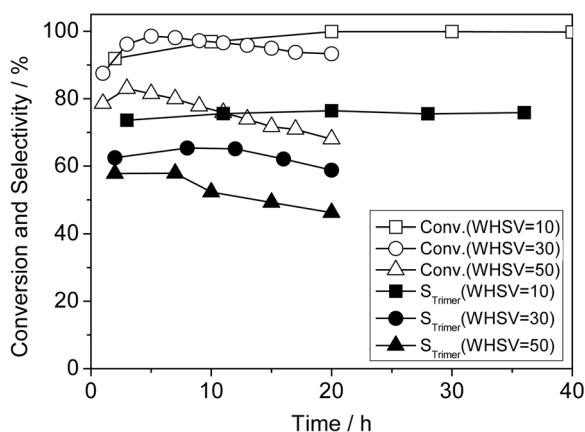
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respectively, and the catalysts were used without further purification. The extra water (~50 wt%) that remained in the cation exchange resins was not removed or replaced because water-containing cation exchange resins does not show bad performance after the water is replaced with reactants.[13] Catalysts (0.2-0.5 g on dry base, together with five times of quartz beads for dilution) were loaded in the reactor as beads (cation exchange resins) or pellets (zeolite).

The ferrierite catalyst was calcined at 550 °C for 8 h in a muffle furnace to convert an ammonium form into a proton form. Prior to the commencement of the reaction, the zeolites loaded in the reactor were dehydrated at 300 °C for 10 h under the flow of nitrogen.
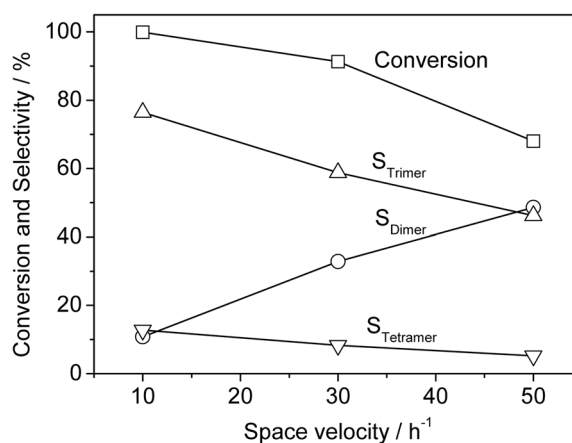
The conversion of isobutene was determined by analyzing frequently the composition of the off-gas stream by using a GC equipped with a TCD and an alumina column (J&W Scientific, 30 m × 0.53 mm). The conversion was cross-checked by measuring the total flow rates of isobutene and the diluent, after condensing liquid products, with a mass flow meter (Brooks, 5850 E). Liquid products were analyzed by a FID GC containing a PONA column (HP, 50 m × 0.20 mm). In this study, the selectivity for dimer, trimers and tetramers is described in wt%. Unless otherwise specified, the reaction temperature, pressure and catalyst were 70 °C, 15 bar and Amberlyst-35, respectively.

Results and Discussion

The productivity of a reaction is greatly depends on the space velocity. Figure 1 compares the isobutene conversion and trimers selectivity with the isobutene WHSV. Figure 2 illustrates the conversion and selectivities with the isobutene WHSV at the time on stream of 20 h. As the WHSV increases, the conversion and trimers selectivity decrease even though the throughput may be high. Moreover, the stability of catalytic performance is low with higher WHSV (Figure 1). The low stability and trimers selectivity at high WHSV are more noticeable for the reaction over a zeolite such as ferrierite (Figure 3) probably because the pore size of FER is much smaller than that of a cation exchange resin,
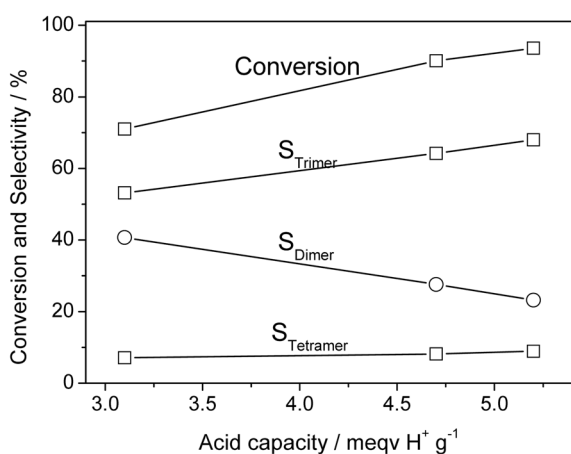

Figure 2. Effect of space velocity (isobutene WHSV) on the conversion and selectivities (catalyst: Amberlyst-35, time on stream: 20 h).
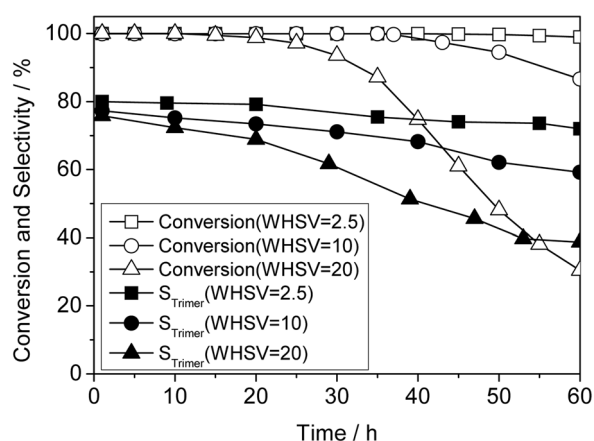

Figure 3. Effect of space velocity (isobutene WHSV) on the conversion and selectivities (catalyst: FER zeolite).

Amberlyst-35. The low trimers selectivity at high WHSV can be related to the low isobutene conversion because the selectivity increases with the isobutene conversion.[13,17,18] Therefore, optimum isobutene concentration should be chosen for stable operation, trimers selectivity and throughput. The low conversion at the beginning of the reaction (Figure 1), especially for low WHSV, is due to the necessary activation of Amberlyst-35 or the replacement of entrapped solvent (water) with reagent such as isobutene and diluent.[13] High WHSV is helpful to replace water solvent for stable operation, especially at the beginning of the reaction.

Figure 4 depicts the conversion and selectivities with acid capacity of cation exchange resins (Amberlyst-35, Amberlyst-15 and Amberlyst-DT)[19] at the reaction time of 3 h. As the acid capacity increases, the conversion, trimers selectivity and tetramers selectivity increase, whereas, the dimer selectivity decreases instead, showing the efficiency of acid catalysts with high concentration of acid sites. A cation exchange resin with even high acid capacity will be interesting for the trimerization reaction even though the physical properties of the cation exchange resin may be a problem. The high capacity is not so helpful for the case of a beta


Figure 1. Effect of space velocity (isobutene WHSV) on the conversion and selectivities (catalyst: Amberlyst-35).

Figure 4. Effect of acid capacity of cation exchange resins on the conversion and selectivities (time on stream: 3 h, space velocity: 50 h^{-1}).
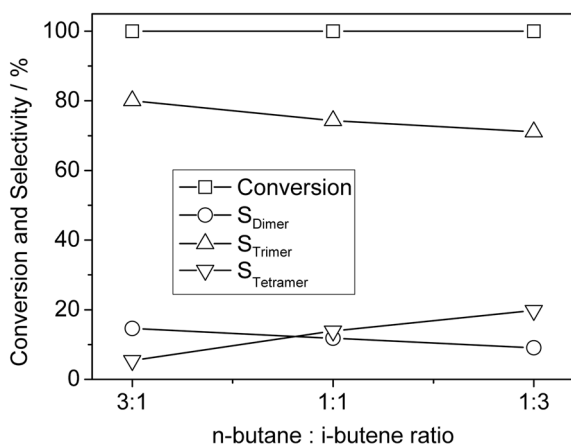
Figure 5. Effect of isobutene concentration on the conversion and selectivities (catalyst: Amberlyst-35, time on stream: 20 h).

zeolite which needs suitable Lewis acid/Bronsted acid ratios.[17] This difference in the performance of trimerization in the reactions over cation exchange resins and zeolites should be studied in more detail.

Figure 5 shows the reaction results over Amberlyst-35 with the reactant compositions (isobutene/*n*-butane ratio). The trimers selectivity increases with the decrease of iso-butene concentration and reaches the selectivity of about 80% from the reactants containing low isobutene concen-tration of 25%. The low trimers concentration at high isobutene is mainly due to the high selectivity for tetramers. The oligomerization of isobutene can be regarded as a consecutive reaction from monomer to dimers, from dimers to trimers, and trimers to tetramers, etc.[2,13] Therefore, the oligomers with high molecular weight can be obtained easily from the feed containing high concentration of isobutene. However, the concentration of tetramers or pentamers does not increase steadily with the isobutene concentration because of steric hindrance[13,18] by the crowded alkyl groups since the reaction occurrs in the inside of the porous cata-lysts. Moreover, the trimers selectivity cannot be increased steadily at low isobutene concentration because the dimer
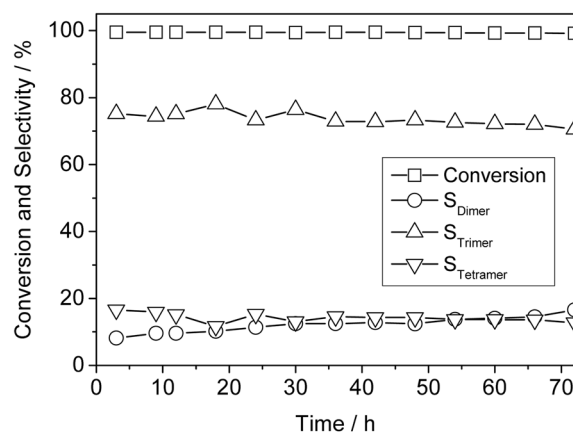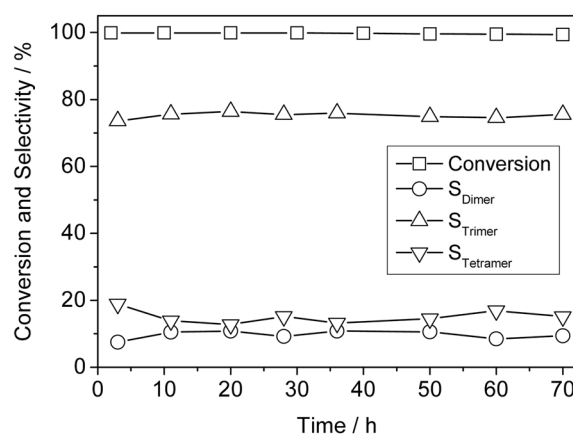
Figure 6. Conversion and selectivities over two cation exchange resins (space velocity: 10 h^{-1}): The upper and lower figures show the results over Amberlyst-35 and Amberlyst-15, respectively (space velocity: 10 h^{-1}).

can be the main product of isobutene oligomerization when the isobutene concentration is low or especially when commercial C$_4$ streams are utilized for oligomerization.[20]

Long term stability is very important to implement a reaction in a commercial plant, especially for large scale production. Figure 6 illustrates the typical performances over two cation exchange resins (Amberlyst-15 and Amber-lyst-35) with relatively high acid capacities. Both catalysts show stable performances for the reaction time up to 70 h. However, the trimers selectivity is slightly higher over Amberlyst-35 than over Amberlyst-15, especially at the later stage of reaction, showing the importance of the high acid capacity for the stable operation. This might be related with the deactivation of an acid site with the progress of the reaction and concomitant deactivation of the catalyst. On the contrary, the selectivity for dimers is relatively high for the catalyst with low acid capacity (Amberlyst-15 in this study). A catalyst may be resistant to deactivation if it has high concentration of acid sites, as for the case of Amberlyst-35 in this study.

Conclusion

The oligomerization of isobutene has been investigated

under wide reaction conditions over several cation exchange resins and a zeolite in order to find efficient conditions for the production of triisobutenes. High trimers selectivity can be obtained from reactant mixture with low isobutene concentration at low WHSV with catalysts containing high acid capacity. However, the time needed for the activation of a catalyst is long in the case of low WHSV because of the necessary replacement of the exisiting water solvent. A cation exchange resin with high acid capacity shows stable performace for the isobutene trimerization.

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