

Trimerization of isobutene over cation exchange resins: Effect of physical properties of the resins and reaction conditions

Ji Woong Yoon^a, Jong-San Chang^{a,*}, Hee-Du Lee^b, Tae-Jin Kim^b, Sung Hwa Jung^{a,**}

^a Research Center for NanoCatalysts, Korea Research Institute of Chemical Technology, P.O. Box, 107, Yuseong, Daejeon 305-600, Republic of Korea

^b R&D Center, SK Corporation, 140-1, Wonchon-Dong, Yuseong, Daejeon 305-712, Republic of Korea

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Abstract

Oligomerization of isobutene has been investigated using several cation exchange resins in order to produce triisobutenes that are useful feedstock for heavy alkylates and neo-acids. Trimers selectivity increases with increasing isobutene conversion. High isobutene conversion is obtained at high temperature and low space velocity by using macroporous cation exchange resins that have high concentration of sulfonic acid groups. Under selected conditions (viz., isobutene WHSV: 10 h⁻¹; temperature: 70 °C; catalyst: Amberlyst-35), the isobutene is quantitatively oligomerized with higher than or equal to 70% selectivity for trimers. The wet resin catalysts containing water or ethanol are very stable for the oligomerization up to about 70 h contrary to the gradual decrease in the conversion with dehydrated catalysts.

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1. Introduction

Recently, trimerization of light olefins has attracted considerable attention as a method for the production of fuel additives [1] and separation of isoolefins from other olefins [2]. Moreover, triisobutenes, for example, are considered to be highly useful for the synthesis of special chemicals including neo-acids [2]. Heavy alkylates containing C₉ or higher carbons are usually by-produced in an alkylation process (reaction between isobutene and butane) in the presence of concentrated sulfuric acid or hydrogen fluoride that is used as a liquid acid catalyst [3,4]. The demand for heavy alkylates increases sharply due to their uses as prime solvents and additives to kerosene and jet fuels. However, the production of heavy alkylates by alkylation is limited because most of the products in the alkylation process are C₈ isomers that are used as a blending stock for gasoline [3–5]. Moreover, the present alkylation process suffers from inherent drawbacks such as corrosion, toxicity, and environmental prob-

lems. The replacement of the liquid acids with a solid acid does not seem to be so promising or economics should be improved for commercialization even though there have been numerous studies [3,4,6]. Additionally, due to the increase in the capacity of ethane cracking unit in the production of ethylene [7], the relative contribution of production of heavy alkylates by the alkylation process will be decreased gradually.

The blending of MTBE (methyl *tert*-butyl ether) in gasoline has been banned in California [8] since 2004 due to the dissolution of MTBE in underground water thus causing its contamination. The surplus of isobutene is therefore expected because it is one of the main raw materials for the synthesis of MTBE.

Hence, the oligomerization of isobutene, especially trimerization, is a very promising reaction not only for the utilization and separation of isobutene but also for the production of heavy alkylates (after hydrogenation of oligomers). However, the trimerization of isobutene has not been studied widely even though there are many studies on the dimerization of olefins [10–15]. Several solid acids including cation exchange resins (CERs) [2], sulfated titania [1,16,17], Al-TS-1 zeolite [18], heteropoly acid [19], and zirconia [20] have been suggested as catalysts for the trimerization. Very recently, ZSM-22 has been used to produce mono-branched trimers of propene due

* Corresponding author.

** Corresponding author. Tel: +82 42 860 7674; fax: +82 42 860 7676.

E-mail addresses: jschang@kriict.re.kr (J.-S. Chang),
sung@kriict.re.kr (S.H. Jung).

Table 1
Analytic conditions for GC

Analysis target (detector)	Column	Detector temperature (°C)	Injector temperature (°C)	Column temperature program				
				Initial temperature (°C)	Initial time (min)	Ramping rate (°C/min)	Final temperature (°C)	Final time (min)
Off gas ^a (TCD)	Alumina	200	200	90			90	
Liquid product ^b (FID)	PONA	250	250	40	15	10 20	Step 1: 130 Step 2: 220	26 10

^a To analyze the isobutene and diluent (*n*-butane). The column temperature was constant.

^b To analyze isobutene, dimers, trimers and tetramers of isobutene.

to shape selective catalysis because of the uniform tubular pore (10-membered ring) of ZSM-22 [21].

CERs have been widely utilized as an acid catalyst for many reactions [13,22–24] such as etherification, oligomerization, hydration, hydrolysis and alkylation, etc. A commercial CER, Amberlyst-15, has been studied as a catalyst for trimerization [2] and dimerization [15] of isobutene. Several CERs have also been compared for the dimerization reaction [12,25]. However, detailed studies to understand the effect of porosity, acid capacities, and acid strength on the trimerization are not reported yet. Moreover, effect of the process parameters such as conversion, temperature and space velocity on the selectivity has not been analyzed in detail.

In this study, the effect of porosity, acid concentration, acid strength, temperature, space velocity and conversion on isobutene trimerization is studied in order to find suitable catalysts and process conditions for isobutene trimerization.

2. Experimental

Trimerization of isobutene (99%, Rigas, Korea) was carried out in the liquid phase using a fixed bed continuous flow reactor (OD 3/8 in., stainless steel 316) equipped with a back pressure regulator (Tescom). The reaction temperature and pressure used for the reaction were 30–110 °C and 15 bar, respectively. The reactor temperature was kept constant by a water jacket in which water, kept at a constant temperature, was flowing continuously by 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 catalyst/h), was varied between 10 and 100 h⁻¹ by controlling the flow rates of isobutene and *n*-butane. The feeding rates of the isobutene and the diluent were equal (50/50 wt.%). Otherwise specified, the temperature and space velocity were 70 °C and 50 h⁻¹, respectively.

The conversion of isobutene was determined by analyzing periodically 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 rate of isobutene and the diluent, after condensing liquid products, with a mass flow meter (Brooks, 5850 E). Liquid products were analyzed by an FID GC containing a PONA column (HP, 50 m × 0.20 mm). The detailed GC analytical conditions are summarized in Table 1. A typical chro-

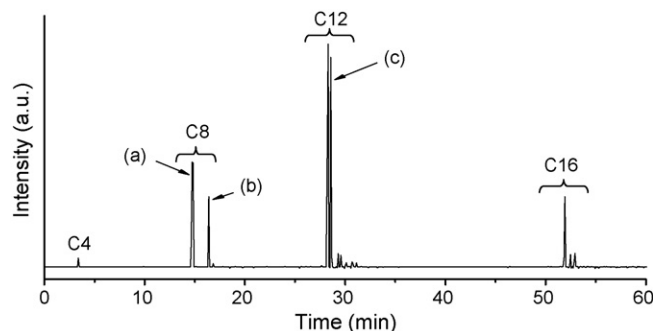


Fig. 1. Typical GC chromatogram of a liquid product. Some of the identified products are shown: (a) 2,4,4-trimethyl-1-pentene, (b) 2,4,4-trimethyl-2-pentene and (c) 2,2,4,6,6-pentamethyl-3-heptene.

matogram of a liquid product is shown in Fig. 1. The assignment of each peak of the chromatogram was done by using authentic samples (2-methyl-1-undecene, 1-dodecenen, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2,2,4-trimethyl pentane, All from Aldrich) and a GC/MS (HP-5890A GC, Jeol JMS-DX303 MS).

Several commercial solid catalysts including CERs and a zeolite mordenite (Zeocat, ammonium form, SiO₂/Al₂O₃ = 25) that were used in this study are summarized in Table 2. The catalysts were used without further purification. The extra water (~50 wt.%) that remained in the CERs was exchanged with ethanol (residual content: ~40 wt.%) or removed by drying at 105 °C in a vacuum oven for some cases. 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 (CERs) or pellets (zeolite). The mordenite was calcined at 550 °C for 8 h in a muffle furnace to convert the ammonium form to a proton form. Prior to the reaction, the zeolite loaded in the reactor was dehydrated under the flow of nitrogen at 300 °C for 10 h.

3. Results

Fig. 2 shows the general trends of isobutene conversion and selectivities over Amberlyst-35, exchanged with ethanol, as a function of reaction temperature and space velocity. The conversion and trimers selectivity increase with increasing temperature and decreasing space velocity. The dimers selectivity decreases accordingly. The tetramers selectivity changes with process conditions in a similar manner to the trimers selectivity; however, the dependence on process parameters is relatively

Table 2
Specification of catalysts used in this study and oligomerization results

Category	Name	Maker ^a	Functional group	Acid capacity (mequiv. H ⁺ /g) ^b	Pore type ^c	Conversion (%)	S _{trimer} (wt.%)
CERs ^d	Amberlyst-35	R-H	–SO ₃ H	5.2	Macroporous	91	66
	Amberlyst-15	R-H	–SO ₃ H	4.7	Macroporous	90	64
	Amberlyst-DT	R-H	–SO ₃ H	3.1	Macroporous	71	50
	Amberlyst-31	R-H	–SO ₃ H	4.8	Gel	<5	36
	WK-40	Diaion	–COOH	3.7	Macroporous	<1	NA ^e
Zeolite ^f	Mordenite	Zeocat	AlOH	See below ^g	Microporous	70	16

^a R-H: Rohm and Haas.

^b Obtained from <http://www.rhomanhaas.com/ionexchange/IP/sac.htm> and http://www.chemical.samyang.com/index_chemical.asp.

^c Macroporous or gel type for cation exchange resins.

^d Reaction conditions: temperature 70 °C; isobutene WHSV 50 h⁻¹; time-on-stream 10 h.

^e NA: selectivity was not analyzed because the product was very little.

^f Reaction conditions: temperature 70 °C; isobutene WHSV 10 h⁻¹; time-on-stream 10 h.

^g The SiO₂/Al₂O₃ ratio of the mordenite was 25.

small. Several CERs such as Amberlyst-15 and Amberlyst-DT show dependence on the temperature and space velocity similar to Amberlyst-35.

Fig. 3 presents the isobutene oligomerization results over various CERs and a zeolite, mordenite. All cation exchange resin catalysts illustrated in Fig. 3 show stable conversions after 3 h due to activation or replacement of the solvent, ethanol, with reactants during 3 h. The CER catalysts containing residual water require similar induction periods. The conversion of isobutene and trimers selectivity decrease in the order of Amberlyst-35 ≥ Amberlyst-15 > Amberlyst-DT. This dependence correlates well with the acid capacities (Table 2) like the isobutene dimerization where the high conversion of isobutene was obtained with CERs containing high concentration of acid sites [12,15,25]. The performance over mordenite is very poor even at low isobutene WHSV (Fig. 3d) as previously reported [9]. The conversion and trimers selectivity over mordenite decrease very sharply with increasing reaction time probably due to micropore blocking arising from deposition of cokes or high molecular weight oligomers probably formed over strong acid sites of a zeolite [24]. The conversion over mordenite is high at the very beginning of the reaction because isobutene WHSV was low and the mordenite was fully dehydrated by a pretreatment at 300 °C under the nitrogen flow.

The summarized results after 5 and 10 h of reaction using various CERs are compared in Fig. 4 and Table 2, respectively. Contrary to the results with Amberlyst-35, Amberlyst-15 and Amberlyst-DT catalysts, the conversion and trimers selectivity over CERs such as WK-40 (Diaion) and Amberlyst-31 are very low, and the dimers selectivity is very high. The WK-40 contains weak acid sites of carboxylic acid (–COOH) rather than sulfonic acid (–SO₃H). On the other hand, the pore structure of Amberlyst-31 is a gel type rather than a macroporous one [22]. Compared with gel type CERs, macroporous materials contain wide pore structure allowing free diffusion of molecules and preventing pore-blocking due to cokes and larger molecules.

The oligomerization reactions were also conducted over dried or wet (containing water) CERs to evaluate the influence of pretreatment conditions on the trimerization. As shown in Fig. 5, the conversion over dried Amberlyst-35 decreases gradually with increasing reaction time. Amberlyst-15 is very similar in the conversion tendency to Amberlyst-35. However, like the change of catalytic activity observed in the mordenite, the activity is found to be high from the very beginning of the reaction because it is not necessary to replace water or ethanol with feeds such as isobutene and *n*-butane. The conversion of isobutene over CERs containing water increases during about 3 h and then remains constant until 12 h just like the reaction over ethanol-replaced CERs.

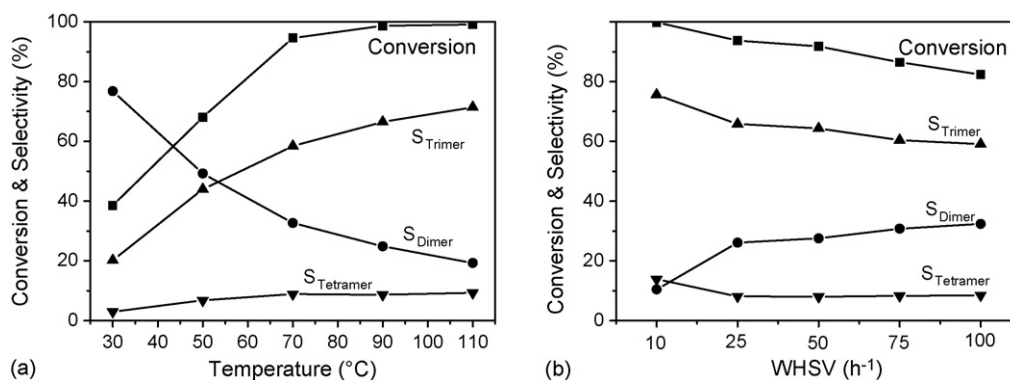


Fig. 2. Oligomerization of isobutene over Amberlyst-35: (a) effect of temperature at isobutene WHSV of 50 h⁻¹ and (b) effect of space velocity, isobutene WHSV, at reaction temperature of 70 °C.

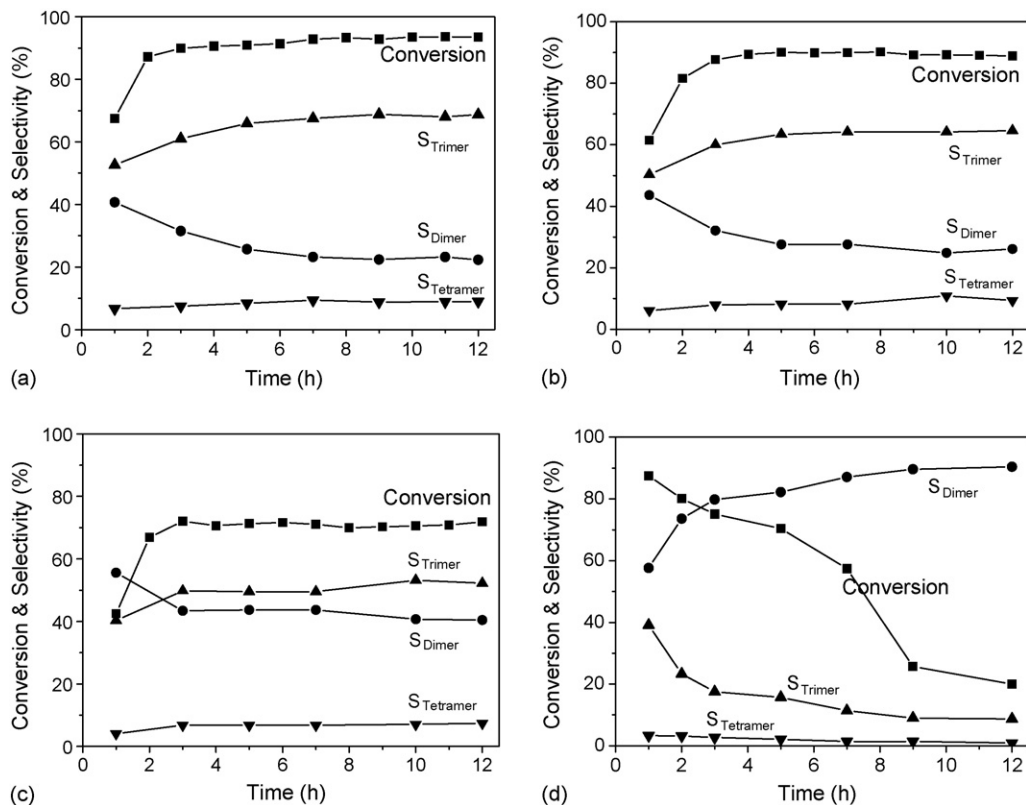


Fig. 3. Oligomerization of isobutene over various solid acid catalysts: (a) Amberlyst-35, (b) Amberlyst-15, (c) Amberlyst-DT and (d) dehydrated mordenite. Reaction conditions: temperature 70 °C; isobutene WHSV 50 h⁻¹ (isobutene WHSV of (d) is 10 h⁻¹).

Since the oligomerization of isobutene can be considered as a consecutive reaction (from monomer to dimers, dimers to trimers, trimers to tetramers, etc.) occurring via carbenium ions and neither tetramers nor pentamers form appreciably in the isobutene oligomerization [2], the trimers concentration is increased at high isobutene conversion. Moreover, because the tetramers selectivity does not change appreciably under the conditions investigated in this study (Figs. 2, 3 and 5), the high

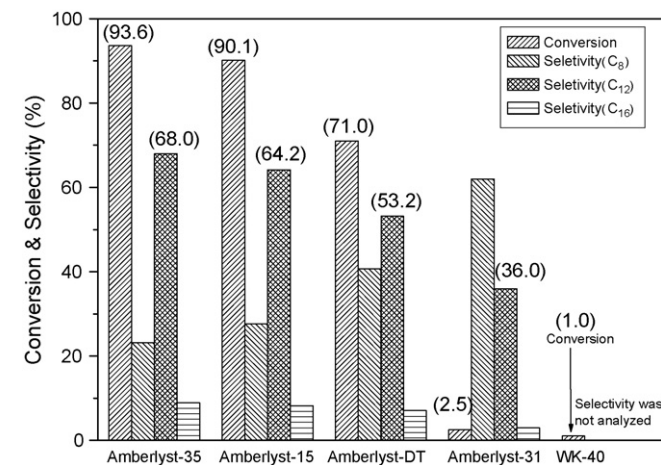


Fig. 4. Comparison of isobutene oligomerization over various CERs. Reaction conditions are temperature: 70 °C; WHSV: 50 h⁻¹; time-on-stream: 5 h; diluent: *n*-butane. The figures in parentheses are the conversion or trimers selectivity in percentage.

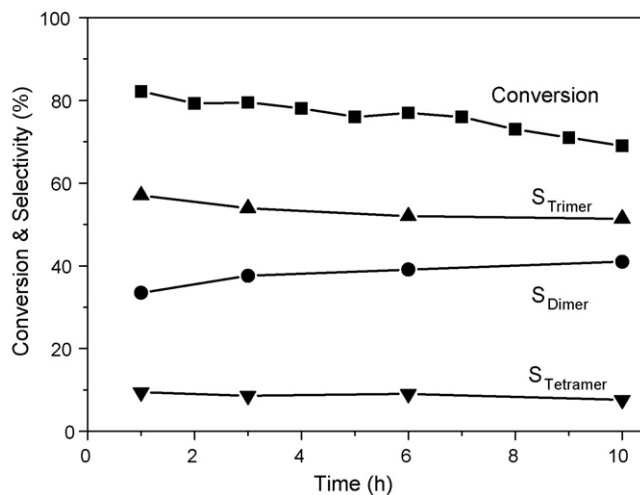


Fig. 5. Oligomerization of isobutene over dried Amberlyst-35.

trimers selectivity is obtained at high conversion. The trimers selectivity is plotted as a function of conversion over Amberlyst-35, Amberlyst-15 and Amberlyst-DT, and, as shown in Fig. 6, the trimers selectivity really increases with the conversion irrespective of the catalyst and temperature, etc.

4. Discussion

The oligomerization of isobutene has been carried out in wide reaction conditions including temperature, space velocity,

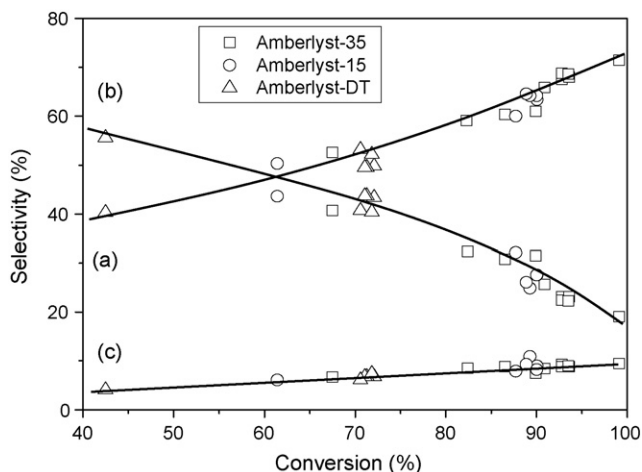


Fig. 6. Dependence of selectivities on the isobutene conversion: (a) trimers selectivity, (b) dimers selectivity and (c) tetramers selectivity.

type of catalysts, catalyst pretreatment and reaction time, etc. As shown in Fig. 2, the conversion and trimers selectivity are high at high temperature and low space velocity. Moreover, the trimers selectivity is also high when at high isobutene conversion (Fig. 6) because the oligomerization is a successive reaction via carbenium ions [2]. Low selectivity of tetramers or pentamers even at high conversion might be due to the steric hindrance by the crowded alkyl groups. Hence, it is very important to increase the conversion in achieving the high trimers selectivity. The high conversion can be obtained by not only high temperature or low space velocity but also by using CERs having high concentration of sulfonic acids ($-\text{SO}_3\text{H}$). As summarized in Table 2 and Fig. 4, the macroporous resins rather than gel type resins are suitable for the isobutene oligomerization, in a quite similar manner to the beneficial roles of mesoporosity of MCM-41 and MTS-type porous materials in the hex-1-ene or 1-butene oligomerization [14,26]. In contrast, microporous materials such as zeolite mordenite are not suitable due to rapid deactivation as previously reported [9]. The conversion of oligomerization over CERs containing weak acid sites ($-\text{COOH}$) is negligible (Table 2 and Fig. 4), suggesting the importance of acid strength of resin catalysts in the reaction. The conversion increases monotonously (Amberlyst-35 \geq Amberlyst-15 $>$ Amberlyst-DT) with the increase in the acid capacities of the CERs (Table 2 and Fig. 4) just like the dimerization of isobutene [12,15,25]. The dried resin catalysts are not suitable because of the rapid deactivation probably due to the shrinkage or partial collapse of the pore structure on drying. The CERs containing water show very similar performance to the ethanol-replaced catalysts even though alcohol (such as methanol)-washed resins are used commercially in an industrial process such as MTBE production unit [27].

Based on the above results, selective trimerization (trimers selectivity >70 wt.%) can be accomplished by using Amberlyst-35 catalyst at low space velocity of 10 h^{-1} . The conversion is nearly quantitative and there is a negligible decrease in the conversion and trimers selectivity within 70 h (Fig. 7). Therefore, it is expected that trimerization of isobutene may be commer-

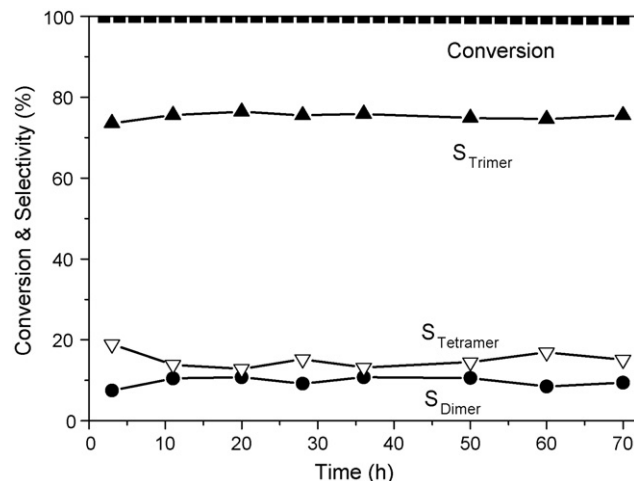


Fig. 7. Oligomerization of isobutene over Amberlyst-35 in a selected condition (WHSV: 10 h^{-1} ; temperature: 70°C). The conversion is nearly quantitative and the trimers selectivity is higher than 70 wt. %.

cialized by using the CERs such as Amberlyst-35. Moreover, heavy alkylates or neo-acids can be produced efficiently from isobutene, the feedstock that will be surplus in near future, through trimerization by using CERs.

5. Conclusion

The oligomerization of isobutene has been investigated under wide reaction conditions over cation exchange resins to find efficient catalysts and optimum process conditions for the triisobutenes production. The trimers selectivity increases with increasing isobutene conversion because the oligomerization is a consecutive reaction. Resin catalysts with several properties such as macroporosity, strong acidity (from sulfonic acid group) and high acid capacity are necessary for the efficient conversion of isobutene to triisobutene. The conversion of isobutene is nearly quantitative and the trimers selectivity is higher than 70 wt.% for selected process conditions (temperature: 70°C , isobutene WHSV: 10 h^{-1}) over Amberlyst-35 as a catalyst. There is only a negligible decrease in conversion and selectivity within 70 h of time on stream. Dried resin catalysts show poor performance with rapid deactivation even though the activity at the beginning of the reaction is high. The cation exchange resins containing water show similar catalytic performance (viz., rate of deactivation, conversion and selectivity) to those of ethanol-exchanged resins.

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