

Etherification of glycerol by isobutylene. Effects of the density of acidic sites in ion-exchange resin on the distribution of products

Hee Jong Lee*, Doyoung Seung*, Igor N. Filimonov*[†], and Hwayong Kim**[†]

*GS-Caltex Corporation, R&D Center, Daejeon 305-380, Korea

**School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Korea

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Abstract—Etherification of glycerol by isobutylene was performed using ion-exchange resin Amberlyst 15, partially neutralized Amberlyst 15 as heterogeneous catalyst, and *p*-toluenesulfonic acid as a homogeneous catalyst. Amberlyst 15 exhibited strong internal diffusion limitations for the initial composition of reaction mixture. Diffusion limitations decrease in the course of reaction due to the accumulation of mono-ether having excellent solubilizing properties. Oligomerized isobutylene is a dominant by-product for high isobutylene-to-glycerol ratio and long contact time in the case of Amberlyst 15. Density reduction of acidic protons in Amberlyst 15 by partial ion exchange with sodium ions leads to considerable reduction of isobutylene affinity to Amberlyst 15, and as a result, it reduced losses of isobutylene. This partial neutralization leads to lower space-time yields of target products, but enhances selectivity to higher ethers with maintaining conversion of glycerol over 95%.

Key words: Glycerol, Etherification, Density of Acidic Sites, Amberlyst 15, Isobutylene

INTRODUCTION

Biodiesel has recently attracted considerable attention as an alternative transportation fuel in the view of modern market and environmental trends in fossil energy consumption. If biodiesel is to be used in motor fuels, then production of biodiesel should significantly increase. Glycerol is a by-product of the transesterification of triglycerides during production of biodiesel and the amount of liberated glycerol is about 10% of produced biodiesel. At present, the management of crude glycerol produced via biodiesel route is a problem in terms of economics. It is estimated that supplies of the glycerol for only the EU is up to one million tons per year in 2010 [1]. Therefore, development of glycerol-based chemical processes is important and a number of attempts have been made to transform glycerol into more valuable products such as glycerol tertiary butyl ethers, propylene glycol, and glycerol carbonate [1-6].

Etherification of glycerol by isobutylene to di-*t*-butyl ether and tri-*t*-butyl ether (termed as higher ethers of glycerol) may be a method for the production of “clean” fuel additives both for diesel and internal combustion engines. Etherification of glycerol in acidic media produces a mixture of mono-*t*-butyl ether, di-*t*-butyl ether, and tri-*t*-

butyl ether (Fig. 1). Taking into account possible isomers, five individual ethers may be formed. Good solubility of higher ethers in diesel and gasoline as well as oxygen content of glycerol ethers makes these ethers attractive candidates for the fuel additives as oxygenates.

It is known that acidity of a catalyst is a key factor for the etherification of glycerol by isobutylene and *tert*-butanol. Thus acid catalysts such as sulfuric acid, *p*-toluenesulfonic acid, acidic ion exchange resins, wide pore zeolites, and acid-functionalized mesostructured silicas have been used in the etherification of glycerol. Among acid catalysts readily affordable *p*-toluenesulfonic acid as homogeneous catalyst and ion exchange resin as heterogeneous catalyst show good activity [1,7-11].

Typical parameters for this process such as temperature, isobutylene-to-glycerol ratio, and addition of co-solvents have been studied and a number of catalysts have been characterized [1,8-11]. It appears that effects of the acid site density in Amberlyst material have not been evaluated yet for this process. In our study, Amberlyst 15, a sulfonated divinylbenzene resin, was used for the liquid phase etherification of glycerol by isobutylene. Amberlyst 15 is advantageous assuming its availability, ease of separation and purification steps, but it has lower selectivity compared to *p*-toluenesulfonic acid

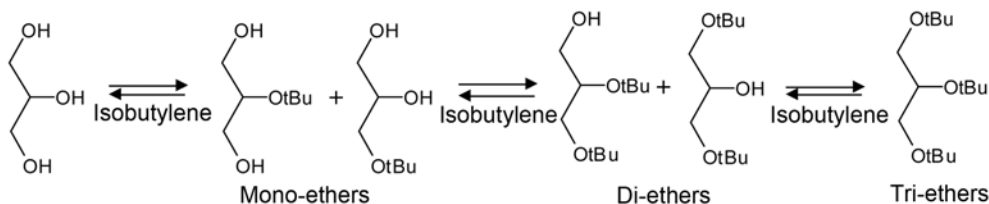


Fig. 1. Reaction scheme of glycerol etherification by isobutylene.

[†]To whom correspondence should be addressed.

E-mail: C16635@gscaltex.co.kr, hwayongk@snu.ac.kr

due to the formation of diisobutylenes (mixture of 2,4,4-trimethyl-1- and 2,4,4-trimethyl-2-pentenenes). Simple change of the specific acid content of catalysts was performed via ion exchange of H^+ to Na^+ . Though the loss of acidity results in the loss of space-time yields, nevertheless decrease of the density of acidic sites may be advantageous at high isobutylene-to-glycerol ratio and long contact times.

Certain important ideas related to the general mechanism and specific features of alcohol etherification using isobutylene catalyzed by acidic ion exchange resins may be traced in the numerous works on MTBE synthesis. Mechanistic aspects of this reaction may be found in [12]. Dimerization of isobutylene in the presence of alcohol was studied by Honkela et al. [13]. Effects of the density of acidic sites in ion-exchange resins were studied by Panneman et al. [14] in MTBE synthesis and by Holub et al. [15] in transesterification reaction.

EXPERIMENTAL

Glycerol (99%), isobutylene (99%), *p*-toluenesulfonic acid, and Amberlyst 15 beads were purchased from Sigma-Aldrich. Partially neutralized Amberlyst 15 was prepared via Na^+ ion exchange using the following procedure. Amberlyst 15 was washed with deionized water, methanol and dried at 70 °C for 12 h. The amount of acidic protons was evaluated by potentiometric titration with sodium hydroxide solution. Amberlyst 15 was gently stirred in 0.2-0.5 mol/L sodium chloride solution for 12 h. Partially neutralized Amberlyst 15 was washed with deionized water and dried at 70 °C for 12 h. Additional drying was conducted under vacuum at 60 °C for 12 h. (A more exact way to achieve the desired degree of ion exchange is by direct neutralization with diluted NaOH solution. Both methods give comparable catalysts in terms of catalytic activity.) The acidity of ion-exchanged Amberlyst 15 was checked again by potentiometric titration with sodium hydroxide solution (Titrimo 721 NET, Metrohm AG). Ion exchanged Amberlyst 15 was abbreviated as XNa-Amb, where X means degree of ion exchange. 25Na-Amb, 51Na-Amb, and 77Na-Amb were prepared with 25%, 51%, and 77% degree of exchange, respectively.

The interaction of the solid samples with isobutylene was measured using pulse technique by Autochem II 2920 automated catalyst characterization system (Micromeritics). Amberlyst samples were pretreated in helium flow for 1 h at 110 °C and solid *p*-toluenesulfonic acid was not thermally treated, only flushed in helium flow.

A train of 10 pulses of isobutylene (0.5 mL each in helium flow 20 mL/min) was applied at 0 °C, 30 °C, 60 °C and the response was obtained by TCD.

Glycerol etherification by isobutylene was performed in stainless steel stirred autoclaves (80 mL), equipped with thermocouples, cooling coil, sampling valve, and 6-blade mechanical stirrer (100-1,200 rpm). To ensure the liquid phase reaction, autoclaves were pressurized to 20 bar using nitrogen. In the standard procedure 11.50 g glycerol, 28.2 g isobutylene and 0.86 g catalyst (7.5% of catalyst with respect to glycerol, isobutylene : glycerol=4 : 1) were placed into the autoclave and the process was conducted at 60 °C for 20-50 h, depending on the activity of the catalyst. In the initial stage of reaction the liquid is biphasic, but upon the progress of the conversion the reaction mixture becomes monophasic. The data in this study were obtained mostly via the sampling of the homogeneous phase. Only in cases when it was important to analyze the initial stage of conversion, the reactor was quickly cooled, depressurized, the phases were separated, their weight, volume and composition were determined separately.

The samples of the reaction mixture were analyzed by GC in two ways. Standard analysis of all the components was performed in an Agilent 7890 system equipped with Agilent DB-WAX column (30 m×0.32 mm×0.25 μm). 1-Octanol was used as internal standard.

To increase the sensitivity and reliability of determination of glycerol and its derivatives a modified procedure of Plank et al. [16] was used. Glycerol and its mono- and di-ethers were transformed to trimethylsilyl derivatives. In brief, the samples were 2-3-fold diluted with 1,4-dioxane (for homogeneous non-viscous samples this step may be omitted); 20 μL of pyridine with internal standard (either 1,2,4-butanetriol or 1,3-propanediol was used as internal standard); 0.5-1.5 μL of the sample and 10 μL MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide) was placed into 1.5 mL GC vial, capped and left for 30 min at room temperature for the completion of silylation. 1 mL of heptane was added to the vial and thus the obtained solution was analyzed using an Agilent HP-5 column (35 m×0.32 mm×0.25 μm).

The response factors for all the individual ethers were determined using home-made high-purity samples. Mono- and di-ether were prepared via epichlorohydrin route. Tri-ether was made via excessive *t*-butylation of di-ether by isobutylene and subsequent distillation over metallic sodium under rough vacuum.

Table 1. Properties of the catalysts

Catalyst	H_0^a [reference]	Acidity, meq/g ^b	% of Ion exchange ^b	Conversion of glycerol within 7 h ^c	Selectivity to diisobutylene within 7 h ^c
<i>p</i> -Toluenesulfonic acid	-2.6 [17]	5.3		99	0.2
Amberlyst 15, powder	-2.2 [18]	4.9	0	99	22
Amberlyst 15, beads	-	4.9	0	98	17
25Na- Amb, beads	-	3.7	25	95	4
51Na- Amb, beads		2.4	51	95	0.3
77Na- Amb, beads		1.2	77	96	0.2

^aHammet acidity values taken from the literature

^bDetermined by titration

^cCatalytic run under the standard conditions

Conversion of glycerol was determined as $X_G = 1 - (G_t/G_0)$, where G_t - amount of glycerol at the moment t , G_0 - initial amount of glycerol.

Selectivity to ether i (mono-, di-, tri-ether) was determined as $S_i = (m_i / \sum_i m_i)$, where m_i - amount of i -th ether.

Selectivity to diisobutylenes was determined as $S_{DIB} = (2 \cdot m_{DIB} / (2 \cdot m_{DIB} + m_{TBA} + (\sum_{i=1}^3 i \cdot m_i)))$, where m_{DIB} - amount of diisobutylenes, m_{TBA} - amount t -butyl alcohol.

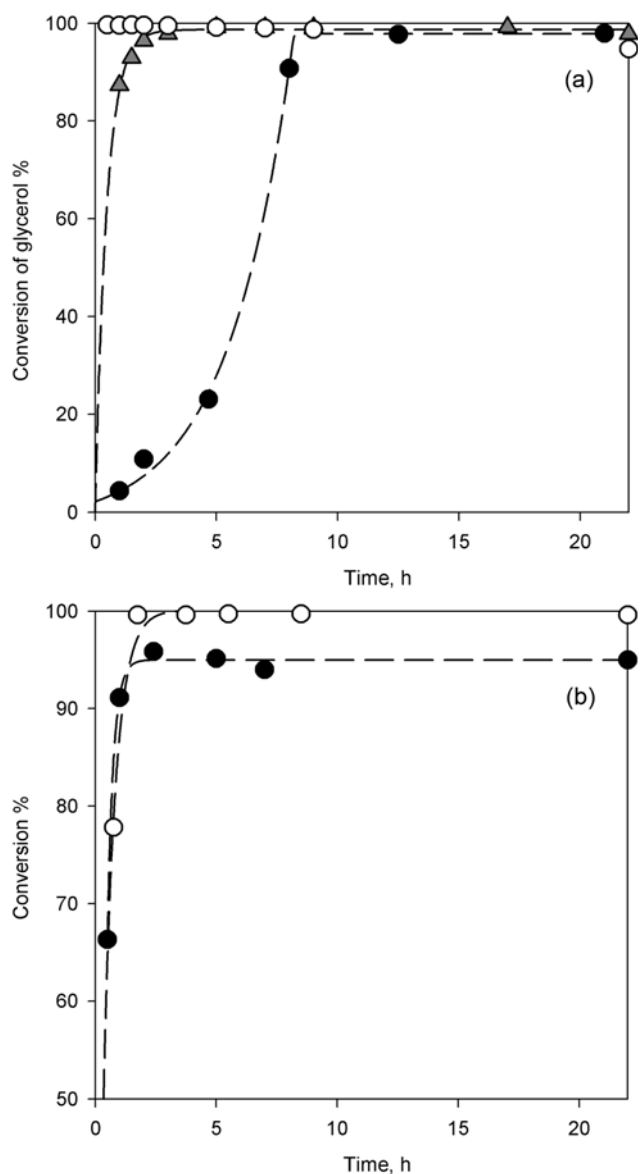


Fig. 2. (a) Conversion of glycerol under the standard conditions (isobutylene : glycerol=4 : 1, 7.5% weight of catalyst with respect to glycerol); Amberlyst 15 beads 1 mm (●), Amberlyst 15 powder (○), *p*-toluenesulfonic acid (▲). (b) Conversion of pure mono-*t*-butyl glycerol ether (isobutylene : mono-ether=2.7 : 1, 3.1% weight of catalyst with respect to mono-ether) (●), conversion of glycerol in 50% wt solution of glycerol/mono-*t*-butyl glycerol ether (isobutylene : glycerol=5.7 : 1, 10.6% weight of catalyst with respect to glycerol) (○).

RESULTS AND DISCUSSION

Some key properties of the catalysts are summarized in Table 1; conversion of glycerol is presented in Fig. 2(a). Amberlyst in the form of the beads (1 mm) shows comparatively low conversion during the first 5 h of reaction. Upon the time progress the rate of conversion increases and conversion becomes well above 95% after ca. 7 h. *p*-Toluenesulfonic acid shows complete conversion after 2 h of reaction. But the most considerable behavior is shown for Amberlyst in the form of the fine powder (<0.18 mm). The reaction is so fast that we observed small exo-effects during the onset of reaction in the case of powdered Amberlyst. It means that upon heating to ca. 50 °C during the start of the catalytic run we observed

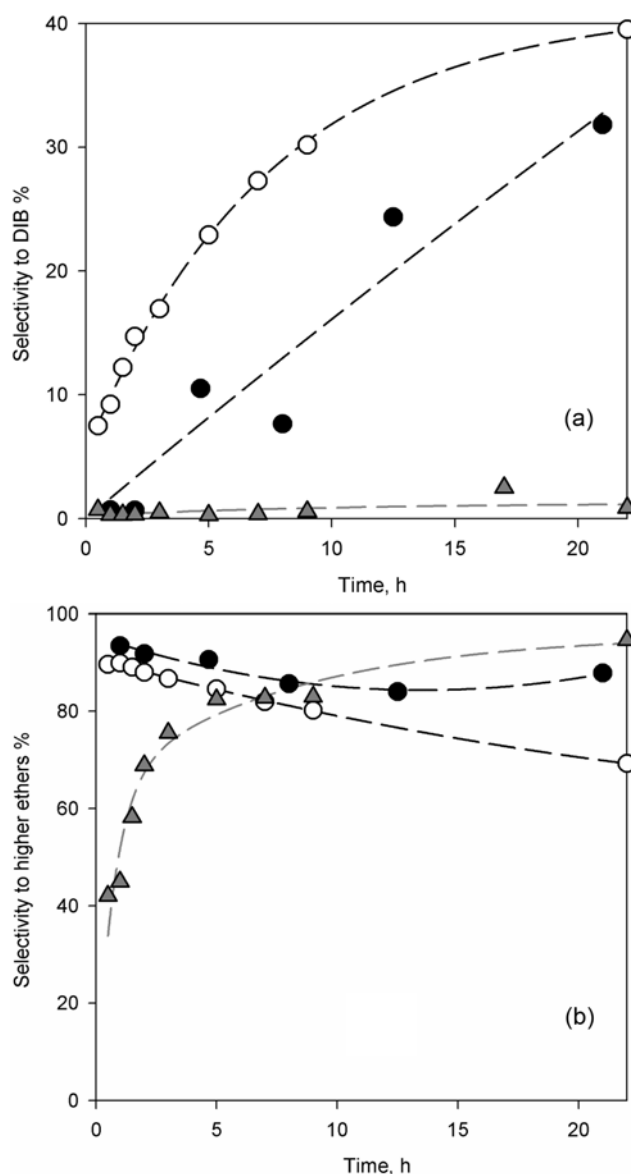


Fig. 3. (a) Selectivity to diisobutylenes under the standard conditions (isobutylene : glycerol=4 : 1, 7.5% weight of catalyst with respect to glycerol); (b) Selectivity to higher ethers (di- and tri-) under the same conditions Amberlyst 15 beads 1 mm (●), Amberlyst 15 powder (○), *p*-toluenesulfonic acid (▲).

a sharp temperature spike to ca. 70 °C for about 10 minutes, and then temperature decreased to the target point 60 °C. We could not observe the same behavior for the other catalysts.

The lag-period in glycerol conversion by Amberlyst beads is probably related to the accumulation of mono-ether in the reaction mixture. To check this hypothesis we evaluated the conversion of mono-*t*-butyl ether of glycerol (Fig. 2(b)). Clearly, there is no lag-period for the conversion mono-ether, though it is a bulkier molecule. According to the literature [11], mono-ether is an excellent solvent that can dissolve both glycerol and isobutylene. Since liquid isobutylene has very small solubility in glycerol, then addition of mono-ether can induce mutual solubility of reactants and thus decrease diffusion limitations. Indeed, when we studied the conversion of glycerol with added mono-ether, lag-periods disappeared (Fig. 2(b)). When we used 50% wt mixture of glycerol in mono-ether, complete conversion of glycerol occurred within 2 h in case of Amberlyst used in the form of the beads.

tert-Butanol and oligomers of isobutylene are main side-products. Selectivity to *t*-butanol is less than 5% and does not change with the time. Obviously, this side reaction on one hand is determined by the amount of water in the system, and on another hand *t*-butanol may be consumed for the etherification of glycerol as well. Oligomers of isobutylene are accumulated during the catalytic run as shown by the curves of selectivity to diisobutylene in Fig. 3. Clearly, acidic form of Amberlyst 15 has much higher selectivity to diisobutylene than its homogeneous analogue, *p*-toluenesulfonic acid. This happens due to the adsorption of isobutylene on the hydrophobic divinylbenzene matrix of Amberlyst and subsequent transformations of adsorbed species on acidic centers. We tested this hypothe-

Table 2. Consumption of isobutylene (in milliliters per gram of sample) during sequential pulsing at 0 °C

Sample Pulse # (°C)	Amberlyst 15	<i>p</i> -Toluenesulfonic acid	⁵¹ Na- Amberlyst 15
1 (0 °C)	>0.47	0.01	0.07
10 (0 °C)	>0.47	0.0	0.03
1 (30 °C)	0.48	0.0	0.09
10 (30 °C)	0.46	0.0	0.06
1 (60 °C)	0.41	-	0.05
10 (60 °C)	0.40	-	0.06

sis using pulse chemisorption technique. Indeed, high consumption of isobutylene occurs at 0 °C, 30 °C, and 60 °C (Fig. 4). In contrast to Amberlyst, consumption by the solid *p*-toluenesulfonic acid is negligible (Fig. 4, Table 2). Though it is not a good idea to make a direct correlation of these data with the isobutylene-catalyst interaction in the real reaction mixture, nevertheless the data on isobutylene chemisorption are a good starting point for the interpretation of catalytic data. Fig. 5 shows the effects of the composition of reaction mixture on the selectivity to isobutylene oligomerization. The formation of mono-ether in the reaction mixture clearly promotes formation of diisobutylene. At high conversions of glycerol, therefore, when the reaction mixture has reached in the ethers, the reaction of isobutylene oligomerization is induced. It is clear as well that at long contact time and excess of isobutylene over the gly-

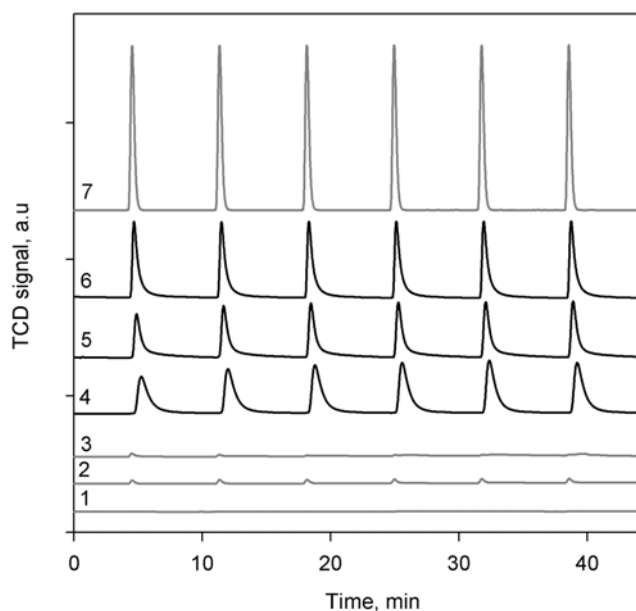


Fig. 4. Pulse responses for a train of 0.5 mL pulses of isobutylene on Amberlyst 15 taken in the amount of 0.4 g (lines 1-3), ⁵¹Na-Amb taken in the amount of 0.9 g (lines 4-6), and *p*-toluenesulfonic acid taken in the amount 0.4 g (line 7); 1 - 0 °C, 2 - 30 °C, 3 - 60 °C; 4 - 0 °C, 5 - 30 °C, 6 - 60 °C; 7 - 0° and 30 °C (the responses are same for these two temperatures).

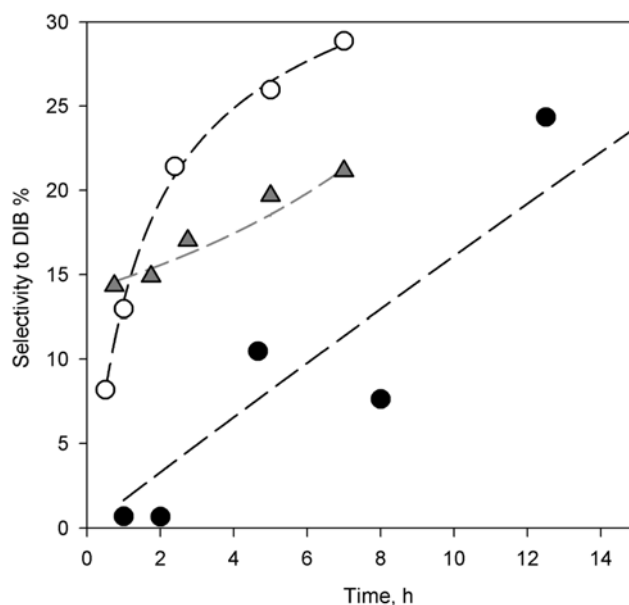


Fig. 5. Selectivity to diisobutylenes for Amberlyst 15 in the form of the beads: (○) - for the conversion of pure mono-*t*-butyl glycerol ether (isobutylene : mono-ether=2.7 : 1, 3.1% weight of catalyst with respect to mono-ether); (▲) - for the conversion of 50% wt solution of glycerol/mono-*t*-butyl glycerol ether (isobutylene : glycerol=5.7 : 1, 10.6% weight of catalyst with respect to glycerol); (●) - for the conversion of glycerol under the standard conditions (isobutylene : glycerol=4 : 1, 7.5% weight of catalyst with respect to glycerol).

erol (that is necessary to achieve high yield of target ethers), we are facing the problem of isobutylene losses (in amount of 20-30%) due to side process of oligomerization.

To modify the selectivity pattern, we tried to vary the density of acidic sites in Amberlyst 15 using partial ion exchange of acidic protons with sodium cations. This procedure inevitably leads to lower activity of the catalyst and thus lower space-time yields, but target and side reactions are suppressed in somewhat different mode; and using this approach it is possible to get better performance in terms of selectivity. The selectivity to diisobutylene is demonstrated in Fig. 6(a). Partial suppression of acidity clearly leads to the suppression of diisobutylene formation. On the other hand, the conversion of gly-

erol is well above 95% for all the catalysts for the same time-scale (Fig. 6(b)), both for partially neutralized and fully acidic Amberlyst 15. The somewhat strange effect of decreasing conversion with time may be attributed to the gradual removal of isobutylene from the media due to oligomerization and leading to the shift of the equilibrium towards reactants. Clearly, this trend is dominating for the fully acidic Amberlyst.

Decreased selectivity for diisobutylene in case of Na-modified Amberlyst correlates well with the results of the pulse chemisorption of isobutylene (Fig. 4). Though the amount of acidic sites in the pulse experiment was comparable for modified and unmodified Amberlyst, the Na-modified sample shows considerably decreased consumption of isobutylene compared to fully acidic Amberlyst 15 (Table 2). Therefore, not only the absolute amount of acidic sites is important but the density of acidic sites as well.

Another important feature of the partial neutralization is the certain possibility to tune up the relative yields of individual glycerol ethers (Fig. 7(a)-(c)). The patterns for the mono-ether formation are noteworthy for the Na-modified samples. As expected, relatively slow decay of mono-ether is observable for 77Na-Amberlyst sample due to very low activity. Clear increase of mono-ether content for fully acidic sample is related to the shift of the equilibrium due to isobutylene oligomerization. The highest yield for di-ether was found for 51Na-Amberlyst. Relatively slow decay of di-ether by equilibrium shift in the case of fully acidic sample and slow conversion to tri-ether in case of the lowest acidic catalyst are contributed. The highest yield of tri-ether was found for 51Na-Amberlyst sample. Decay of tri-ether was found for fully acidic catalyst, which is readily ascribed to the equilibrium shift. In general 51Na-Amberlyst sample provided the highest yields of higher ethers of glycerol (ca. 90%) combined with relatively low conversion of isobutylene to oligomers. This result is a clear trade-off for the lower catalytic activity due to the removal of significant number of acidic sites.

CONCLUSIONS

Etherification of glycerol by isobutylene in the liquid phase is investigated using Amberlyst 15, series of partially neutralized Amberlyst 15 catalysts, and *p*-toluenesulfonic acid.

Heterogeneous catalyst demonstrates considerable internal mass transfer limitations that may be alleviated using fine powder of the catalyst or using co-solvent. The best co-solvent is mono-*t*-butyl ether of glycerol that has good solubilizing properties both for isobutylene and glycerol. Since mono-ether is an intermediate product of the reaction, the reaction of etherification proceeds slowly in the beginning and accelerates upon the progress of the catalytic conversion.

Main side process is oligomerization of isobutylene that may be considerable at high isobutylene-to-glycerol ratio and long contact time. While, isobutylene is readily oligomerized in the case of fully acidic Amberlyst 15 and considerable amount of isobutylene (c.a., 15-30%) may be lost as a result of this process. Homogeneous analogue, *p*-toluenesulfonic acid, gives very low amount of isobutylene oligomers. Pulse chemisorption study of isobutylene interaction with the catalysts reveals high affinity of isobutylene to Amberlyst 15 and very low affinity of isobutylene to solid *p*-toluenesulfonic acid under the identical conditions.

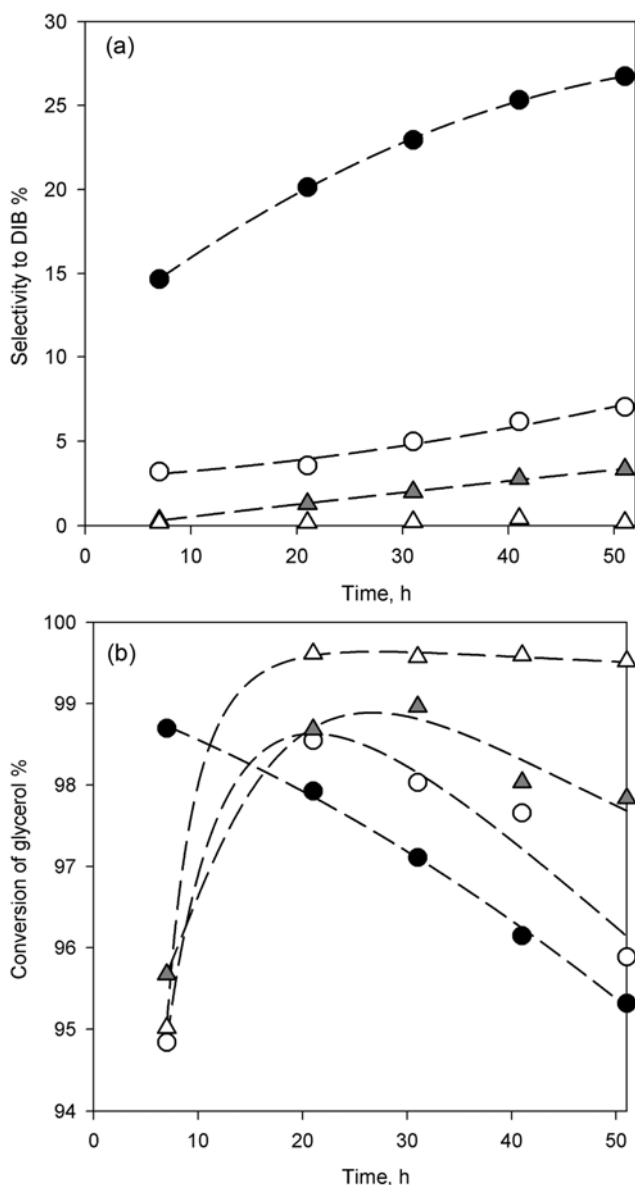


Fig. 6. (a) Selectivity to diisobutylenes for Amberlyst 15 in the form of the beads under the standard conditions (isobutylene : glycerol=4 : 1, 7.5% weight of catalyst with respect to glycerol); (b) Conversion of glycerol under the same conditions. (●) - Amberlyst 15, (○) - 25Na-Amb, (▲) - 51Na-Amb, (△) - 77Na-Amb.

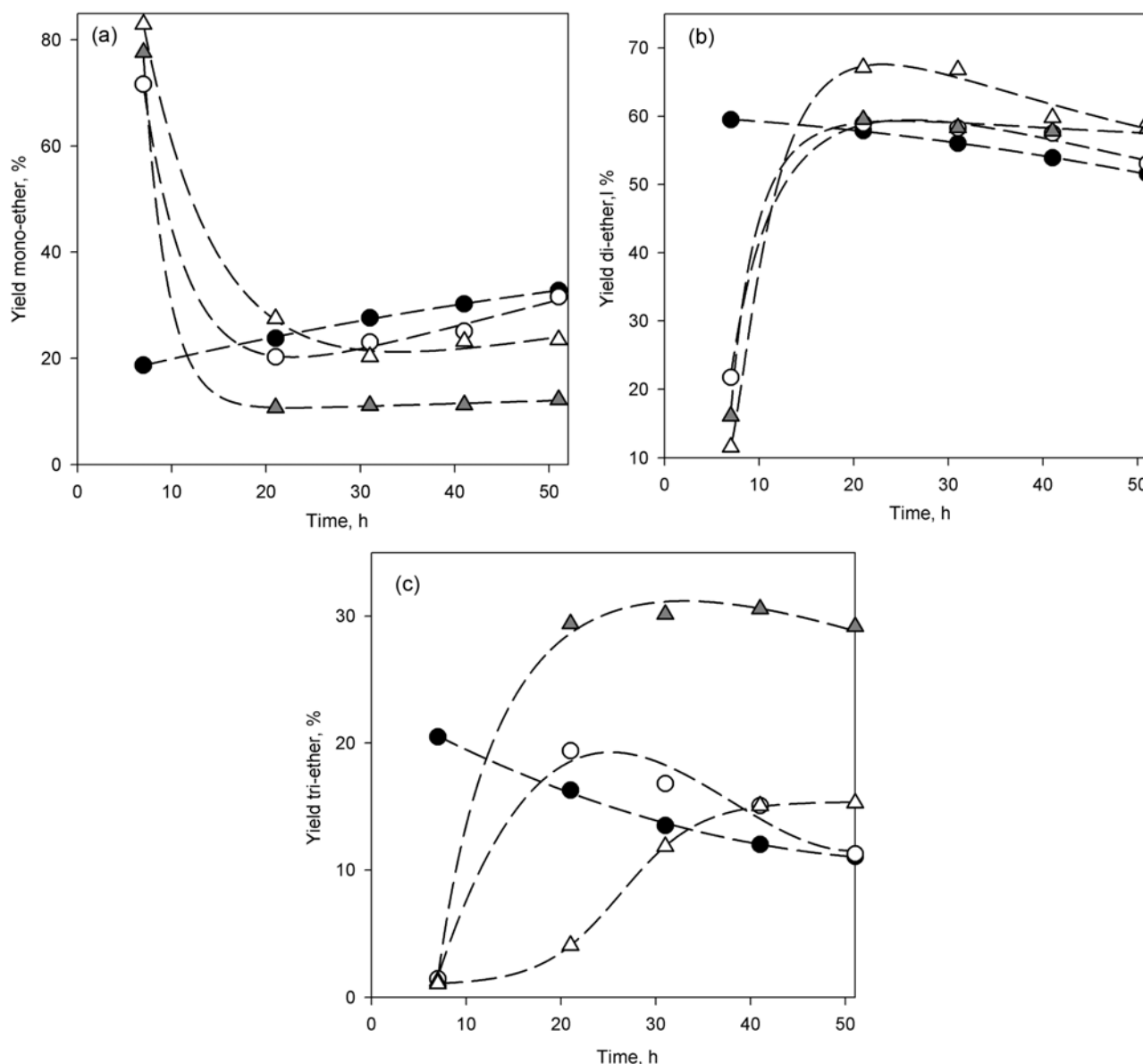


Fig. 7. (a) Yield of mono-*t*-butyl glycerol ether for Amberlyst 15 in the form of the beads under the standard conditions (isobutylene : glycerol=4 : 1, 7.5% weight of catalyst with respect to glycerol); (b) Yield of di-*t*-butyl glycerol ether for Amberlyst 15 in the form of the beads under the same conditions; (c) Yield of tri-*t*-butyl glycerol ether for Amberlyst 15 in the form of the beads under the same conditions; (●) - Amberlyst 15, (○) - 25Na-Amb, (▲) - 51Na-Amb, (△) - 77Na-Amb.

Removal of acidic sites in the matrix of Amberlyst 15 using partial ion exchange with sodium reveals inevitable loss of catalytic activity. At the same time, considerable improvement in terms of selectivity is observed while high conversion of glycerol is maintained. Pulse chemisorption of isobutylene reveals that the density of acidic sites is important for the interaction of isobutylene with Amberlyst 15. According to our study, c.a. 50% degree of ion exchange in the catalyst provides c.a. 90% yields of higher ethers of glycerol and induces losses of isobutylene due to oligomerization within 5%.

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