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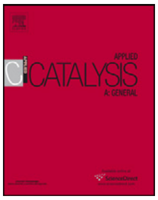

Etherification of glycerol by isobutylene: Tuning the product composition

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ABSTRACT

Etherification of glycerol by isobutylene was conducted in a batch mode using acidic and partially neutralized Amberlyst-15 ionic resin, *p*-toluenesulfonic acid, silicotungstic acid, cesium salt of silicotungstic acid, and ionic liquid containing sulfonic acid groups. All the catalysts are comparable in terms of the initial rate of glycerol conversion into mono-ether (except cesium salt of heteropolyacid), but differ substantially with respect to the yields of higher ethers of glycerol.

Ionic liquid and heteropolyacid are immiscible/insoluble in higher ethers of glycerol. As a result they have unique capability of suppressing the formation of tri-ether during the initial stage of glycerol conversion.

Acidic Amberlyst-15 in the form of fine powder has the highest activity per unit weight for glycerol etherification and relatively high activity in isobutene oligomerization. Partial exchange of acidic protons with cations Na^+, Ag^+, Mg^{2+}, and Al^{3+} decreases the rates of all the processes, but isobutylene oligomerization is suppressed more efficiently. Ag^+- and Al^{3+}-modified Amberlyst demonstrates higher yields of tri-ether and has specific pattern of interaction with gaseous isobutene distinctive to other metal-substituted Amberlysts.

1. Introduction

Components of engine fuel from sustainable sources became a business area in the last decades. With the introduction of biodiesel to the market substantial "overproduction" of glycerol resulted in the corresponding downtrend in the price of crude glycerol making the latter an attractive platform chemical.

A number of value-added products derived from glycerol are already proposed and some of them are commercialized [1–6]. A well-known possibility for the upgrade of glycerol to fuel additives is its transformation into higher (di- and tri-) tertiary butyl ethers. Di- and tri-tert-butyl ethers of glycerol have good potential for the usage as fuel components and have been under investigation for the last decade in several laboratories, both academic and industrial [7–13].

t-Butylation of glycerol may be realized via the contact of glycerol and isobutylene in the batch-type reactor under the modest heating (50–100 °C) and pressure in the presence of a suitable acidic catalyst. Ethers of glycerol (GE) are formed as a result of 3 consecutive steps and currently the following reaction scheme is accepted:

$$\mathrm{G + IB \leftrightarrows MTBGE} \quad (1)$$

$$\mathrm{MTBGE + IB \leftrightarrows DTBGE} \quad (2)$$

$$\mathrm{DTBGE + IB \leftrightarrows TTBGE} \quad (3)$$

Two side reactions give rise to the formation of tert-butyl alcohol (TBA) and oligomers of isobutylene (mainly dimers – DIB).

$$\mathrm{IB + H_2O \leftrightarrows TBA} \quad (4)$$

$$\mathrm{2IB \rightarrow DIB} \quad (5)$$

Assuming that MTBGE and DTBGE may have two isomers, in general case a mixture of five different glycerol ethers is obtained.

Higher ethers (di- and tri-) of glycerol are preferred as fuel components due to their miscibility with conventional fuel and high octane and cetane numbers. It is important to note that octane num-

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Abbreviations: IB, isobutylene; HSiW, silicotungstic acid $H_4SiW_{12}O_{40}$; G, glycerol; $Cs_{2.5}SiW$, cesium salt $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$; DIB, diisobutylene (mixture of 2,4,4-trimethyl-1- and 2,4,4-trimethyl-2-pentenes); IL-6, 1-(4-sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate; GTBE, glycerol tert-butyl ethers; TsOH, para-toluenesulfonic acid; MTBGE, mono-tert-butyl glycerol ether; TBA, tert-butyl alcohol; DTBGE, di-tert-butyl glycerol ether; Na(50)Amb, 50% ion-exchanged Amberlyst-15 sodium form; TTBGE, tri-tert-butyl glycerol ether; H-Amb, acidic form of Amberlyst-15.

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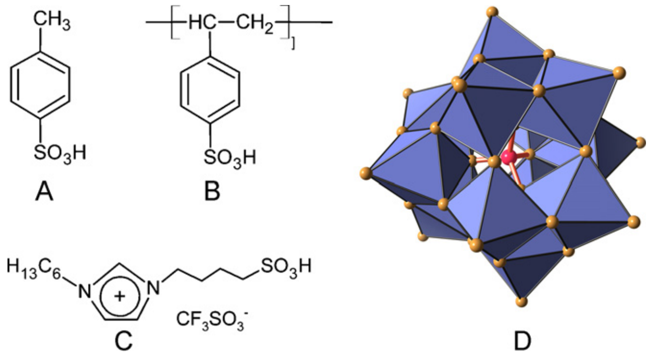

Fig. 1. Structure of catalysts used in the study: (A) *p*-toluenesulfonic acid (TsOH); (B) Amberlyst 15 (H-Amb); (C) 1-(4-sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate (IL-6); (D) Keggin unit of silicotungstic acid $H_4SiW_{12}O_{40}$ (HSiW).

bers of di- and tri-ethers are very close. On the other hand, glycerol is relatively cheap and renewable component, while isobutylene is more expensive and is not renewable. This simple consideration reveals the necessity of manufacturing preferentially di-ether pool of GTBE.

Recently we have tried to find the ways for a more selective production of individual ethers in GTBE process.

This publication is devoted to the comparison of different types of catalysts; applicability of the general reaction scheme (reactions (1)–(3)) for the catalysts under study; and evaluation of the catalytic activity of partially neutralized Amberlyst-15.

2. Experimental

2.1. Materials

Glycerol (99%), isobutylene (99%), p-toluenesulfonic acid, Amberlyst-15 beads were obtained from Sigma–Aldrich; silicotungstic acid hydrate was obtained from Fluka. All the chemicals were used as received. Supplementary solvents (methanol, dioxane, and others) were analytical grade purity.

2.2. Catalysts

Ionic liquid with Brønsted acidity: 1-(4-sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate was synthesized according to the known protocols [14,15]. In brief, N-hexylimidazole was prepared from imidazole and freshly distilled 1-bromohexane using ethanol solution of sodium ethoxide as a base [16]. Equimolar amounts of N-hexylimidazole and 1,4-butane sultone were stirred solvent free at room temperature for 3 days. The solid mass formed was washed three times with toluene and dried under vacuum. Thus obtained 3-hexyl-1-(butyl-4-sulfonate)-imidazolium betaine was reacted with trifluoromethanesulfonic acid for 2 h at 40 °C under stirring. Viscous colored ionic liquid thus obtained was washed with toluene and ether to remove non-ionic residues, and dried under vacuum at 80 °C, ~10 mm Hg. Structure of IL-6 is presented in Fig. 1 together with the other types of catalysts used in this study for a comparison.

Amberlyst-15 beads were washed with deionized water (Milli-Q), methanol and dried at 70 °C overnight. The content of acidic protons was checked by potentiometric titration (Titrino 721 NET, Metrohm AG). Ion exchange was performed using diluted (0.2–0.5 mol/L) solutions of metal nitrates or chlorides at ambient temperature overnight under gentle stirring. Modified Amberlyst was washed with deionized water, dried overnight at 70 °C, and vacuum dried at 60 °C. Acid content of modified Amberlyst was rechecked by potentiometric titration and the results of titration were used for the estimation of the degree of ion exchange. The notation of modified Amberlyst follows the example: Na(50)Amb means 50% replacement of acidic protons by Na^+ cations.

Cesium salt of silicotungstic acid, $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ was obtained according to the procedure of Okuhara et al. [17]. Aqueous solution of Cs_2CO_3 (0.2 M) was added to the appropriate amount of $H_4SiW_{12}O_{40}$ (0.08 M) at a pump rate of 0.1 ml/min under stirring. Resulting precipitate was dried at 85 °C overnight. The concentration of heteropolyacid in the solution was estimated by the titration procedure described in Ref. [18].

2.3. Characterization of samples

The distribution of metals in Amberlyst matrix was checked by energy-dispersive X-ray (EDX) spectroscopy using Quanta FEG 250 scanning electron microscope.

The interaction of the solid samples with isobutene was estimated using pulse technique in Autochem II 2920 automated catalyst characterization system (Micromeritics). Before analysis samples were pretreated in helium flow for 1 h at 110 °C. A train of 10 pulses of isobutene (0.5 ml each in helium flow 20 ml/min) was applied at 0 °C, 30 °C, 60 °C and the response was followed by TCD. All condensable materials in the effluent gas were trapped at 0 °C. The data on catalyst characterization are presented in Supplementary Materials.

2.4. Catalytic tests

Etherification of glycerol was performed in stainless steel stirred autoclaves (80 ml each), equipped with thermocouples, cooling coil and sampling valve. Each autoclave was equipped with 6-blade mechanical stirrer (100–1200 rpm). Before the experiment the reactor was flushed with nitrogen and adjusted to 20 bar when introducing liquid isobutylene. In typical runs conditions of Klepáčová et al. [9] were used: 11.50 g (0.125 mol) of glycerol, 0.86 g dry catalyst (7.5 wt%/glycerol), 28.2 g (0.503 mol) isobutylene; 60 °C; 1200 rpm (above 1000 rpm the product distribution does not depend on stirring speed). These conditions will be termed as standard throughout the paper. All variations of conditions with respect to catalyst, feed composition, temperature, etc. are reflected in the text.

Since reaction system initially separates into two liquid phases (glycerol/isobutylene) and typically becomes visibly homogeneous within 1–2 h, the most part of the data in this paper represent homogeneous case. In certain cases e.g., when it is important to analyze initial conversions or slow reactions, the process was stopped and the autoclave was quickly cooled to the room temperature and depressurized. The phases were separated, their weight, volume and composition were determined separately.

2.5. Analysis

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

In order to increase the sensitivity and reliability of determination of glycerol and its derivatives a modified procedure of Plank and Lorbeer [19] 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 were used as internal standards); 0.5–1.5 μL of the sample and 10 μL MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide) were

Table 1
Properties of the catalysts.

Catalyst (abbreviation)	H_0[a] [reference]	Acidity, meq/g	Conversion of glycerol within 5 h[b]	Selectivity to DIB within 5 h[b]
p-Toluenesulfonic acid (TsOH)	−2.6 [20]	5.3	99	0.2
Amberlyst-15 (H-Amb)	−2.2 [21]	4.8	99	22
$H_4SiW_{12}O_{40}$ (HSiW)	−3.4 [20]	1.4	94	17
$Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ ($Cs_{2.5}$SiW)	<−8.2 [22]	0.5	50	37
1-(4-Sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate (IL-6)	0.23[c]; −0.02[d] [23]	2.3	76	0.5

[a] Hammet acidity values taken from the literature.
[b] Catalytic run under the standard conditions.
[c] Hammet acidity for 3-methylimidazolium analogue.
[d] Hammet acidity for 3-decylimidazolium analogue.

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 obtained solution was analyzed using 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 DTBGE by isobutylene and subsequent distillation over metallic sodium under rough vacuum.

3. Results and discussion

3.1. Characterization of catalysts

Some characteristics of the catalysts are summarized in Table 1; structural types of the catalysts are presented in Fig. 1. The distribution of metal cations within the matrix of Amberlyst according to EDX does not depend on the nature of cation (see Supplementary Materials).

Interaction of isobutene with the solid samples was investigated using a pulse technique. Typical TCD responses are presented in Fig. 2. Absence of responses was observed for the original Amberlyst 15 in acidic form and cesium salt of heteropolyacid indicating very high affinities of these catalysts to isobutene. Interaction of isobutene with catalysts is exothermic reaction and clear exo-effects are observed (see Supplementary Materials). Isobutene consumption is a result of chemisorption of isobutene followed by the secondary processes like oligomerization and these processes are more pronounced for the Amberlyst with high density of the acidic sites and cesium salt of heteropolyacid. It is necessary to note that acid content of cesium salt per weight base is by the order of magnitude lower than that of Amberlyst. Therefore, when normalized by the acid content, $Cs_{2.5}$SiW should have the highest affinity for isobutene during the pulse experiment. This is a clear indication that the content of the strong acid sites is not a key factor in the process of isobutene interaction with a catalyst.

Density of acidic sites and nature of the metal cation seem to be important. Despite the fact that we used increased amount of partially neutralized Amberlyst to compensate the change of acidity, Fig. 2 clearly shows the difference between partially neutralized Amberlyst and unmodified Amberlyst. Analysis of the shape of responses suggests that the effect of counter-cations cannot be excluded. Ag(62)Amb shows very broad responses and almost complete consumption of isobutene during the first pulse. Al(57)Amb shows somewhat reduced amplitude of responses compared to the other samples. Li-, Ba-, Mg- and Na-modified samples show comparable responses though the shape of the first pulse shows certain dependence on the nature of metal cation as well.

According to Fig. 2 we can point out certain qualitative differences for the Amberlyst samples having comparable acid content but different metal cations used for the ion-exchange. Quantitative difference is presented in Fig. 3. For the sake of brevity we will term isobutene consumed by the sample during the first pulse as “consumption by the clean sample”, while the amount of isobutene consumed during the 10th pulse as “consumption by the saturated sample”. Among partially neutralized Amberlyst samples silver-modified catalysts have the highest consumption by the clean sample and the lowest consumption by the saturated sample. Al-

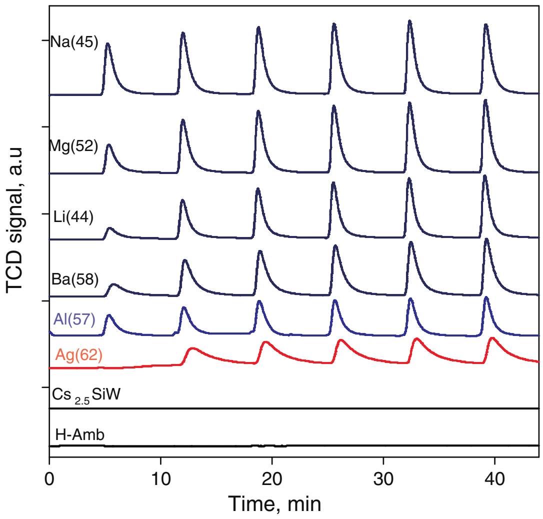

Fig. 2. Pulse responses for a train of 0.5 mL pulses of isobutene at 0 °C. $Cs_{2.5}$SiW and H-Amb taken in the amount of 0.4 g, all the other samples taken in the amount of 0.9 g.

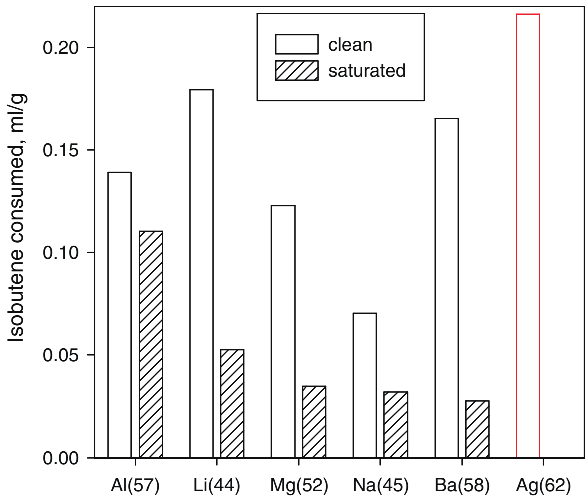

Fig. 3. Comparison of isobutene consumption for the 1st pulse (“clean sample”) and the 10th pulse (“saturated sample”).

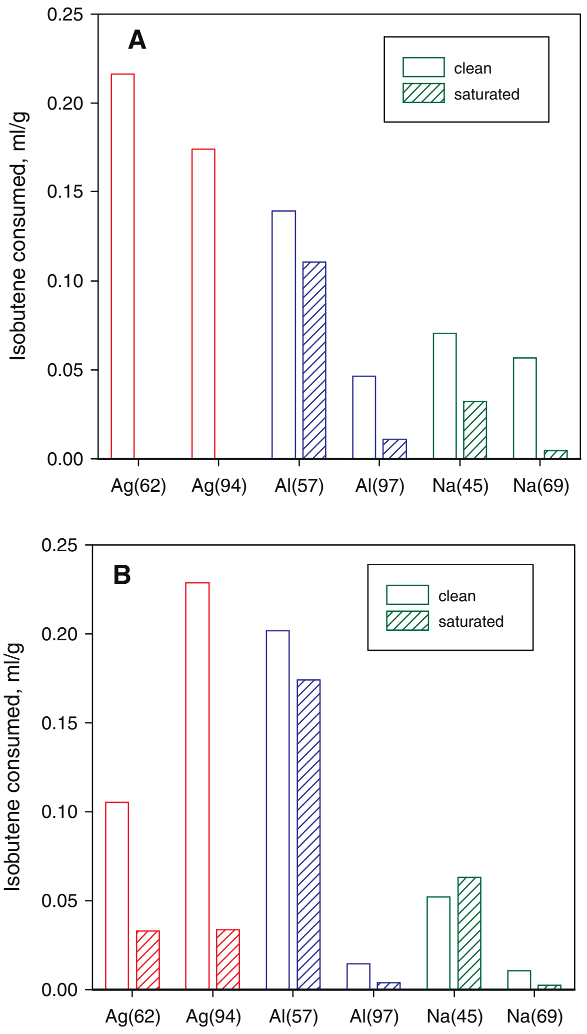

Fig. 4. Effect of the metal loading (Ag, Al, and Na) on the isobutene consumption by "clean sample" and "saturated sample" at 0 °C (A) and 60 °C (B).

modified Amberlyst has the highest consumption of isobutene by the saturated sample.

Effects of temperature and metal content on the isobutene consumption are presented in Fig. 4(A) and (B). Silver and aluminium tend to increase consumption by the clean sample compared to sodium-modified sample. Increase of the silver content does not have suppressing effect on the consumption by the clean sample. On the other hand, increase of metal content in the case of sodium and aluminium clearly leads to the suppression of the interaction of isobutene with Amberlyst. Partially Al-exchanged Amberlyst has the highest consumption of isobutene by the saturated sample among all the modified Amberlysts and the increase of temperature induces this effect.

The shape of the responses in pulse experiments is sensitive to the degree of ion-exchange for all the ions except silver (Fig. 5). Ag(62)Amb and Ag(94)Amb show almost identical responses.

Taken all together, Ag- and Al-modified samples have certain unique properties with respect to the interaction with isobutene compared to the other samples. This leads to certain specific features in catalysis as well (see lower).

3.2. Conversion of glycerol and oligomerization of isobutylene

Fig. 6 and Tables 1–2 show conversions of glycerol and selectivities of DIB formation. In general, conversion exceeding 80% is

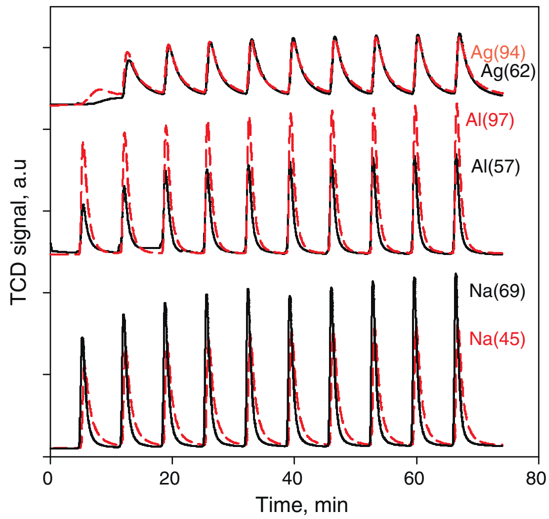

Fig. 5. Effect of the metal loading (Ag, Al, and Na) on the shape of responses. Solid lines – lower amount of metal, dashed lines – higher amount of metal.

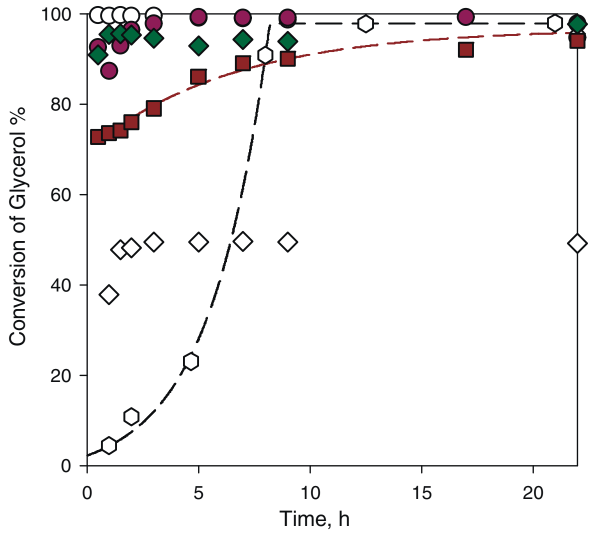

Fig. 6. Conversion of glycerol under the standard conditions (IB:G = 4:1, 7.5% weight of catalyst with respect to glycerol); empty symbols – heterogeneous catalysts, filled symbols – homogeneous catalysts H-Amb beads 1 mm (⬡), H-Amb powder (○), TsOH (●), IL-6 (■), HSiW (♦), Cs$_{2.5}$SiW (◊) taken in the amount of 2 g.

Table 2
Selectivity to diisobutenes under standard conditions.

Catalyst	S_{DIB} (2 h of reaction)	S_{DIB} (22 h of reaction)
TsOH	0.3	0.9
H-Amb (powder)	14.7	39.5
H-Amb (beads)	0.7	31.8
HSiW	14.3	32.9
Cs$_{2.5}$SiW[a]	33.8	44.8
IL-6	0.6	1.6
H-Amb (powder)[b]	5.0	11.3
Al(57)Amb	1.0	8.9
Mg(52)Amb	0	1.9
Ag(62)Amb	1.0	11.0
Na(45)Amb	0.8	3.2

Figures on DIB formation are presented in Supplementary Materials.

[a] Catalyst taken in the amount of 2 g.

[b] Catalyst taken in the amount corresponding to 10% of the standard.

reached within 2 h under the standard conditions with two exceptions: Amberlyst-15 in the form of the beads (1 mm in diameter) and insoluble cesium salt of silicotungstic acid. Amberlyst-15 in the form of the beads shows a lag period due to severe internal diffusion limitations. This period of a very slow reaction may be explained by a slow transport of reactants within the cross-linked matrix of Amberlyst-15. After 5 h of reaction, when sufficient amount of mono-ether (MTBGE) is accumulated, the rate of etherification increases due to the solvent effect. MTBGE is a very good solvent both for glycerol and isobutylene [11] and facilitates the transport of reactants within the pores. The more MTBGE is accumulated, the higher is the reaction rate, and after 7 h of reaction almost all glycerol is converted by the beads of Amberlyst.

Particle size of Amberlyst is of crucial importance for the fast glycerol conversion. When beads of Amberlyst-15 are ground into the fine powder, internal diffusion control becomes negligible and complete conversion of glycerol occurs within 30 min (Fig. 6). Powdered Amberlyst-15 has superior rate of conversion per weight unit among all the catalysts studied and considerably more active than its homogeneous analogue, *p*-toluenesulfonic acid (Fig. 6). This effect may be attributed to (i) higher local concentration of the acidic sites (discussed lower) and (ii) to the increased concentration of isobutylene within the hydrophobic backbone of Amberlyst-15. Both effects lead to the enhanced formation of isobutylene oligomers. Indeed, according to Table 2 Amberlyst-15 demonstrates much higher rate of isobutylene oligomerization compared to *p*-toluenesulfonic acid.

Insoluble cesium salt of heteropolyacid ($Cs_{2.5}SiW$) has the poorest performance among all the catalysts studied (Fig. 6). Conversion of glycerol is never complete even when high catalyst loading is used. The reaction mixture remains all the time biphasic. The lower phase is comprised mostly of viscous glycerol-rich media with particles of catalyst, and the upper phase is transparent and is comprised mostly of higher ethers of glycerol and oligomers of isobutylene. $Cs_{2.5}SiW$ provides the highest activity in side reaction of isobutylene oligomerization according to Table 2. GC analysis revealed as well formation of many unidentified peaks that probably belong to the condensed molecules of glycerol. Evidently the introduction of Cs^+ cations leads to the creation of basic sites that are facilitating condensation reactions of glycerol. These high molecular weight products probably deactivate the catalyst within ca. 1 h of catalytic run.

In contrast to $Cs_{2.5}SiW$, parent homogeneous silicotungstic acid (HSiW) is very active and glycerol conversion is over 90% after 1 h of catalytic run. HSiW shows much higher yields DIB in contrast to the other homogeneous catalysts: TsOH and IL-6 (Table 2). According to theoretic and experimental studies [24,25] there is quite high affinity of isobutylene for Keggin anion due to the protonation of isobutylene and formation of the alkoxy state bound to Keggin anion. These bound alkoxy-species may couple with a next isobutylene molecule [26] producing dimeric species. Another route for dimerization is through π-bound state of olefin found for the catalysts with strong acid sites [27]. According to Table 1 HSiW and $Cs_{2.5}SiW$ have the strongest acidity in terms of Hammett function, and thus tend to promote isobutylene oligomerization.

Amberlyst has lower acid strength compared to heteropolyacid, nevertheless it shows elevated yields of DIB. According to [28] isobutene dimerization is a second order reaction with respect to the Amberlyst acid concentration. Spatially fixed sulfonic groups of Amberlyst provide higher local concentration of acidic protons compared to homogeneous case and thus the probability of IB dimerization is increased. Higher local concentration of acidic sites may be attributed to $Cs_{2.5}SiW$ where acidic centers are confined. Alcohols are suppressing oligomerization of olefins [28,29], but complete suppression of DIB formation in the case of Amberlyst is achieved at ratio olefin/alcohol < 0.6 [30]. In our study IB/G = 4, therefore we expect high probability of isobutene oligomerization over H-Amb. For homogeneous acids with moderate acidity (TsOH and IL-6) lower concentration of alcohol is sufficient for the suppression of isobutylene oligomerization. Hydrophobic interaction is an additional factor that may play some role in the oligomerization and probably needs some speculation. Addition of cesium induces hydrophobicity of the surface of the heteropolyacid salt [31], as well as hydrophobic divinylbenzene matrix of Amberlyst may favor adsorption of isobutene and may promote the formation of DIB.

Finally, our pulse experiments on the interaction of isobutene with catalysts (Fig. 2) revealed the highest affinity of isobutene to $Cs_{2.5}SiW$ and H-Amb among all the catalysts studied and provide a clear interpretation of catalytic data.

3.3. *Product distribution*

The distribution of products depends on the ratio of isobutylene to glycerol (Fig. 7A). Mostly tri- and di-ethers are formed at high IB/G ratio and mostly mono- and di-ethers are formed at low IB/G ratio. It is difficult to obtain single ether at the high level of glycerol conversion. If the equilibrium in reactions ((1)–(3)) is established, then the distribution of glycerol ethers should not be dependent on the nature of the catalyst. We can see that after 20 h of reaction there is still considerable difference in the product distribution (Fig. 7B). Therefore, the system is not in the equilibrium in general even after long reaction runs.

Figs. 8 and 9 show time-dependent yields of mono-, di-, and tri-ethers of glycerol. It is important to note that experimental patterns in general do not follow the simplified kinetic model developed by Behr and Obendorf [11] for the same process. According to reactions (1)–(3), the following rates may be written:

$$r_1 = k_1 C_G \cdot C_{IB} - k_{-1} \cdot C_{MTBGE} \quad (6)$$

$$r_2 = k_2 C_{MTBGE} \cdot C_{IB} - k_{-2} \cdot C_{DTBGE} \quad (7)$$

$$r_3 = k_3 C_{DTBGE} \cdot C_{IB} - k_{-3} \cdot C_{TTBGE} \quad (8)$$

Concentration profiles of ethers then should be found according to the system of equations:

$$\frac{dC_G}{dt} = -r_1 \quad (9)$$

$$\frac{dC_{MTBGE}}{dt} = r_1 - r_2 \quad (10)$$

$$\frac{dC_{DTBGE}}{dt} = r_2 - r_3 \quad (11)$$

$$\frac{dC_{TTBGE}}{dt} = r_3 \quad (12)$$

$$\frac{dC_{IB}}{dt} = -r_1 - r_2 - r_3 \quad (13)$$

Fig. 10 shows example of satisfactory fit in the case of TsOH and example of unsatisfactory fit demonstrated by IL-6. Powdered Amberlyst shows clearly deviations from the expected patterns (Fig. 8). In this case almost immediate formation of the reaction mixture (~10 mol% MTBGE, ~60 mol% DTBGE and ~30 mol% TTBGE) occurs followed by the gradual decay of TTBGE and corresponding rise of MTBGE concentration. After 20 h of reaction the composition of the reaction mixture changes to ~30 mol% MTBGE, ~55 mol% DTBGE and ~15 mol% TTBGE. This behavior may be attributed to a very high activity of powdered Amberlyst in the target and side reaction. We observed a temperature spike from ca. 55 °C to ca. 65 °C during initial 15 min of catalytic run when the autoclave is heated from room temperature to 60 °C. This temperature spike is short (about 5–10 min) and is observed only in the case of powdered Amberlyst. All the other catalysts show smooth temperature

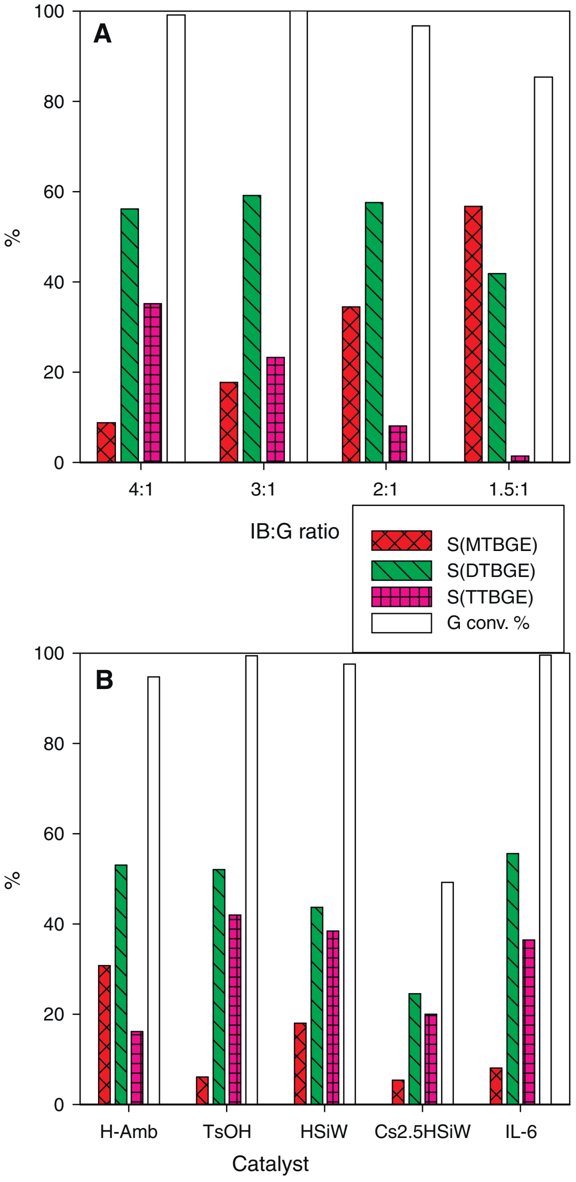

Fig. 7. (A) Conversion of glycerol and selectivity to glycerol ethers after 1 h of reaction; H-Amb powder-catalyst, variable ratio of IB:G; standard conditions ($P = 20$ bar, 7.5% weight of catalyst with respect to glycerol). (B) Conversion of glycerol and selectivity to glycerol ethers after 20 h of reaction, ratio of IB:G = 4:1; standard conditions: $P = 20$ bar, 7.5% weight of catalyst (with exception of $Cs_{2.5}SiW$ taken in the amount corresponding 17% weight with respect to glycerol).

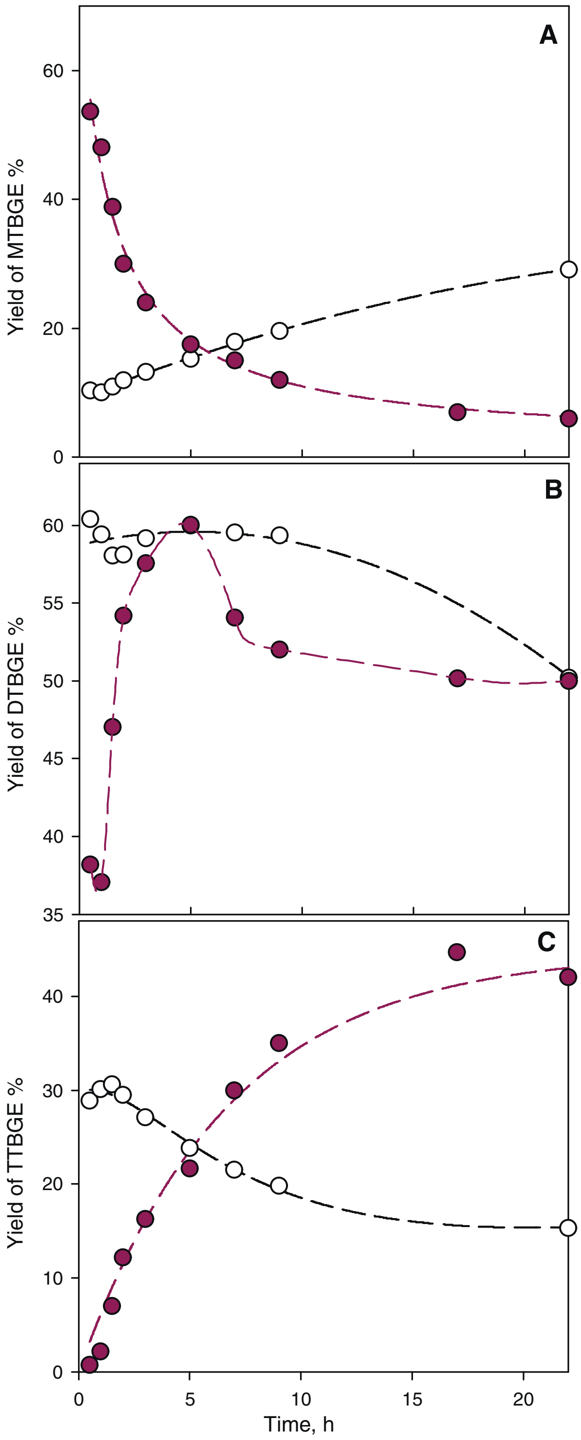

Fig. 8. Yields of glycerol ethers under the standard conditions ($P = 20$ bar, IB:G = 4:1, 7.5% weight of catalyst with respect to glycerol); empty symbols – heterogeneous catalysts, filled symbols – homogeneous catalysts H-Amb powder (○), TsOH (●). (A) Yield of MTBGE; (B) yield of DTBGE; (C) yield of TTBGE.

profile during the onset of the catalytic run. This is a clear indication that reaction starts violently and finishes within 10 min when it is driven by powdered Amberlyst. As a result the system arrives to the equilibrium (or overshoots the equilibrium) very fast but then, due to the steady process of isobutylene removal in the form of DIB, the equilibrium is perturbed to the left in a more gradual manner. This is indicated by the decay of TTBGE and slow accumulation of MTBGE (Fig. 8). In contrast to H-Amb, TsOH with higher content of acidic sites of comparable strength shows the concentration profiles that agree with the expected simplified kinetic scheme presented in Fig. 10A. There is no decay of TTBGE since isobutylene removal in the form of DIB is negligible for TsOH-driven reaction (Table 2).

Heteropolyacid exhibits concentration profiles that cannot be fitted by the simple kinetic scheme. TTBGE profile in this case has certain deviation from the expected pattern. Despite the fast accumulation of DTBGE, the TTBGE profile shows a relatively long lag-period in the beginning of the run. Though DTBGE concentration reaches maximum within 2 h, formation of TTBGE is suppressed to ~5 mol% for initial 7 h of reaction. Only after 20 h the concentration of TTBGE increases up to 35 mol%.

Ionic liquid demonstrates the same feature of suppressed TTBGE formation during the first 7 h of reaction. DTBGE and MTBGE profiles have plateaus during initial 3 h of the run (Fig. 9). These lag-periods and plateaus probably correspond to the solvent effects

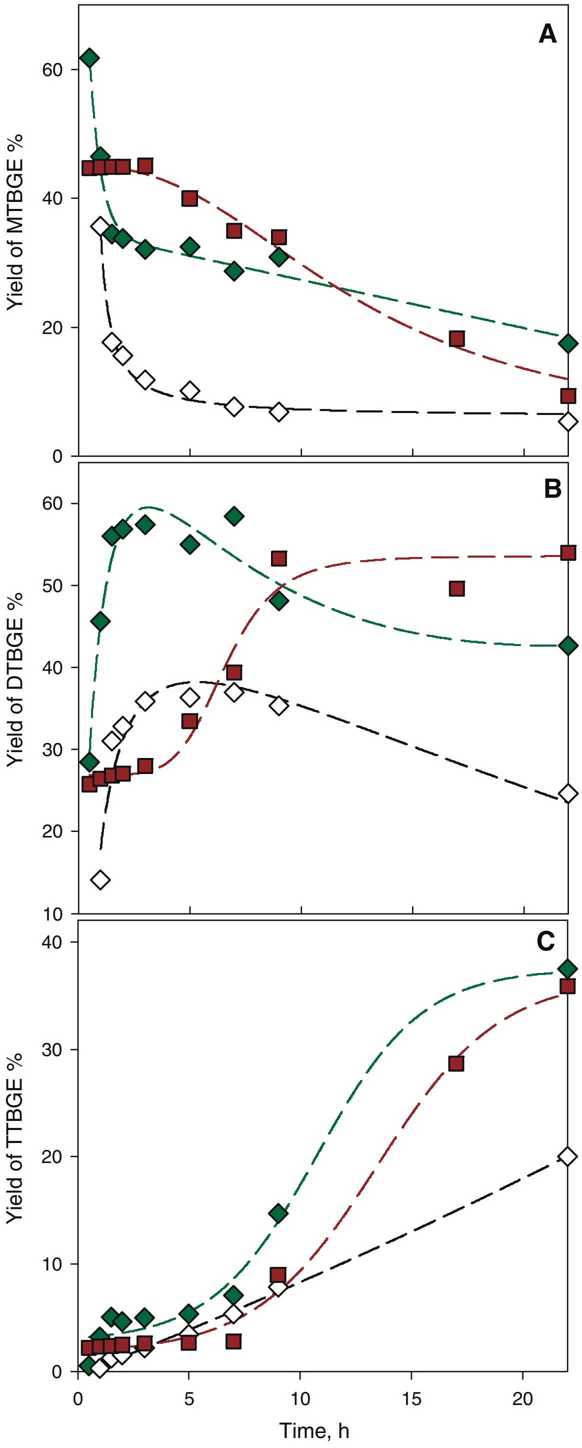

Fig. 9. Yields of glycerol ethers under the standard conditions ($P = 20$ bar, IB:G = 4:1, 7.5% weight of catalyst with respect to glycerol); empty symbols – heterogeneous catalysts, filled symbols – homogeneous catalysts IL-6 (■), HSiW (♦), $Cs_{2.5}SiW$ (◊) taken in the amount of corresponding to 17% with respect to glycerol. (A) Yield of MTBGE; (B) yield of DTBGE; (C) yield of TTBGE.

and cannot be fitted according to the simplified kinetic scheme (Fig. 10B). Ionic liquid has good solubility in glycerol and MTBGE, but poor solubility in higher ethers of glycerol (Fig. 11). Thus in the beginning, the reaction of glycerol etherification is fast and ~75% of glycerol is converted into MTBGE and DTBGE. DTBGE is expelled from the polar phase rich in catalyst resulting in a very slow reaction of TTBGE formation. The same explanation holds for heteropolyacid since it is as well soluble in glycerol and MTBGE, but not soluble in higher ethers of glycerol (Fig. 11). Plateaus observed in MTBGE and DTBE profiles in the case of IL-6 are less clear for the interpretation. Solubility of IL-6 in MTBGE is good therefore, the solvent effect is excluded. It is clear that initial conversion of glycerol is fast until 60% of glycerol is converted. Then etherification of the second hydroxyl-group of glycerol becomes slower according to the slow rate of MTBGE decay (Fig. 9A) demonstrated by both IL-6 and HSiW.

We may speculate on the possible changes of the system of hydrogen bonds when bulky *t*-butyl groups appear near the active centers. According to the common views on the mechanism of etherification of alcohols by olefins, concerted action of several protons is required resulting in the very complicated ensemble in the transition state [30,32]. When *t*-butyl group is inserted into the molecule of glycerol it may distort the ensemble of the transition state and change the rate constant. Probably the same changes in the structure of “active ensemble”, when ca. 60 mol% of MTBGE is converted into DTBGE, lead to the corresponding sigmoid shape of TTBGE profile.

Product distribution in the case of insoluble $Cs_{2.5}SiW$ salt should be treated with caution (or in a semi-quantitative manner) since in this case we get considerable errors due to the formation of a big number of unidentified products. Excessive oligomerization of isobutylene may promote glycerol etherification by a variety of IB oligomers. Glycerol condensation to polyglycerols cannot be excluded as well. We expect that these high molecular weight products lead to the fast deactivation of the catalyst.

3.4. *Recycling of the catalyst*

Amberlyst-15 may be recycled several times without any loss of activity. This catalyst may be recovered by filtration, washing with methanol and drying.

p-Toluenesulfonic acid is more difficult to recycle. For example, it may be extracted by glycerol from the product mixture, but still traces of *p*-toluenesulfonic could not be removed. The latter deteriorates the yields of ethers during the distillation step [8].

Catalytic activity of $Cs_{2.5}SiW$ vanishes after a single catalytic run indicating severe deactivation.

Heteropolyacids and ionic liquids are easily separated from the products due to their low solubility in higher ethers of glycerol. They form liquid lower phase or solid sediment in the case of HSiW, which may be removed via simple decantation (Fig. 11). Though phase separation is easily obtained, gradual loss of the catalyst occurs during multiple runs. This gradual loss is attributed to the small solubility of these acids in the product mixture. Treatment of the products with glycerol greatly improves the recovery of these catalysts.

3.5. *Partially neutralized Amberlyst-15*

Fine powder of Amberlyst-15 provides the best activity and may be easily separated from the products. Unfortunately, it gives elevated levels of side products due to isobutylene oligomerization (Table 2). Behr et al. [8] also reported higher levels of IB oligomerization for heteropolyacid and Amberlyst compared to TsOH.

We tried to modify the density of acidic sites in order to suppress the formation of DIB and other oligomers. Ion exchange using aqueous solutions containing single-charged cations (Na^+, Ag^+), double-charged cations (Mg^{2+}), and triple charged cations (Al^{3+}) diminished the number of acidic sites and resulted in the loss of catalytic activity. Conversions of glycerol catalyzed by partially neutralized Amberlyst samples are above 80% within 2 h and above 90% within 4 h of reaction (see Supplementary Materials for the illustration). All the catalysts with 50% reduced acidity show comparable rate of conversion. This rate of conversion is equivalent to ca. 10% of the standard amount of H-Amb. Ag(62)Amb has the high-

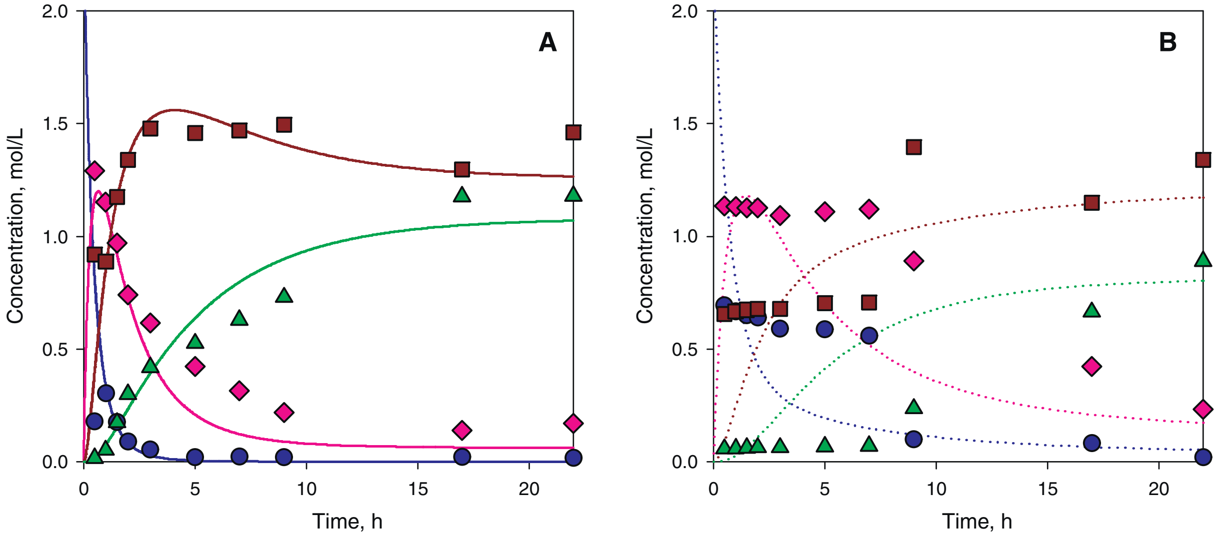

Fig. 10. Experimental concentrations of glycerol (●), MTBGE (◊), DTBGE (□),and TTBGE (△) fitted by the simplified kinetic model (Eqs. (6)–(13)). (A) Satisfactory fit in case of TsOH. (B) Unsatisfactory fit in case of IL-6.

est rate of etherification compared to the other partially neutralized samples of Amberlyst.

Selectivity to DIB exhibited by partially neutralized Amberlyst samples is presented in Table 2. All the samples show lower rates of DIB formation compared to parent H-Amb. Ag(62)Amb and Al(57)Amb have higher level of DIB formation compared to Na- and Mg-samples. This catalytic effect clearly corroborates our data on the specific features of isobutene interaction with these catalysts during pulse experiments.

Yields of MTBE, DTBGE, and TTBGE exhibited by modified Amberlyst are summarized in Fig. 12(A)–(C). Comparison with the unmodified H-Amb indicates that 50% reduction of acidic sites caused by ion-exchange corresponds to 90% reduction of production rate of ethers. According to Panneman and Beenackers [33] 90% decrease of acidity caused by the neutralization of Amberlyst leads to 200 times lower production rate of MTBE formation from methanol and isobutene. Second order with respect to TsOH concentration was found by Kogelbauer et al. [34] for the acid catalyzed hydrolysis of MTBE. Ancillotti et al. found higher than third order reaction rate with respect to the acid content of Amberlyst for alcohol etherification by isobutylene [35,36]. All these features in general imply that associates of acidic sites act as catalytic center.

Analysis of the yields of tri-ethers (Fig. 12C) reveals that in the case of Na(45)Amb and Mg(52)Amb the concentration of TTBGE is gradually increasing until the probable equilibrium level. But in the case of Al(57)Amb and especially Ag(62)Amb TTBGE concentration "overshoots" the equilibrium level and after reaching maximum it gradually decreases. The same but "mirrored" effect is clearly observed for MTBGE (Fig. 12A). The yields of MTBGE go below the equilibrium level for Al(57)Amb and Ag(62)Amb samples.

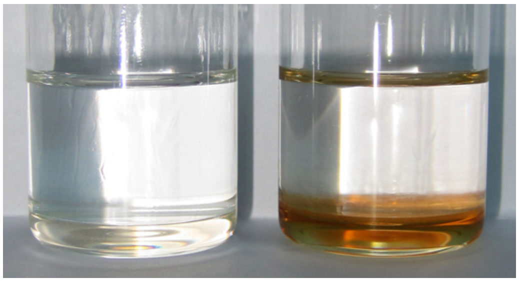

Fig. 11. Liquid phase separation of products and catalysts: left – HSiW, right – IL-6.

The effect of "overshooting" the equilibrium is more pronounced for the Ag-modified Amberlyst. This effect is further enhanced when the loading of catalyst is increased 4 times (see Supplementary Materials). In this case the overall amount of acidic sites is 2 times higher compared to the standard amount of unmodified Amberlyst. According to the data on the consumption of isobutene during the pulse experiments, silver-modified Amberlyst catalysts show enhanced consumption of isobutene by the clean sample and enhanced consumption of isobutene at high metal loadings. While Al(97)Amb sample has no catalytic activity in the target reaction, Ag(94)Amb sample has measurable catalytic activity despite very low content of acidic sites. Enhanced adsorption of ethylene by Ag-modified Amberlyst 15 was revealed by Wu et al. studied in equilibrium adsorption–desorption mode [37]. Ag^+ ions are often used in membranes for the separation of olefin/paraffin mixtures [38,39] due to the specific interaction of olefins with Ag^+. Then it is possible to explain the mechanism of "overshooting" the equilibrium due to the increased possibility of simultaneous etherification of mono-ether by two isobutylene molecules producing tri-ether in one step. Since Ag^+ ions have increased affinity to isobutene, and then this effect is more evident for Ag(62)Amb sample. Probably the same mechanism operates for Al(57)Amb since this sample also revealed enhanced interaction with isobutene in pulse experiments. Al(57)Amb, unlike the other modified samples, shows wide distribution of weak acidic sites. Probably these weaker sites have certain affinity to olefin molecules.

According to Figs. 8, 9 and 12 there is certain possibility to vary the yields of individual ethers using suitable catalysts or fine tuning H-Amb by partial ion exchange. It is clear that certain variations of the individual rates (i.e., rates of reactions (1)–(3)) are observed according to different product distributions on different catalysts with the same number of acidic sites. Different counter-cations used for the neutralization of H-Amb are changing the reaction rates in the individual manner. According to the literature, partial neutralization of Amberlyst 31 revealed the influence of the nature of amine, taken as neutralizing agent, on the catalytic activity in esterification [40]. Therefore, the nature of the cation used for the ion-exchange and the distribution of the remaining acidic sites are important factors for fine tuning the catalytic activity.

Cation exchange decreases the density of acidic sites in Amberlyst and deteriorates the catalysis by associated acidic protons leading to the non-linear dependence of the reaction rates upon the concentration of acid centers in Amberlyst. The rates of

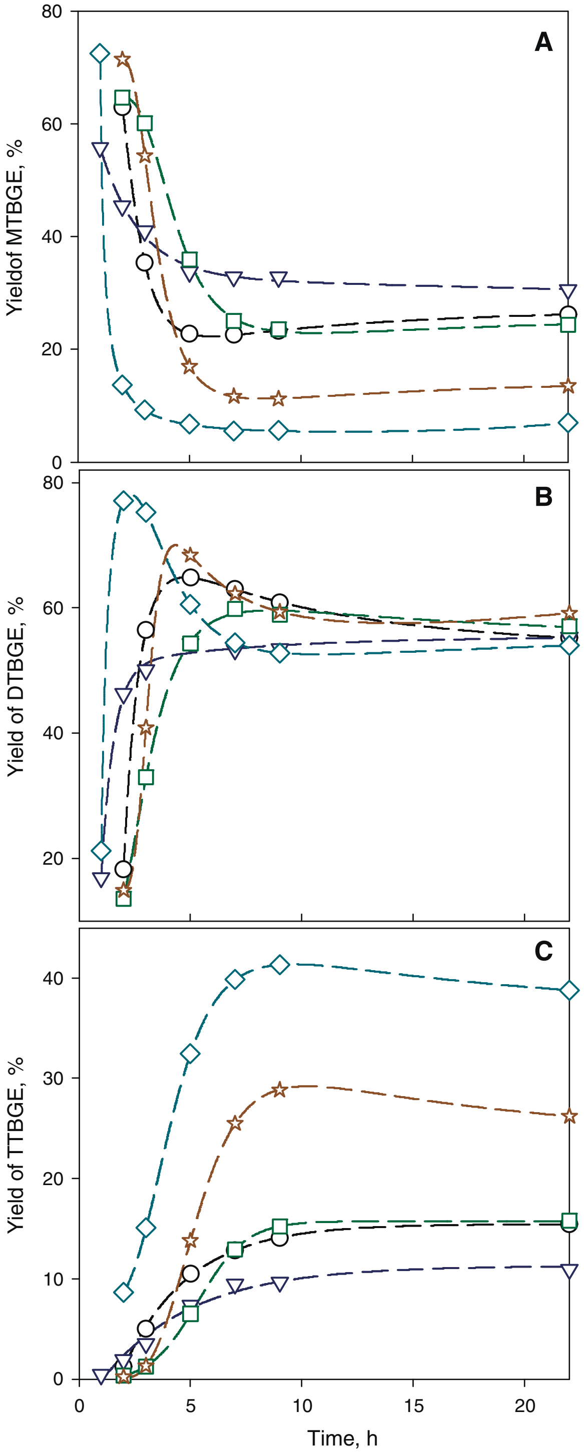

Fig. 12. Yields of glycerol ethers under the standard conditions ($P = 20$ bar, IB:G = 4:1) for powered Amberlyst based catalysts: H-Amb, taken as 10% amount with respect to standard conditions (○); Na(45)Amb (▽); Ag(62)Amb (◊); Mg(52)Amb (□); Al(57)Amb (☆). (A) Yield of MTBGE; (B) yield of DTBGE; (C) yield of TTBGE.

individual reactions may have different dependence on the concentration of acidic sites; and thus certain reactions (e.g., formation of DIB) are suppressed more effectively. Solvent effect is another factor that plays important role in the catalysis by homogeneous acids. Depending on the solubility in glycerol (starting material) and glycerol ethers (product of reaction) different homogeneous catalysts may provide different yields of higher ethers of glycerol.

4. Conclusions

Comparison of the performances of different solid and liquid acids in the etherification of glycerol by liquid isobutylene in a batch reactor was performed and revealed that equilibrium is not reached in general case.

The most active catalyst per weight basis was fine powder of Amberlyst-15. It may be “fine tuned” using partial exchange of acidic protons with suitable metal cations. This tuning leads to the suppression of isobutylene oligomerization and provides a possibility to vary the product distribution of glycerol ethers.

Some liquid acids (heteropolyacid and ionic liquid with Brønsted acidity) are immiscible/insoluble in higher ethers and thus have unique feature of suppressing the formation of tri-ethers of glycerol.

These catalytic characteristics give the possibility to tune within certain limits the yields of mono-, di-, and tri-ethers of glycerol at fixed IB/G ratios.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.10.014.

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