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Synthesis of long alkyl chain ethers through direct etherification of biomass-based alcohols with 1-octene over heterogeneous acid catalysts

Agnieszka M. Ruppert [a,1], Andrei N. Parvulescu [a], Maria Arias [a], Peter J.C. Hausoul [a,b], Pieter C.A. Bruijnincx [a], Robertus J.M. Klein Gebbink [b], Bert M. Weckhuysen [a,*]

[a] *Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3508 TB Utrecht, The Netherlands*
[b] *Chemical Biology & Organic Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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ABSTRACT

Heterogeneous etherification of various biomass-based alcohols with 1-octene was investigated as a direct route for the synthesis of long alkyl chain ethers. Several acid catalyst materials including Amberlyst resins and various zeolites were screened as etherification catalysts in a solventless system. It was found that H-Beta zeolites are the most selective catalysts for the etherification of biomass-based alcohols with 1-octene to the corresponding *mono*-ethers. With H-Beta the conversion of neat glycerol was around 15–20% and increased to 54–89% for glycols such as ethylene glycol and 1,2-propylene glycol, with high selectivities to *mono*- and *di*-octyl ethers of 85–97%. Other linear alkenes like 1-dodecene and 1-hexadecene were successfully employed in the direct etherification of glycols as well. Crude glycerol was also etherified, albeit with low conversions. The influence of several reaction parameters on the etherification activity of H-Beta has been investigated together with catalyst recovery and re-use.

1. Introduction

In recent years, a growing interest in the use of biomass as raw material for the chemical industry has developed [1,2]. Biomass is the primary renewable source of carbon besides carbon dioxide and can therefore be a sustainable alternative to the depleting fossil resources for the production of both transport fuels and chemicals [3]. In this way, new platform molecules can be obtained from biomass and further used as starting materials for bulk and fine chemicals [4,5]. In contrast to fossil-derived feedstock, some of these molecules are highly oxygenated compounds, such as polyols. An important example of the latter is glycerol. The increase in biodiesel production and development of the vegetable oil industry results in the production of glycerol in large quantities as a by-product. For example, about one kilogram of glycerol is obtained for each ten kilograms of biodiesel produced. In order to have a sustainable biodiesel production, new processes for the conversion of glycerol to value added products are absolutely necessary [2]. Besides glycerol other polyols, such as glycols, also represent important starting materials for various chemical syntheses and they are readily available from biomass sources via fermentation, thermochemical or catalytic processes [5].

Etherification of glycerol or bio-based glycols represents an important application, as it will directly afford compounds that can be used as either fuel additives [6], intermediates in the pharmaceutical industry, agrochemicals [7] or as non-ionic surfactants [2,8]. More specifically, the direct etherification with long linear alkenes like 1-octene will produce C8-chain *mono* and *di*-ethers which have valuable properties and potential large scale applications [9–13]. Indeed, C8 *mono*-ethers of glycerol or ethylene glycol in particular were found to present remarkable antimicrobial and antiseptic properties [13,10] and C8 *mono*-ethers of glycerol and glycols have in general found wide application as non-ionic surfactants or solvents [13,9,12,14].

Long alkyl ethers of glycerol are classically obtained indirectly using several synthetic steps or by employing environmentally hazardous compounds, using strong mineral acids or alkaline bases [15] as catalysts and alkyl chlorides as etherification agents. Corresponding alkyl ethers of ethylene glycol and propylene glycol are generally obtained using oil-based ethylene oxide or propylene oxide as starting materials [9]. These routes are not only time-consuming, but produce stoichiometric amounts of waste as well. Products with similar properties have been recently obtained by telomerization of 1,3-butadiene with glycerol and glycols, using homogeneous Pd/phosphine catalysts, but an extra hydrogenation step is needed in this case to obtain the saturated C8-ethers [16,17]. A direct one-step etherification process of glycols and glycerol with 1-octene catalyzed by a heterogeneous system is

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[*] Corresponding author. Fax: +31 30 251 1027.
E-mail address: b.m.weckhuysen@uu.nl (B.M. Weckhuysen).

[1] On leave from Institute of General and Ecological Chemistry, Technical University of Lodz, ul. Zeromskiego 116, 90-924, Lodz, Poland.

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therefore desired as it will represent a greener and more straightforward route to these valuable compounds.

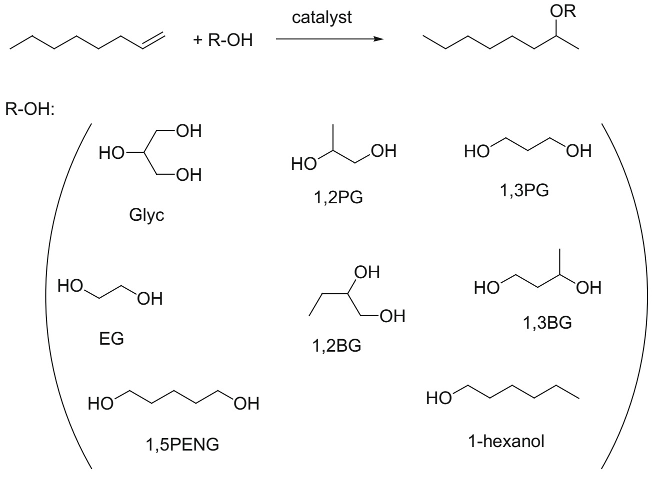
Until now most of the reports concerning heterogeneous etherification of such alcohols with alkenes involve the use of isobutene or butene [18,20], or cyclic alkenes [21] using acid catalysts such as ion-exchange resins, zeolites (i.e. H-Beta and HY) or mesoporous sulfonated silica. Recently, Corma and co-worker [19] reported the direct synthesis of the 1-octyl ether of methanol from the direct reaction of methanol with 1-octene in the presence of a homogeneous $AuCl_3/CuCl$ catalyst system. Knifton [12] reported the etherification of ethylene glycol and 1,2-propylene glycol with α-olefins over homogeneous heteropolyacid catalysts and a heterogeneous montmorillonite clay material. Both the homogeneous and heterogeneous acid catalysts presented high etherification activity for ethylene glycol, but needed to use an organic solvent and a continuous flow system and very low activities were reported for 1,2-propylene glycol. Surprisingly, there is no detailed investigation of the direct etherification of glycerol with long linear alkenes, although one report indicates H-Beta as an active catalyst for the etherification of glycerol with 1-dodecene [22].

Given the little attention hitherto paid to direct etherification and its large potential for biomass-based alcohol valorization, we have decided to investigate the direct synthesis of C8-chain *mono*- and *di*-ethers of glycerol and a number of renewable glycols from the reaction with 1-octene (Scheme 1). This complementary route would provide an attractive alternative to our research effort on glycerol, polyols and sugars telomerization [16]. The reactions were performed in a solventless system in the liquid phase and various commercial solid acids such as zeolites and ion-exchange resins were tested as heterogeneous etherification catalysts.

2. Experimental section

2.1. Chemicals and catalysts

Glycerol (>99%), 1,2-propylene glycol (>99%) and 1-octene (99+%) were purchased from Acros, while 1,3-propylene glycol (>99%) and ethylene glycol (>99%) were purchased from Fluka. Crude glycerol (15 wt.% water) was received as a gift from DOW Chemical. Amberlyst-70 was a gift from Sabic. The wet ion-exchange resin was washed with methanol and dried for 6 h at 60 °C before reaction. Zeolite NH_4^+-Beta (Si/Al = 12.5) CP814E, H-Beta (Si/Al = 37.5) CP811E, NH_4^+-ZSM-5 (Si/Al = 15) CBV3024E, H-Y (Si/Al = 40) CBV 910 were purchased from Zeolyst and NH_4^+-USY (Si/Al = 25) was a gift from Albermarle. The zeolites that were in the NH_4^+ form were calcined before reaction and transformed into the H^+ form. The following calcination program was used: heating from 25 °C to 500 °C with a rate of 1 °C/min and keeping the temperature at 500 °C for 6 h. From here on, zeolites will be denoted as e.g. H-Beta (37.5) instead of H-Beta (Si/Al = 37.5).



Scheme 1. Etherification of alcohols with 1-octene.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was performed using a Bruker-AXS D8 Advance powder X-ray diffractometer, equipped with automatic divergence slit, Våntec-1 detector and Cobalt Kα1,2 (λ = 1.79026 Å) source. The specific surface areas and pore volume were determined by N_2 sorption measurements using a Micromeritics ASAP 2400 instrument. Surface areas were calculated using the BET model.

2.3. Catalytic experiments and analytical methods

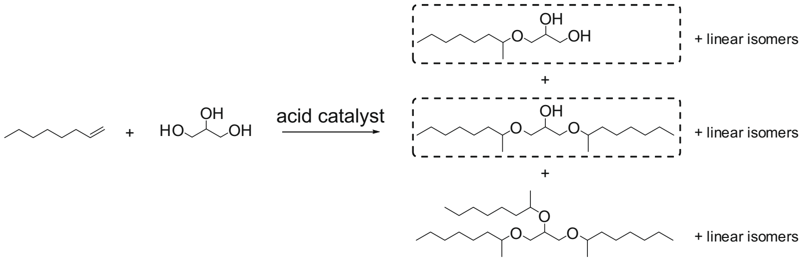
In a typical etherification reaction 0.12 mol of glycerol, 0.24 mol of 1-octene and 1 g of catalyst were loaded in a 100 mL stainless steel Parr autoclave. The autoclave was flushed with Ar three times and then pressurized with an additional 10 bar of Ar. The autoclave was heated to 120 °C or 140 °C under continuous mechanical stirring (750 rpm). The starting point of the reaction was taken when the autoclave reached the reaction temperature. When the reaction was considered finished, the autoclave was cooled to 40 °C and the reaction mixture was dissolved in a known amount of ethanol. The catalyst was separated by filtration, and a sample of the solution was taken for further analysis. The conversions were calculated using a GC 2010 system from Shimadzu with a CP-WAX 57CB column (25 m × 0.2 mm × 0.2 μm). Identification of the products was done by a GC–MS from Schimadzu with a Supelcowax 10 column (30 m × 0.2 mm × 0.2 μm) and a HPLC-ESI-MS from Schimadzu with a CP-WAX 57CB column (25 m × 0.2 mm × 0.2 μm). Since the main product of glycerol etherification (mono octyl-ether (3-(2-octyloxy)propane-1,2-diol) (C8Glyc)) is not commercially available, it was isolated and purified by column chromatography. The purity was checked by ^{13}C NMR, ^{1}H NMR, and GC–MS. Calibration was done using the pure compound and the correction factor of the *mono*-ether was considered to be the same for the *di*-ether and other by-products. The same procedure was used for the other tested alcohols.

3. Results and discussion

3.1. Catalyst screening

As part of our recent efforts aimed at catalytic glycerol valorization, the etherification of glycerol with 1-octene was chosen as a test reaction. The aim was to develop an alternative route for the synthesis of long alkyl chain ethers complementary to our previous telomerization studies [16]. Solid acid catalysts, such as zeolites and ion-exchange resins, were previously reported as active catalysts for the etherification of glycerol with isobutene [18,20]. Therefore, these solid acids were screened in the direct etherification of glycerol with 1-octene and the catalytic activities were benchmarked against a homogeneous acid catalyst, *para*-toluene sulfonic acid (*p*TSA). The etherification reactions were performed at 120 °C or above since no significant conversion to octyl-ethers was observed at lower temperatures for any of the tested catalysts. The reaction time was fixed at 10 h. The conversions and yields were calculated based on glycerol.

Etherification of glycerol with 1-octene over the acid catalyst can result in the formation of a mixture of *mono*-, *di*- and *tri*-ethers according to Scheme 2 and, additionally, in the formation of some



Scheme 2. Etherification of glycerol with 1-octene over acid catalysts. *Tri*-octyl ether of glycerol was not observed as a reaction product.

unwanted by-products (vide infra). The product distribution was found to depend strongly on the type of acid catalyst employed. The only observed octyl-ethers of glycerol were the *mono*-ether C8Glyc and *di*-ether C16Glyc, however. The *tri*-octyl ether of glycerol was not formed, most probably because of steric constrains. Since at temperatures above 120 °C 1-octene is in equilibrium between the liquid and the gas phase, glycerol is essentially found in excess in the liquid phase and the reaction will proceed according to the mechanism proposed by Françoise and Thyrion [23] for the etherification of ethanol with isobutene [24]. The alcohol is protonated first and further reaction with the alkene regioselectively gives the C8Glyc and C16Glyc as branched isomers (>95%) with only small traces of linear and mixed linear-branched ethers (<5%) (Scheme 2).

The results of the catalyst screening are presented in Table 1. In the absence of a catalyst (Table 1, entry 1) no conversion was observed irrespective of the reaction conditions. Since water is known [20a] to decrease the activity of etherification catalysts, all catalysts were dried and the reaction mixture was flushed with Ar. The catalytic etherification activities of Amberlyst-70 and *p*TSA were found to be similar (Table 1, entries 2–7). With both catalysts selectivities below 20% to the glycerol octyl-ethers were obtained. C8Glyc was formed with low selectivity and only traces of C16Glyc could be detected with both catalysts, as unwanted by-products made up most of the product. The selectivity for C8Glyc was 12% over Amberlyst-70 at 120 °C, and remained the same with an increase of temperature to 140 °C (entries 2 and 3). The increase in temperature was found to affect only the conversion, which increased from 12% to 38% for Amberlyst-70 (Table 1, entries 2 and 3). As a homogeneous counterpart of Amberlyst-70, the use of *p*TSA resulted in higher conversions of glycerol and also in a higher selectivity to C8Glyc (Table 1, entries 5–7). It should be noted that 1 g of *p*TSA contains 5.81×10^{-3} moles of sulfonic acid groups, whereas 1 g of Amberlyst-70 contains 2.55×10^{-3} moles of acid groups. Therefore, using the same weight loading of catalyst, already at 120 °C the glycerol conversion was 22% with *p*TSA (compared to 12% for Amberlyst-70) and at 140 °C conversion reached 57% (Table 1, entries 2–6). Nonetheless, the homogeneous acid was still more active than Amberlyst-70 even when an equivalent concentration of acid species was used (Table 1, entries 3 and 7). As in the case of Amberlyst-70, by-products were predominantly formed, with selectivities higher than 70%.

In contrast to the results obtained with either Amberlyst-70 or *p*TSA, C8Glyc and C16Glyc were obtained as the main products in the etherification of glycerol with 1-octene when zeolites were employed as heterogeneous catalysts (Table 1, entries 8–18). H-Beta zeolites gave the best etherification activities, with excellent selectivities to the octyl-ethers of glycerol, particularly to the desired C8Glyc. Two H-Beta zeolites with a different Si/Al ratio were tested in the etherification of glycerol to assess their influence on conversion and product distribution (Table 1, entries 8–15). H-Beta (12.5) gave the highest conversion of glycerol at 140 °C, namely

Table 1
Screening of acid catalysts for etherification of glycerol with 1-octene.

Entry	Catalyst	*T* (°C)	Conversion[a] (%)	$\text{Selectivity}_{\text{C8Glyc}}$ (%)	$\text{Selectivity}_{\text{C16Glyc}}$ (%)	$\text{Selectivity}_{\text{other}}$ (%)
1	Blank	140	0	–	–	–
2	Amberlyst-70	120	12	12	0	88
3		140	38	11	1	88
4		140[b]	17	9	1	90
5	pTSA	120	22	20	3	77
6		140	57	19	2	79
7		140[c]	45	19	1	80
8	H-Beta (37.5)	120	10	72	16	12
9		140	14	79	12	9
10		160	14	54	8	38
11		140[b]	13	81	12	7
12		140[d]	17	78	15	7
13	H-Beta (12.5)	140	15	80	14	6
14		140[b]	12	84	13	3
15		140[d]	19	81	14	5
16	H-Y (40)	140	12	47	12	41
17	USY (27.5)	140	10	75	12	13
18	H-ZSM-5 (15)	140	1	83	5	12

Standard etherification conditions: 1 g catalyst, 10 h reaction, 10 bar Ar, 1-octene:glycerol 2:1.

[a] Conversion of glycerol.

[b] 5 h.

[c] 0.5 g of *p*TSA.

[d] Molar ratio 3:1.

15% as well as the highest selectivity for the octyl-ethers (94%). C8Glyc was obtained as the main product with a selectivity of 80% (Table 1, entry 13). A slightly lower conversion of 14% and selectivity of C8Glyc of 79% was obtained at 140 °C with a zeolite with a higher Si/Al ratio, H-Beta (37.5) (Table 1, entry 9). H-USY (27.5) and H-ZSM-5 (15) (Table 1, entries 17 and 18) were less active in the etherification of glycerol with 1-octene, yet the selectivity to octyl-ethers remained high, above 90%. For H-Y (40) a conversion of glycerol of 12% was reached, but compared to the other zeolites the selectivity to C8Glyc dropped to 47%, while the selectivity to C16Glyc remained around 12% (Table 1, entry 16). The screening of the different zeolites clearly indicated that H-Beta zeolites are the most promising etherification catalysts for this particular reaction.

The optimal reaction temperature for the etherification activity of H-Beta zeolites was found to be 140 °C. For H-Beta (37.5), a lower temperature gave a lower conversion, whereas at 160 °C the selectivity to by-products increased rapidly from 13% to 38% (Table 1, entries 8–10). A higher reaction temperature did not increase the amount of *di*-ethers which is in contrast with the results obtained for Beta zeolites in the etherification of glycerol with isobutene [20a]. Inherent differences in reactivity between 1-octene and isobutene and the size of the product may prevent an increase in the amount of C16Glyc in this case. Decreasing the reaction time from 10 h to 5 h had very little influence on the conversion of glycerol with H-Beta (37.5), i.e. 13% instead of 14% (Table 1, entry 11). For H-Beta (12.5) the conversion of glycerol dropped to 12% from 15% but the selectivity to C8Glyc slightly increased to 84% (Table 1, entry 14). Increasing the alkene to glycerol molar ratio to 3:1 improved the etherification activity of both H-Beta zeolites (Table 1 entries 12 and 15). The conversion increased from 14% to 17% for H-Beta (37.5) where it reached 19% for H-Beta (12.5). In both cases the selectivity for C8Glyc remained around 80%.

3.2. Substrate scope and product selectivity

The initial catalyst screening for glycerol etherification activity with 1-octene indicated that H-Beta zeolites presented a high selectivity to the octyl-ethers, whereas Amberlyst-70 and *p*TSA showed higher conversions of the alcohol but a very low selectivity to the desired products. To follow up on this encouraging lead, we intended to explore the substrate scope of the system. Indeed, besides glycerol, other alcohols are also easily available from biomass and may form ethers with non-ionic surfactant properties [12] (Table 2).

For all substrates higher yields of ethers were obtained compared to glycerol. The conversions and selectivities to the octyl-ethers were influenced by both the alcohol and the catalyst that was used.

In fact, the change of substrate increased the etherification activity considerably for the H-Beta zeolites, while maintaining the high selectivity for the octyl-ethers (Table 2, entries 6–18). Conversions between 40% and 90% were obtained using the two H-Beta zeolites depending on the alcohol. These conversions are considerably higher than those obtained for glycerol for which maximum conversion under the same conditions was 16% (Table 2, entry 6).

Similar conversions of 70% were obtained for both H-Beta zeolites in the etherification of ethylene glycol (EG) (Table 2, entries 7 and 12). H-Beta (37.5) gave a higher selectivity for the *di*-ether (21%), where H-Beta (12.5) presented an excellent selectivity (81%) for the *mono*-ether. 1,2-Propylene glycol (1,2PG) also proved a very good substrate for the etherification with 1-octene with both H-Beta zeolites. With H-Beta (12.5) a 76% conversion of 1,2PG was obtained after 5 h of reaction and the selectivity to C8-ether was 82%. For H-Beta (37.5) the conversion was 87%, but the selectivity to C8-ether dropped to 70% (Table 2, entries 8 and 13). For 1,2-butylene glycol (1,2BG) a lower conversion of the alcohol (59%) was obtained with H-Beta (12.5), but the selectivity for the C8-ether increased to 90%. In contrast, H-Beta (37.5) presented the highest conversion when 1,2BG was used as a substrate, i.e. 89% after just 5 h of reaction. The selectivity for the C8-ether was still 76% in this case (Table 2, entry 15). 1,3-Propylene glycol (1,3PG) turned out to be a more difficult substrate for both H-Beta zeolites, as conversions of 52% and 46% were obtained for H-Beta (12.5) and H-Beta (37.5), respectively (Table 2, entries 9 and 14). Other glycols, 1,3-butylene glycol (1,3BG), for example, could also be successfully etherified with H-Beta (37.5) (Table 2, entry 16). Larger alcohols, like 1,5-pentylene glycol (1,5PENG) and 1-hexanol, were also etherified with 1-octene with good results (Table 2, entries 17 and 18). The conversion of 1,5-pentene glycol was 71% over H-Beta (37.5) again with a very high selectivity for the C8-ether of 92% (Table 2, entry 17); 1-hexanol selectivity for the C8-ether was 91%.

Although the selectivity to C8-ethers was somewhat higher for the glycols than for glycerol with Amberlyst-70 and *p*TSA, the by-

Table 2
Substrate screening in etherification with 1-octene.

Entry	Catalyst	Substrate	Conversion (%)	$\text{Selectivity}_{\text{c8-ether}}$ (%)	$\text{Selectivity}_{\text{c16-ether}}$ (%)	$\text{Selectivity}_{\text{other}}$ (%)
1	pTSA	Glycerol	40	10	2	88
2		1,2PG	80	42	8	50
3	Amberlyst	Glycerol	35	5	1	93
4		EG	68	33	1	66
5		1,2PG	85	26	7	67
6	H-Beta (12.5)	Glycerol	16	83	13	3
7		EG	70	81	17	2
8		1,2PG	76	82	6	9
9		1,3PG	51	70	11	19
10		1,2BG	59	90	3	7
11	H-Beta (37.5)	Glycerol	14	78	14	8
12		EG	71	74	21	4
13		1,2PG	87	70	17	13
14		1,3PG	46	78	12	10
15		1,2BG	89	76	13	12
16		1,3BG	54	71	14	15
17		1,5PENG	71	92	5	3
18		1-Hexanol	65	91	–	9

Reaction conditions: 1 g catalyst, 0.12 mol substrate, 0.36 mol 1-octene, 140 °C, 5 h, 10 bar Ar.

products were still formed predominantly (Table 2, entries 1–5). For 1,2-propylene glycol (1,2PG) a conversion of 80% was obtained with *p*TSA with a selectivity of just 42% for the *mono*-ether. As previously observed, *p*TSA was generally more selective than Amberlyst-70. The conversion of 1,2PG was 85% with Amberlyst-70, but the selectivity for the C8-ether just 26%. Like in the case of glycerol, with both *p*TSA and Amberlyst-70 the *di*-ether was formed with very low selectivities (Table 2, entries 1–5).

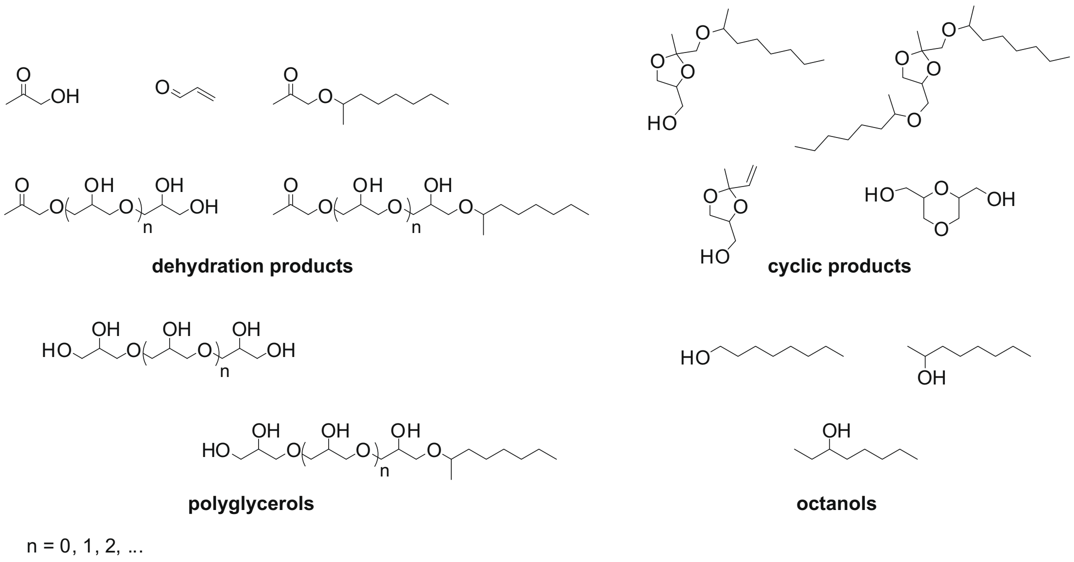
The size of the alcohol and the hydrophilic/hydrophobic properties clearly influence the etherification activity of the heterogeneous catalysts. Glycols are more hydrophobic than glycerol [25] and in the absence of a solvent they will mix better with the alkene. The hydrophobic character increases in the series glycerol < ethylene glycol < 1,2-propylene glycol < 1,2-butylene glycol. The activity of the etherification catalysts is following a similar trend. For *p*TSA and Amberlyst-70 the conversion increased from glycerol towards 1,2PG. The same trend was observed for H-Beta zeolites with few exceptions. With 1,5PENG and 1-hexanol smaller conversions were obtained even though these alcohols are the most hydrophobic ones. The size of the alcohol and of the products may be responsible for this exception.

In addition to the physicochemical properties of the alcohol, the catalyst properties are also very important. For instance, *p*TSA and Amberlyst-70 are more hydrophilic than H-Beta zeolites. This difference is reflected in the product distribution over these materials and especially by the high amounts of by-products, which were obtained for *p*TSA and Amberlyst-70. Particularly for glycerol the selectivity for these by-products can go up to 90%. A closer look at the type of by-products (Scheme 3) shows that most of them are formed by glycerol dehydration, condensation or etherification of the polyglycerols. Moreover, the interaction with glycerol is enhanced by the highly hydrophilic character of Amberlyst-70 [26] making the adsorption of 1-octene on the catalyst more difficult. Indeed, Amberlyst catalysts are highly hydrophilic materials that are known to concentrate polar compounds such as alcohols in their structure [24,27]. Polyglycerol ethers were also found in the complex mixture of products in the reaction catalyzed by *p*TSA and Amberlyst-70. They were found to be formed from the etherification of polyglycerols and not from successive reactions of C8Glyc as indicated by the results obtained after 5 h of reaction with Amberlyst-70. The polyglycerols consist mostly of tetra- or penta-glycerol units and their formation was favored by the macroporous structure of Amberlyst-70. The same types of by-products were obtained for the other glycols with Amberlyst-70 and *p*TSA, albeit to a lesser extent (Table 2, entries 1–5).

Only small amounts of by-products were obtained for H-Beta zeolites (Tables 1 and 2). Dehydration products and traces of polyglycerol derivatives were obtained in the etherification of glycerol with H-Beta zeolites with selectivities below 10% (Table 2, entries 6–11). The C8Glyc was predominantly formed with selectivities around 80% and only a small amount of bulky polyglycerols of low oligomerization degree (two to maximum three glycerol units). The uniform microporous structure of H-Beta, with pore dimensions of around 7.5 Å, is thus likely inducing a shape selectivity effect. In addition to the shape selectivity effect, the selectivity is influenced by the fact that due to its high Si/Al ratio H-Beta is more hydrophobic than Amberlyst-70. Furthermore, H-Beta also has a higher surface area. Indeed, the nitrogen sorption measurements indicated that the tested H-Beta had surface areas higher than 500 m^2/g whereas for Amberlyst-70 this amounted to just 36 m^2/g. Both the hydrophobic properties and the high surface area allow a better adsorption of 1-octene over H-Beta zeolites compared with Amberlyst-70. The low selectivity for the by-products of H-Beta zeolites was kept for the other alcohols as well. For glycols the main by-products were found to be dehydration products, cyclic products and low oligomers of the alcohols. The different Si/Al ratio influences the etherification activity of the two zeolites. With H-Beta (12.5) the etherification activity with hydrophilic substrates, like glycerol or 1,3-propylene glycol was higher compared to the one of H-Beta (37.5) for the same substrates. Also the selectivity for the C8-ether of H-Beta (12.5) was always higher compared to H-Beta (37.5). As a result of its higher Si/Al ratio, H-Beta (37.5) has both a higher acid strength and is more hydrophobic. As a result, higher conversions are obtained with more hydrophobic alcohols like 1,2PD and 1,2BD (table 2, entries 13 and 15). The C16-ethers were also formed in higher amounts since the C8-ether can more easily interact with the more hydrophobic H-Beta (37.5) and be further transformed. This indicates that an optimum combination between the properties of the catalyst and substrate must be achieved in order to have a maximum yield of desired product.

3.3. Influence of the reaction parameters on the etherification activity of H-Beta zeolites

Since the reactions were carried out in the absence of a solvent it was essential to exclude any influence of external mass transfer



Scheme 3. Observed by-products of glycerol etherification with 1-octene.

limitation on the performance of the heterogeneous catalysts. The influence of stirring speed and the amount of catalyst on the etherification activity was therefore carefully analyzed. An extra pressure of inert gas (10 bar Ar) was used in order to maintain 1-octene in the liquid phase during the whole reaction.

The most sensible substrate to study the possible influence of external mass transfer limitations is certainly glycerol as it is the most viscous and hydrophilic of the tested alcohols. Above 500 rpm no influence of stirring rate on conversion of glycerol was observed (Table 3, entries 1 and 2). Using a lower stirring rate like 200 rpm resulted in both a lower conversion and selectivity for the C8Glyc (Table 2, entry 3). A stirring rate of 750 rpm was therefore subsequently employed in all the etherification reactions. The influence of the amount of catalyst was also checked. A loading 1 g of zeolite proved to be the optimum amount in order to have a good combination of conversion and selectivity for etherification of the various alcohols (Table 3, entries 1, 4–9). For both glycerol and ethylene glycol the conversion increased linearly with the amount of catalyst which suggests that the reaction is not influenced by external mass transfer limitations.

The effect of the 1-octene to glycerol molar ratio was already pointed out to influence the etherification activity of H-Beta zeolites (see Table 1). Since no solvent is used it is necessary to adjust the ratio between the two reactants to optimize the access to the active sites of the catalyst and desorption of the reaction products. The influence of the 1-octene:alcohol molar ratio was exemplified in the etherification of glycerol and 1,2-propylene glycol with 1-octene over H-Beta (12.5). A 1:1 molar ratio led to a lower conversion for both alcohols (Table 4, entries 1 and 5). An increase of the 1-octene:alcohol molar ratio to 3:1, resulted in higher conversions for both substrates. A 6% and 20% increase of conversion was obtained for glycerol and 1,2PG, respectively (Table 4, entries 1–3 and 5–7). Besides conversion, also the selectivity for the C8-increases for both alcohols (>80%) with an increase of the 1-octene:alcohol molar ratio to 3:1. Further increase of the 1-octene amount gave rise to a decrease in the conversion of the two alcohols.

3.4. Catalyst recovery and re-use

The reduced etherification activity of the H-Beta catalysts in the etherification of glycerol with 1-octene is most probably caused by deactivation of the catalyst due to the formation of some coke-like compounds. After the reaction a change in color of the H-Beta catalysts was observed. The brown-yellow color is more pronounced in the case of glycerol compared with the other alcohols and with an increase in the Si/Al ratio. Most probably this change of color is caused by the oligomerization of the alkene on the acid catalyst and irreversible adsorption of these products. Similarly, oligomerization of isobutene was previously observed in the etherification of glycerol even at reaction temperatures of 90 °C [20a]. Recent reports also suggest that glycerol and its polyglycerols may irreversibly adsorb on the zeolite [28]. Irreversible adsorption of glycerol was found to be less than 2% in our studies, but the complex mixture of polyglycerols and etherified polyglycerols (Scheme 3) may irreversibly adsorb and deactivate the solid catalyst. Further spectroscopic work is currently ongoing to identify the species that are causing this deactivation and to elucidate how the process occurs.

The deactivation of the H-Beta zeolites was followed in time for four alcohols (Fig. 1). The strongest deactivation was found for glycerol where after 15 h of reaction conversion reached a maximum of 22% (Fig. 1a). From 5 h to 15 h the conversion increases with 6% and the selectivity to C8Glyc slightly decreased from 83% to 81%. For the glycols tested deactivation of the H-Beta catalyst is less pronounced (Fig. 1b–d), as conversions over 72% are being easily obtained. A maximum in conversion different for each of the alcohols was obtained after 10 h of reaction. For example, the conversion reached 90% after 10 h for 1,2PG (Fig. 1c) and just 72% for EG. In time the selectivity for C8-ether is slightly decreasing and an increase of the C16-ether selectivity and by-products was observed.

In order to investigate if the deactivation of the zeolite was reversible, the catalyst was recovered and re-used. The recovered H-Beta (37.5) presented a lower etherification activity for glycerol in the second run, with a 70% loss of the initial activity (Table 5,

Table 3
Stirring speed and catalyst weight influence on the etherification activity of H-Beta (37.5).

Entry	Substrate	Weight catalyst (g)	Stirring rate (rpm)	Conversion (%)	Selectivity$_{C8\text{-}ether}$ (%)	Selectivity$_{C16\text{-}ether}$ (%)	Selectivity$_{other}$ (%)
1	Glycerol	1	750	12	84	13	3
2		1	570	12	83	13	4
3		1	200	6	75	8	17
4		0.5	750	8	81	14	5
5		1.6	750	15	79	13	9
7	EG	0.5	750	34	92	6	2
8		1	750	61	80	18	2
9		2	750	72	64	31	5

Reaction conditions: 5 h, 1-octene:substrate 2:1, 140 °C, EG – ethylene glycol.

Table 4
Molar ratio 1-octene:alcohol *versus* the etherification activity of H-Beta (12.5).

Entry	Catalyst	1-Octene:alcohol[a]	Conversion (%)	Selectivity$_{C8\text{-}ether}$ (%)	Selectivity$_{C16\text{-}ether}$ (%)	Selectivity$_{other}$ (%)
1	Glycerol	1:1	10	71	12	17
2		2:1	12	84	13	3
3		3:1	16	83	13	3
4		5:1	11	82	16	2
5	1,2PG	1:1	57	80	9	11
6		2:1	62	86	7	7
7		3:1	76	82	6	9
8		5:1	61	86	4	10

Reaction conditions: 1 g catalyst, 5 h, 10 bar Ar, 140 °C.
[a] Molar ratio 1-octene:alcohol.

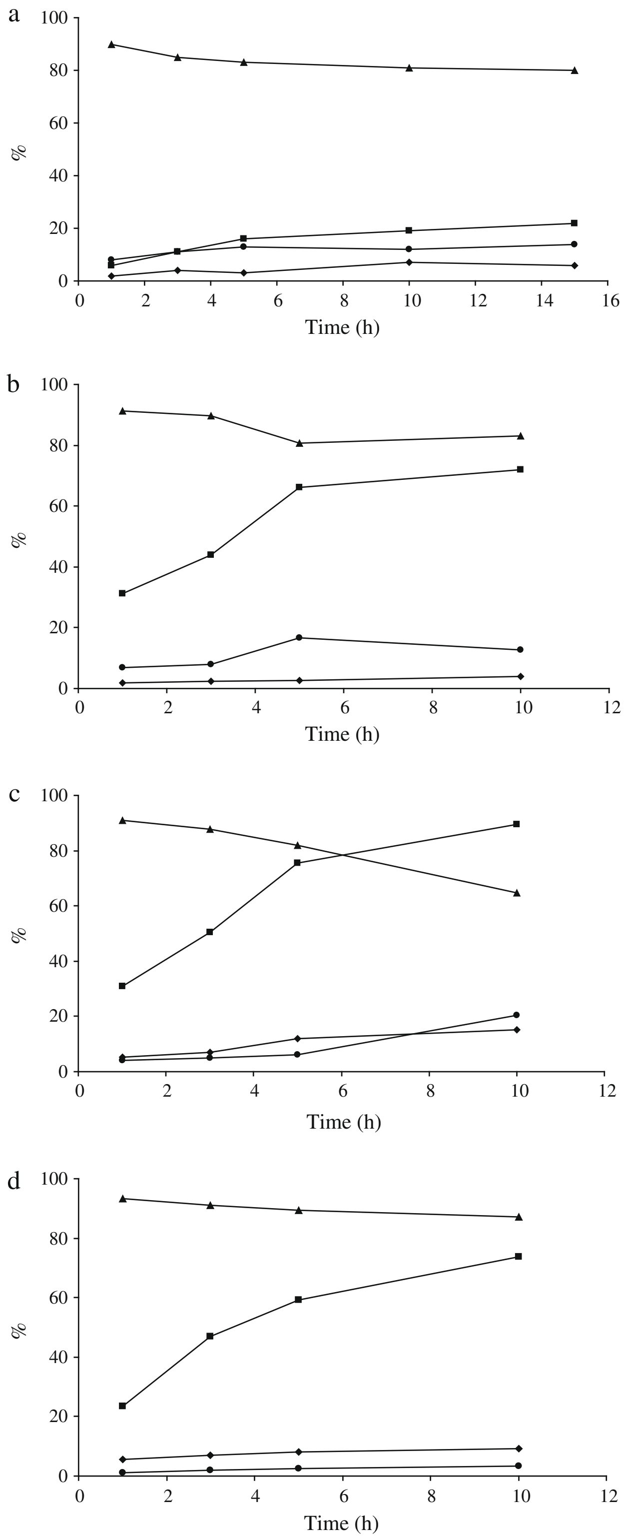


Fig. 1. Time vs. etherification of various substrates with 1-octene over H-Beta (12.5) at 140 °C, 10 bar Ar, 1-octene:alcohol 3:1, (a) glycerol; (b) ethylene glycol; (c) 1,2-propylene glycol; (d) 1,2-butylene glycol; ■ – conversion (%), ▲ – selectivity of C8-ether (%); ● – selectivity of C16-ether (%); ♦ – selectivity to other products. The lines are intended as visual aid only.

entries 1 and 3). However, calcination of the zeolite could restore the initial etherification activity completely. In this way, H-Beta (37.5) was successfully recovered and re-used for 3 reaction cycles in the etherification of glycerol with 1-octene. Both conversion and yield of C8Glyc and C16Glyc were found to remain the same (Table 5). XRD measurements indicated that neither the calcination nor the etherification reaction did affect the structure of the zeolite. The re-use of H-Beta (12.5) was also attempted for 1,2PG. As was previously observed from the conversion-time profile for the etherification of 1,2PG, the deactivation of the H-Beta (12.5) is much less pronounced compared to glycerol. The recovery and re-use of the zeolite confirmed this observation. After a second reaction cycle the conversion of 1,2PG was 57% with 90% selectivity for the C8-ether. This corresponds to a drop of 25% of the initial conversion. In a third reaction cycle conversion dropped further to 40%, which nonetheless still represents more than 50% of the initial activity (Table 5, entries 5–7). The type of the alcohol thus influences the extent of deactivation of the H-Beta zeolite and this process is less pronounced for glycols.

3.5. Control of the alkyl chain length

Since our goal is to synthesize compounds with possible non-ionic surfactant applications it would be interesting if ethers with various lengths of the alkyl chain may be obtained. It is known that ethers with chain lengths of C10 or C16 have already found many applications as non-ionic surfactants [9]. Therefore, in addition to 1-octene, alkenes with longer alkyl chain such as 1-dodecene and 1-hexadecene were also tested in the etherification of 1,2PG over H-Beta (12.5) (Table 6). Good conversions after 5 h of reaction and selectivities to the *mono*-ether over 90% were obtained with 1-dodecene and 1-hexadecene (Table 6). The conversion was 71% when 1,2PG was etherified with 1-dodecene and dropped to 46% for 1-hexadecene. With a shorter alkene like 1-hexene the selectivity for the *mono*-ether was just 55% and the *di*-ether was obtained with 40% selectivity. On the contrary, with 1-hexadecene no *di*-ether was obtained at all. The selectivity for the *mono*-ether was therefore found to increase with the chain length of the alkene (Table 6). This result may be correlated with the literature data for etherification of glycerol with isobutene where very high selectivities for the *di*-ethers are normally obtained with H-Beta zeolites [20]. Also the properties of the H-Beta (12.5) may influence this selectivity since it was already shown that this zeolite presented a higher selectivity for the *mono*-ether due to its hydrophilic/hydrophobic properties. With increasing the chain length the interaction of the *mono*-ether with the zeolite may therefore decrease and higher selectivities for the *mono*-ether are obtained.

3.6. Etherification of crude glycerol

Crude glycerol coming from a caustic catalyzed methanolysis plant was also tested in the etherification with 1-octene over H-Beta zeolites (Table 7). When crude glycerol was used as such (Table 6, entry 2) no catalytic activity was observed. Some etherification activity, i.e. 3% conversion, was obtained by partially drying the crude glycerol prior reaction (Table 6, entry 3). This aqueous (15 wt.%) alkaline solution of glycerol affects both the acidity of the zeolite and its structure upon heating [28]. We observed that the presence of the alkali metal in crude glycerol (as alkali salts, soaps, unreacted base), is detrimental for the catalytic activity of H-Beta. That the poisoning effect is due to the alkali metal residues rather than the large amount of water in crude glycerol is further illustrated by the results obtained from the etherification of a 15 wt.% water solution of neat glycerol. Indeed, the etherification activity of the H-Beta (12.5) was not influenced by the presence of water (Table 6, entries 1 and 4) and the selectivity to C8Gly remained around 84%. In order to pinpoint the poisoning effect of the alkali ions on the zeolite etherification activity further tests were performed in which the alkali metal content was controlled. Alkali metals may be found in the crude glycerol as salts of the fatty acids,

Table 5
Re-use of H-Beta zeolites in the etherification of glycerol with 1-octene.

Substrate	Run		Conversion (%)	Selectivity$_{C8\text{-}ether}$ (%)	Selectivity$_{C16\text{-}ether}$ (%)	Selectivity$_{other}$ (%)
Glycerol	1	Fresh	14	78	14	8
	2	Calcined	13	80	13	7
	2	Uncalcined	4	75	11	14
	3	Calcined	14	79	12	9
1,2-PG	1	Fresh	76	82	6	9
	2	Uncalcined	57	90	3	7
	3	Uncalcined	40	91	3	6

Reaction conditions: 1 g of catalyst, 1-octene:glycerol 3:1, 5 h, 10 bar Ar, 140 °C.

Table 6
Alkene screening in etherification of 1,2PG over H-Beta (12.5).

Alkene	Conversion (%)	Selectivity$_{mono}$ (%)	Selectivity$_{di}$ (%)	Selectivity$_{other}$ (%)
1-Hexene	56	55	40	5
1-Octene	76	82	6	9
1-Dodecene	71	93	3	3
1-Hexadecene	46	90	0	10

Reaction conditions: 1 g catalyst, 0.12 mol substrate, 0.36 mol alkene, 140 °C, 5 h, 10 bar Ar.

Table 7
Crude glycerol etherification with 1-octene over H-Beta (12.5).

Entry	Substrate	Conversion (%)	Selectivity$_{C8Glyc}$ (%)	Selectivity$_{C16Glyc}$ (%)	Selectivity$_{other}$ (%)
1	Glycerol	12	84	13	3
2	Glycerol[a]	0	–	–	–
3	Glycerol[b]	3	90	3	7
4	Glycerol[c]	13	83	13	4
5	Glycerol[d]	0	–	–	–
6	Glycerol[e]	5	9	3	88

Reaction conditions: 1 g catalyst, 1-octene:glycerol 2:1, 5 h, 10 bar Ar, 140 °C.
[a] Crude glycerol.
[b] Partially dried crude glycerol.
[c] 15 wt.% aqueous glycerol solution.
[d] 86 wt.% glycerol, 10 wt.% water, 2 wt.% sodium oleate, 2 wt.% NaCl.
[e] 86 wt.% glycerol, 10 wt.% water, 2 wt.% hexanoic acid, 2 wt.% NaCl.

inorganic salts or residual catalyst. Therefore, solutions of glycerol containing water and sodium salts were prepared (Table 6, entries 5 and 6). When a solution of glycerol containing 2 wt.% of sodium oleate and 2 wt.% of sodium chloride was used no transformation of the glycerol was observed. By replacing the sodium oleate with hexanoic acid, some etherification activity was restored and in addition to the octyl ethers some glycerol esters of hexanoic acid were formed. Therefore, the use of crude glycerol resulting from a heterogeneous biodiesel synthesis process is expected to avoid such deactivation problems.

4. Conclusions

The direct etherification of glycerol and glycols with 1-octene in a solventless system is possible by using heterogeneous acid catalysts. The type of the solid acid used strongly influences the activity and selectivity of the etherification process. Several factors were found to influence the activity and selectivity of the acid catalysts in the etherification of glycerol with 1-octene. Foremost, hydrophilicity and pore structure of the catalyst turned out to be the critical parameters. Optimization of other parameters, like reaction time, stoichiometry of reactants, reaction temperature, and the addition of an inert gas resulted in an improved etherification activity of the catalyst as well. H-Beta zeolites proved to be the most selective etherification catalysts, whereas for Amberlyst-70 mainly by-products were formed. Maximum conversions of 19% with 93% selectivity to the octyl-ethers were obtained in the etherification of glycerol with 1-octene over H-Beta zeolites, more particularly with H-Beta (12.5). Switching to other biomass-based alcohols such as glycols resulted in a strong increase in the etherification activity of the H-Beta zeolites, while maintaining the very high selectivity toward the desired octyl-ethers. Conversions up to 89% were obtained for 1,2PD and 1,2BD with H-Beta zeolites and selectivities for the octyl-ethers over 90%. Using alkenes with longer alkyl chains like 1-dodecene and 1-hexadecene also proved possible with the H-Beta zeolites. Crude glycerol was also etherified, albeit with low conversions and the alkaline nature of the substrate was demonstrated to be responsible for this low activity. The H-Beta catalysts were recovered and re-used for three reaction cycles in the etherification of both glycerol and a glycol substrate. These results show the potential of using heterogeneous acid catalysts for the green synthesis of valuable long alkyl *mono*- or *di*-ethers of various bio-based alcohols.

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