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Synthesis of octyl-ethers of biomass-based glycols through two competitive catalytic routes: Telomerization and etherification

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Increasing interest in biomass valorization has triggered a worldwide search for new catalytic routes to transform biomass-based derivatives in transportation fuels and valuable chemicals. It is anticipated that in most cases more than one catalytic pathway can be followed for the synthesis of the desired end products. One such example is the synthesis of octyl-ethers from biomass-based glycols, which can be made either via the telomerization of 1,3-butadiene or the direct etherification of long linear alkenes. For both processes active and selective catalysts have been developed in our groups and their activity and selectivity have been investigated under solvent-free conditions. The telomerization of 1,3-butadiene affords *linear* octyl-ethers with high yields (up to 80%) with a homogeneous Pd/TOMPP (TOMPP = Tris-(*o*-methoxyphenyl)phosphine) catalyst. For the direct etherification of glycols with 1-octene H-Beta zeolites were found to be very promising heterogeneous catalysts to produce *branched* octyl-ethers with yields up to 80%. In this work, a detailed account of the influence of catalyst properties and glycol structure is given and the advantages and disadvantages of both catalytic routes are discussed.

1. Introduction

Biomass valorization has attracted great interest in recent years mainly due to environmental concerns, diminishing crude oil reserves and the increasing demand for transportation fuels and chemicals [1,2]. In the context of a sustainable chemical industry (partially) based on biomass, efficient catalytic technologies have to be developed for the further conversion of biomass-based derivatives into valuable bulk and fine chemicals [1–3]. Besides being greener, the new processes need to create economically attractive value chains based on these biomass-based intermediates. These so-called platform molecules can be obtained from biomass via chemical and/or enzymatic processes. Many of these compounds are highly oxygenated, such as the glycols [4]. Ethylene glycol and propylene glycol are well known examples of such glycols and they have found numerous important applications in chemical industry as building blocks for the synthesis of various valuable chemicals [4c]. In this sense the development of new routes for transforming these and other biomass-based glycols into valuable products through 100% atom-efficient catalytic processes is of major importance.

One way to valorize these glycols is through their transformation into C8 alkyl chain ethers since these products can have important applications such as antimicrobial or antiseptic agents, precursors for polymers, solvents or surfactants [5–10]. Two catalytic routes were recently proposed for the synthesis of such bio-based long alkyl chain ethers; i.e., the telomerization of 1,3-butadiene and the direct etherification with long linear alkenes [11–13]. Both routes can in principle yield the desired ethers with 100% atom efficiency, as illustrated in Scheme 1. In fact, the telomerization of 1,3-butadiene is a process that is already industrially applied for the synthesis of 1-octanol and 1-octene [12,14]. Various homogeneous Pd complexes with phosphines or carbenes ligands are generally used as catalysts [11,12]. Furthermore, the telomerization of 1,3-dienes with biomass-based derivatives, such as alcohols, glycerol, carbohydrates and glycols, has attracted large attention recently as a viable route to valorize these compounds. In this context, we recently introduced a very active telomerization catalyst based on a Pd/TOMPP (TOMPP = Tris-(*o*-methoxyphenyl)phosphine) complex [11,15].

The direct etherification of alcohols with longer linear alkenes, on the other hand, has received rather little attention [8,16]. Recently, we have identified and reported after a large screening of heterogeneous acid catalysts that H-Beta zeolites are very promising catalysts for the etherification of biomass-based alcohols and glycols [13]. The reaction resulted in the formation of saturated C8 ethers with a high selectivity for the desired mono-ether. The

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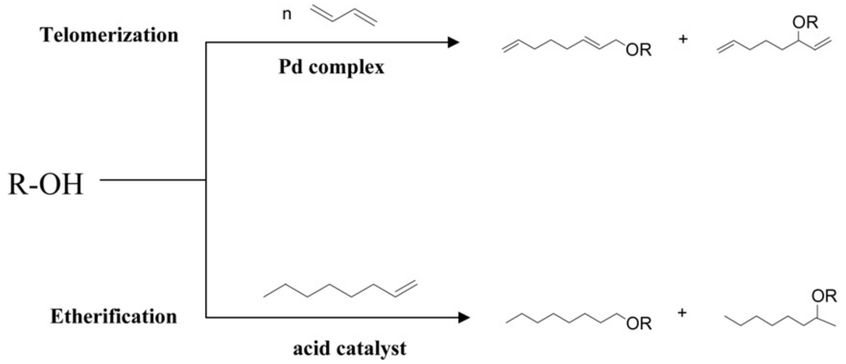


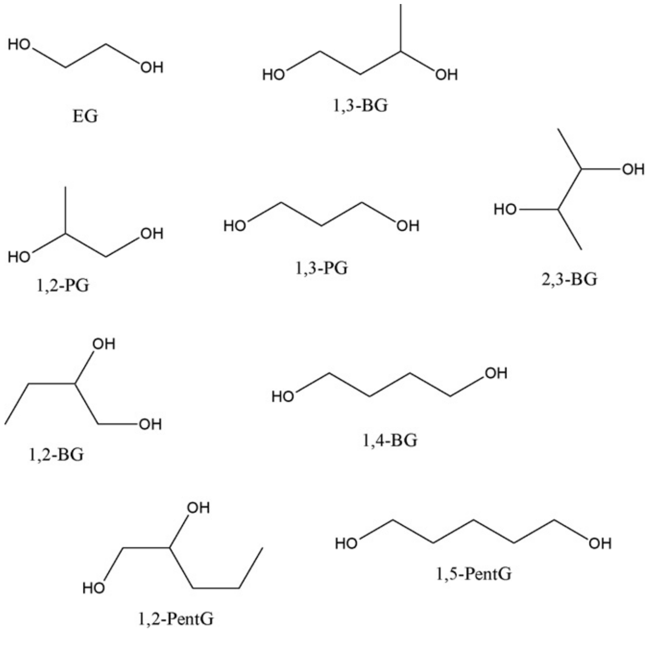
Scheme 1. Synthesis of octyl-ethers through telomerization of 1,3-butadiene or direct etherification with 1-octene.

attractiveness of the telomerization and etherification routes in the context of a sustainable chemical industry is that they can be integrated in a 100% biomass-based process as both butadiene and 1-octene can be derived from renewable sources as well [14,17]. In this paper we aim to analyze these two complementary catalytic routes for the synthesis of the C8 ethers of the various important glycols depicted in Scheme 2. The reactions were performed under solvent-free conditions and special emphasis was placed on the differences in product selectivity between the two routes and the effect of the glycol structure on the product distribution and catalyst activity. The advantages and disadvantages of the two methods will be discussed and a closer look will be given to catalyst activity and stability.

2. Experimental section

2.1. Chemicals and catalyst materials

All chemicals were purchased from commercial sources and used as received: 1,2-propylene glycol (>99%), 2,3-butylene glycol (>99%), 1,4-butylene glycol (>99%), 1,3-butylene glycol (>99%) and 1-octene (99+%) were purchased from Acros, 1,3- propylene glycol (>99%) and ethylene glycol (>99%) were purchased from Fluka and 1,2-butylene glycol (>99%), 1,2-pentane diol (>99%), 1,5-pentane diol (>99%) were purchased from Sigma–Aldrich. 1,3-Butadiene was obtained from Linde Gas Benelux. $Pd(acac)_2$ (Pd (II) acetylacetonate) and $Pd(dba)_2$ (Pd(0)) dibenzylideneacetone) were purchased from Aldrich, Zeolite NH_4^+-Beta (Si:Al = 12.5) CP814E, H-Beta (Si:Al = 37.5) CP811E, were purchased from Zeolyst, H-Beta (Si:Al = 22), H-Beta (Si:Al = 40.5) were a gift from Exxon Mobil, Beta zeolites with Si:Al of 12, 18, 75 were a gift from BASF, Beta zeolite with Si:Al of 19 was a gift from SABIC and H-Beta with Si:Al ratio of 180 was a gift from ESCA. 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 293 K to 773 K with a rate of 1 °C/min and keeping the temperature at 773 K for 6 h. From here on, zeolites will be denoted as, e.g., Beta (Z-37.5) instead of H-Beta (Si:Al = 37.5) from Zeolyst.



Scheme 2. The molecular structure of the biomass-based glycols used as substrates in this study.

2.2. Telomerization reaction

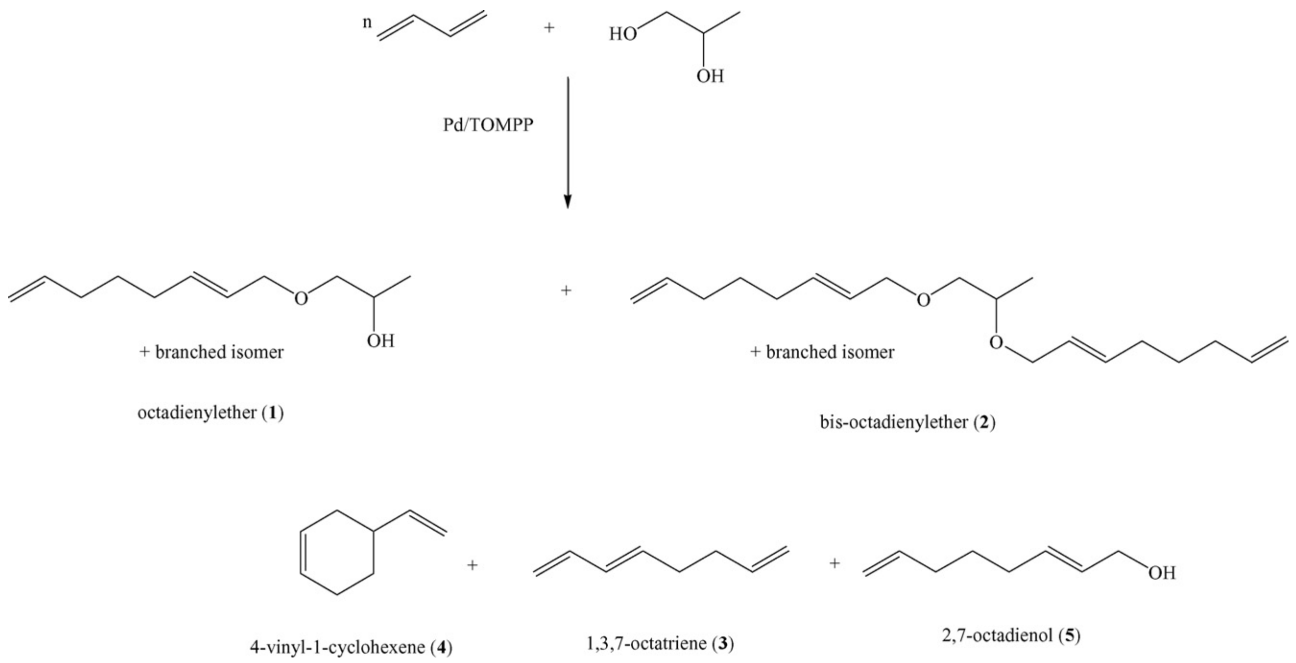
In a typical telomerization experiment, (1.5×10^{-5} mol) $Pd(acac)_2$ and (7.5×10^{-5} mol) of the TOMPP ligand were added to 0.125 mol alcohol. The alcohol, Pd source and the phosphine were directly mixed inside a 100 mL stainless steel Parr autoclave and flushed three times with argon. The autoclave was cooled down to 233 K using an acetone–dry ice mixture. 1,3-Butadiene was directly condensed in the reactor and the autoclave was heated to the reaction temperature of 353 K and kept till the pressure dropped to less than 3 bar. The starting point of the reactions was defined as the time at which the reaction temperature was reached. After the reaction, the reactor system was cooled to room temperature and flushed several times with argon.

2.3. Hydrogenation reaction

To the reaction mixture obtained after the telomerization of 1,3-butadiene with 1,2-propylene glycol was added 0.5 g of 5% Pd/C and the reactor was flushed three times with Ar and loaded with 5 MPa H_2. The reaction was carried out at 343 K for 40 min. The hydrogen consumption was monitored and the pressure was kept constant during the reaction. When the reaction was considered finished the autoclave was cooled to room temperature after which a sample was taken for analysis and the catalyst was filtered off.

2.4. Etherification reaction

In a typical etherification reaction 0.05 mol of 1,2-propylene glycol, 0.15 mol of 1-octene and 0.5 g of catalyst was loaded in a 40 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 413 K under continuous mechanical stirring (750 rpm). As starting point of the reaction the time was taken at which the autoclave reached the reaction temperature. When the reaction was considered finished, the autoclave was



Scheme 3. Telomerization of 1,3-butadiene with 1,2PG with Pd/TOMPP as catalyst.

cooled to 313 K 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.

2.5. 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 ($\lambda = 1.79026$ 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. Scanning electron microscopy (SEM) measurements were performed using a FEI XL30 FEG electron microscope equipped with an EDX detector.

2.6. Analytical methods

The reaction mixtures were analyzed using a GC 2010 system from Shimadzu with a CP-WAX 57CB (25 m × 0.2 mm × 0.2 μm) (internal calibration), GC–MS from Shimadzu with a CP-WAX 57CB column (25m × 0.2 mm × 0.2 μm) and an HPLC–ESI-MS from Shimadzu with Pathfinder PS column (RP-18, 3.5 μm, 4.6 cm × 150 cm). As the reaction products are rarely commercially available, authentic samples of each were prepared, purified using column chromatography and used for calibration [11a–c,13]. Conversions and yields were calculated based on the alcohol. TOF values were measured at initial reaction rates (conv. < 20%) and the conversions at moment *t* were adjusted for the most reactive substrates by subtracting the conversion at moment 0 with the condition that the total conversion at moment *t* to be below or equal to 20%.

3. Results and discussion

3.1. Telomerization of 1,3-butadiene with biomass-based glycols

The telomerization of 1,3-butadiene with 1,2-propylene glycol (1,2PG) is taken as an illustrative example. Both mono- (C8 telomer) and di-telomer (C16 telomer) products can be obtained from this substrate as linear or branched isomers (Scheme 3). The C8 telomer can be formed from either the primary or secondary hydroxyl group and is the product of interest for future application. Using the Pd/TOMPP complex as telomerization catalyst the telomers were obtained as the main reaction products with yields above 98%. Butadiene dimerization products 1,3,7-octatriene (**3**) and 4-vinyl-1-cyclohexene (**4**) (Scheme 3) and the water telomer 2,7-octadienol (**5**) were obtained as main reaction by-products with a combined yield of around 1%. The C8 and C16 telomers were always obtained as mainly linear products as the branched isomers represent less than 3% of the total amount of telomers. An important parameter in controlling the selectivity towards linear over branched telomers was previously found to be the Pd/P ratio [18]. A Pd/TOMPP molar ratio of 1/5 was found to be optimum in order to maximize the selectivity towards the linear telomers and was used in this study [11,18].

Very high telomerization activities were obtained with the Pd/TOMPP complex in the telomerization of 1,3-butadiene with glycols at 353 K (Table 1). Almost total conversions of the glycols were obtained in very short reaction times of less than 90 min under solvent-free conditions and in the absence of base activators. Bases are generally used as additive in telomerization reactions [12,18] implying additional steps for product purification. There is, therefore, a clear advantage in using the Pd/TOMPP system since this catalyst does not require the presence of a base or solvent for obtaining glycol conversions above 80% (Table 1).

In the absence of a solvent the properties of the reactants and their interaction with the catalyst are very important. Indeed, the activity of the Pd telomerization catalyst and the product selectivity was found to be dependent on the structure of the glycol. For all glycols the main reaction product of the telomerization was the mono-telomer (C8 telomer) and highest selectivities were obtained with the branched glycols (Table 1, entries 2–3 and 5–8). Ethylene glycol (EG) gave the highest amount of di-telomer (C16 telomer) 42% (Table 1, entry 1). The primary glycols like 1,3-propylene glycol (1,3PG), 1,4-butylene glycol (1,4BG) and 1,5-pentanediol (1,5PentG) always gave higher selectivities for the C16 telomer compared to their branched isomers (Table 1, entries 4, 9 and 11).

Table 1
Pd/TOMPP-catalyzed telomerization of 1,3-butadiene with various glycols.

Entry	Substrate	Time (min)	Conv.[a] (%)	Yield$_{\text{C8 telom}}$ (%)	Yield$_{\text{C16 telom}}$ (%)	TON[b]
1	EG	66	81	42	38	9831
2	1,2PG	34	82	73	7	7188
3	1,2PG[c]	20	87	78	8	7662
4	1,3PG	27	77	61	15	7584
5	1,2BG	22	83	70	11	7779
6	1,2BG	1	55	50	3	4688
7	1,3BG	2	70	60	9	6500
8	2,3BG	2	67	59	6	6010
9	1,4BG	19	80	64	16	8048
10	1,2PentG	5	51	39	11	5104
11	1,5PentG	1	52	40	11	5181

Reaction conditions: 100 mL autoclave, [Pd] = 0.01 mol%, Pd:TOMPP 1:5, 353 K, 1,3-butadiene:glycol 2:1.

[a] Conversions based on the alcohol.

[b] TON calculated based on nucleophile conversion, where formation of 1 mol of C8 telomer is one reaction cycle TON = 1 and 1 mol C16 telomer TON = 2.

[c] Pd(dba)$_2$.

Shorter reactions times were needed to reach almost full conversion with increasing length of the glycol carbon chain. For butylene glycols such as 1,4BG 80% conversion was achieved in just 19 min (entry 9) where for 1,3PG 27 min and for EG (entries 4 and 1) 66 min were needed to reach comparable conversions. The conversions of higher glycols were already significant after just a couple of minutes of reaction, as observed for 1,2BG, 1,3BG, 2,3BG and 1,5PentG (Table 1). Conversions over 50% were obtained in less than 2 min of reaction. Further increase of the conversion from 50% to 80% for 1,2BG, for example, required more than 15 min of reaction. The high activity and stability of the Pd/TOMPP system is evidenced also by the high turn-over numbers (TON) that were obtained. A loading of 0.01 mol% of Pd (based on the alcohol) was used to obtain these high TONs which correspond to a concentration of 195.5 ppm of Pd in the reaction mixture. Although the TON indicates the activity of the catalyst, a very high value is not necessarily good for the selective mono-telomerization of 1,3-butadiene with glycols. Formation of one mol of C8 telomer accounts for one reaction cycle and corresponds to a TON of 1, where C16 telomer formation corresponds to a TON of 2. The highest TON obtained for EG (entry 1) of 9831, therefore, also corresponds to the formation of the highest amount of C16 telomer. Nonetheless, TONs higher than 7000 were obtained for substrates likes 1,2PG and 1,2BG which presented the highest selectivity for the C8 telomer. Also, very high TONs (over 5000) were already measured after 1 or 2 min of reaction for the butylene glycols and pentane diols. A small increase of the yield of C8 telomer was obtained by changing the Pd precursor. Instead of using Pd(acac)$_2$ as precursor for the Pd/TOMPP system, we also tested Pd(dba)$_2$ as precursor in the telomerization of 1,3-butadiene with 1,2PG (Table 1, entry 3). Under these conditions the yield of C8 telomer increased from 73% to 78% (Table 1, entries 2 and 3). Also, the glycol conversion increased from 82% to 87% and was obtained in 20 min instead of 34 min.

3.1.1. Relationship between the structure of the alcohol and the telomerization activity

More detailed insight into the telomerization activity of the Pd/TOMPP complex can be obtained when considering the TOF values measured at low conversions (<20%). The necessity of measuring this TOF is suggested by the catalytic results obtained in Table 1. The telomerization activity of the Pd complex is very high in the first minutes, as conversions above 50% are obtained, but longer reaction times are required for a 30% further increase. This is caused by the competition between the C8 telomer and glycol for binding to the catalytic active site and to act as reaction substrate. Therefore, in order to differentiate between the activity of the Pd complex in telomerization of 1,3-butadiene with the glycol or the C8 telomer the initial activity needs to be measured at conversions below 20% where mainly the C8 telomer is formed with selectivities above 90%. The measured TOF values for all the glycols are plotted in Fig. 1 and a clear relation with the alcohol properties can be seen. The TOF was found to increase with the number of carbon atoms of the glycol; the highest TOF being obtained for 1,5-pentane diol (close to 400,000 h^{-1}) (Fig. 1a).

The activity of the telomerization catalyst can be nicely correlated with the hydrophobicity of the glycol, but other properties are also important. In the absence of a solvent the hydrophobicity of the glycol determines both the solubility of the TOMPP ligand as well as the interaction with the butadiene. The hydrophobicity/hydrophilicity of a glycol can be described by its E_T^N value which is obtained by measuring the UV/Vis/Near-IR shift of a dye probe molecule (Fig. 1) [19]. Based on this scale, the C4 and C5 glycols are expected to be the most hydrophobic with ethylene glycol being the most hydrophilic [19]. We have previously shown that the solubility of the TOMPP ligand and butadiene increases with the hydrophobicity of the glycol [11c]. The same general trend can be discerned from Fig. 1 which shows that the TOFs increase

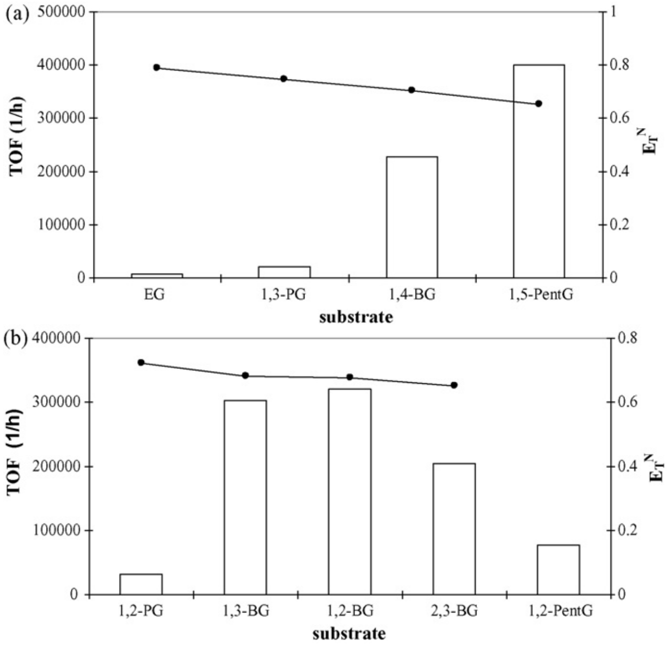


Fig. 1. Relationship between the alcohol hydrophobicity (E_T^N) and TOF (calculated at conversions <20%) for the 1,3-butadiene telomerization with: (a) linear glycols and (b) branched glycols. Columns represent the TOF and dots represent the E_T^N [19] values (see Section 2 on how TOF values are caculated).

Table 2
C8 telomer distribution between the primary and secondary alcohol.

Substrate	C8 telomer on primary OH (%)	C8 telomer on secondary OH (%)
1,2PG	82.9	17.1
1,2BG	85.2	14.8
1,3BG	84.9	15.1
1,2PentG	86.0	14.0

Reaction conditions: 100 mL autoclave, [Pd] = 0.01 mol%, Pd:TOMPP 1:5, 353 K, 1,3-butadiene:glycol 2:1. The selectivities were calculated at glycol conversions below 20%.

Table 3
Influence of the Pd precursor on the catalyst activity in the telomerization of 1,3-butadiene with 1,2PG.

Pd precursor	TOF (1/h)
$Pd(acac)_2$	30,991
$Pd(dba)_2$	36,000

Reaction conditions: 100 mL autoclave, [Pd] = 0.01 mol%, Pd:TOMPP 1:5, 353 K, 1,3-butadiene:glycol 2:1. Conversions based on the alcohol and below 20%.

Table 4
Product distribution before and after hydrogenation of the telomers.

	Conv. (%)	C8 telomer (%)	C16 telomer (%)
Telomerization	87	78	8
	Conv. (%)	C8 ether (%)	C16 ether (%)
Hydrogenation	88	74	7

Reaction conditions: 100 mL autoclave, [Pd] = 0.01 mol%, Pd:TOMPP 1:5, 353 K, 1,3-butadiene:glycol 2:1, 100 mL, 0.5 g 5% Pd/C, 80 bar H_2, 343 K. Conversions expressed based on the initial amount of glycol.

with an increase of the hydrophobicity of the glycol (lower E_T^N) and TOFs of 350,000 and 400,000 h^{-1} are obtained for the butylene glycols and pentane diols. As mentioned above other properties also contribute to the telomerization activity. For example, the position of the hydroxyl group, i.e., the substrate having only primary or primary–secondary hydroxyl groups, has also a strong effect. Higher TOFs values were obtained for the primary–secondary glycols compared to their linear isomers (Fig. 1a and b, note that the TOF are measured for initial reaction rates). For 2,3-butylene glycol (2,3BG) the presence of two secondary vicinal hydroxyl groups is probably causing a lower TOF, where coordination properties are probably responsible for the lower TOF of 1,2-pentanediol.

For branched glycols, such as 1,2PG and 1,2BG, there is a clear difference in the reactivity of the two hydroxyl groups. The secondary hydroxyl group is less reactive than the primary hydroxyl group, as suggested by the results obtained in Table 2. For the primary–secondary glycols the primary hydroxyl reacts predominantly which explains the higher selectivity obtained for the mono-telomer (more than 85%) (Table 1). For linear glycols EG, 1,3PG and 1,4BG both hydroxyl groups are equally reactive so the formation of the C8 telomers and further on the C16 telomers can occur at each of the two hydroxyl groups with enhanced probability. For EG, which is more nucleophilic, this effect was the most obvious and therefore presented the lowest selectivity for the C8 telomer (Table 1, entry 1). The higher activity of the primary hydroxyl group compared to secondary hydroxyl group is evidenced in Table 2 where the selectivities between the C8 telomers formed at the primary –OH or secondary –OH are compared. As expected, in all cases the primary hydroxyl group it is clearly more reactive (>82%) than the secondary one. The selectivity towards the C8 telomer of the primary hydroxyl group increases slightly with the length of the alkyl chain of the glycol, from 83% to 86%.

The Pd precursor was found to influence the TOF too. Using a Pd(0) precursor a higher TOF was obtained compared to the result obtained with a Pd(II) precursor (Table 3). In the latter case, the Pd(II) cation needs to be reduced first before it can enter the catalytic cycle. Part of the phosphine ligands are involved in the reduction of the metal and the in situ complexation. The use of a Pd(0) precursor obviates the need for the reduction step and higher initial telomerization activities can thus be obtained.

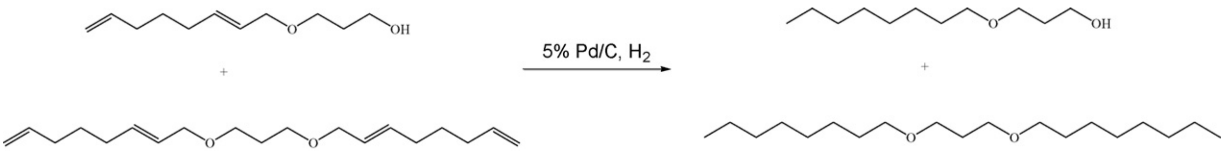
3.1.2. Hydrogenation of the octadienylethers

Several applications are envisaged for the octadienyl-telomers of the glycols. The unsaturated telomers can be used as monomers for polymer synthesis or alternatively they can be hydrogenated and used as precursors for non-ionic surfactants [5,20]. The hydrogenation step was carried out using a heterogeneous hydrogenation catalyst. More specifically, a 5% Pd/C catalyst was used for the hydrogenation of the 1,2PG telomers, as illustrated in Scheme 4. The hydrogenation catalyst was added to the autoclave containing the telomerization mixture after removing all the unreacted butadiene. The reactor was then filled with hydrogen and the reaction was started. After 30 min at 343 K all the telomers were fully hydrogenated. The product distribution (C8 ethers vs. C16 ethers) was found not to be affected during the hydrogenation step (Table 4). Using this approach linear saturated C8 ethers can be readily obtained from biomass-based glycols.

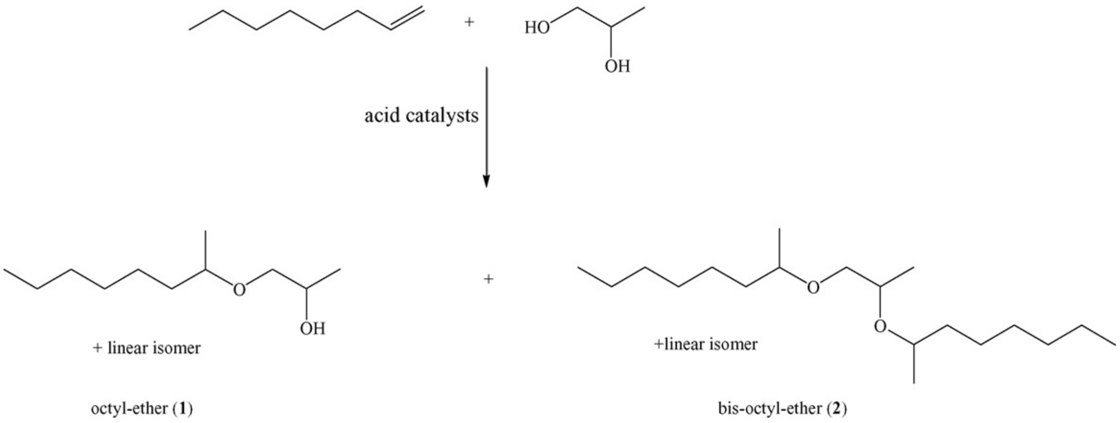
3.2. Etherification of biomass-based glycols with 1-octene

Acid catalysts are generally used for the etherification of alcohols with olefins. The etherification of biomass-based alcohols with isobutene has received a lot of attention in this respect, due to the possible use of the products as fuel additives [21]. In contrast, the etherification of alcohols and particularly glycols with, e.g., longer alkenes such as 1-octene is virtually unexplored [8,16]. In a previous article we have investigated the etherification of various biomass-based alcohols with long linear terminal alkenes and after a screening of solid acid catalysts, such as zeolites and ion exchange resins, we have identified H-Beta zeolites as very active and selective catalysts for this reaction [13]. Taking the etherification of 1,2-propylene glycol (1,2PG) with 1-octene (Scheme 5) as probe reaction, both the mono-ether (C8 ether) and the di-ether (C16 ether) can be formed with this substrate. As in the case of the telomerization the desired products are the C8 ethers.

However, in contrast to the telomerization reaction branched ethers were obtained predominantly in this case, while the linear and mixed linear-branched ethers were obtained in only small amounts (5%). Glycol dehydration and cyclization products and 1-octanols were obtained as the main reaction by-products. In the next step of our investigation, we decided to study various H-Beta zeolite materials differing in their Si:Al ratio and crystal sizes in



Scheme 4. Telomer hydrogenation over a 5% Pd/C catalyst.



Scheme 5. Etherification of 1,2PG with 1-octene.

Table 5
Overview of the catalytic performances of various H-Beta zeolites in the etherification reaction of 1,2PG with 1-octene.

Entry	Si:Al	Source	Conv. (%)	Sel.$_{\text{C8 ether}}$ (%)	Sel.$_{\text{C16 ether}}$ (%)	Other (%)	Particle size (nm)[b]
1	22	Exxon	66	86	5	9	450
2	40.5	Exxon	71	83	8	9	480
3	12	BASF	60	87	7	6	277
4	18	BASF	62	84	7	9	325
5	75	BASF	64	83	10	7	340
6	18[a]	BASF	13	94	2	4	325
7	12.5	Zeolyst	62	86	8	6	90
8	19	Zeolyst	77	84	10	6	130
9	37.5	Zeolyst	80	81	8	11	100
10	180	Zeolyst	2	82	3	15	300

Etherification conditions: 0.5 g catalyst, 3 h, 413 K, 1-octene:1,2PG 3:1, 0.05 mol 1,2PG.

[a] NaH form of the zeolite.

[b] Averaged dimension over 120 particles (±5 nm).

the etherification of various glycols, but 1,2PG in particular, with 1-octene under solvent-less conditions. The results are summarized in Table 5. It is clear that high conversions were obtained for all zeolite materials under study after just 3 h of reaction. For all the H-Beta zeolites, independently of their Si:Al ratio and particle size, the C8 ether was obtained as the main reaction product with selectivities above 80% and the combined selectivity for the octyl-ethers was higher than 90%. However, different conversions were obtained as a function of these two zeolite properties, which will be discussed separately.

3.2.1. *Influence of the Si:Al ratio*

Variation of the Si:Al ratio is known to have a strong influence on the catalytic activity of zeolite materials [22]. It influences both the acid and hydrophilic properties of the zeolite. From Table 5 it can be concluded that a relationship exists between the 1,2PG conversion and the zeolite Si:Al ratio. Taking the H-Beta catalysts from Zeolyst (i.e., zeolites with similar particle sizes) as an example, the 1,2PG conversion increased from 62% to 80% with increasing the Si:Al ratio from 12.5 to 37.5 (Table 5, entries 7–9). Further increase of the Si:Al ratio to 180 lead to an almost total loss of the etherification activity (2%) (Table 5, entry 10). This loss of activity is related to a very strong decrease in the number of acid active sites and in particular of the Brønsted acid sites, which are correlated with the framework Al amount [22,23]. The need to have a certain concentration of Brønsted acid sites for achieving a high etherification activity was also suggested by the result obtained with a partially exchanged Na–Beta zeolite. By partially replacing the H^+ of the H-Beta zeolite with Na^+ the etherification activity is dramatically reduced from 62% to 13% (Table 5, entry 6). No change in the selectivity was observed, however.

The change in the zeolite Si:Al ratio has also an influence on the hydrophilic properties of H-Beta. Since the 1,2PG etherification reaction was performed under solvent-free conditions, the hydrophilic properties of the zeolite material will influence the adsorption of the reactants and product elimination. By increasing

Table 6
Influence of the H-Beta zeolite Si:Al ratio and hydrophilic properties of the alcohol on the etherification activity and related product distribution.

Entry	Catalyst	Substrate	Conv. (%)	Sel.$_{\text{mono}}$ (%)	Sel.$_{\text{di}}$ (%)	Sel.$_{\text{other}}$ (%)	E_T^N[a]
1	H-Beta (Z-12.5)	EG	70	81	17	2	0.790
2		1,2PG	76	82	6	9	0.722
3		1,3PG	51	70	11	19	0.747
4		1,2BG	59	90	3	7	0.676
5	H-Beta (Z-37.5)	EG	71	74	21	4	0.790
6		1,2PG	87	70	17	13	0.722
7		1,3PG	46	78	12	10	0.747
8		1,2BG	89	76	13	12	0.676

Etherification conditions: 0.5 g catalyst, 5 h, 413 K, 1-octene: alcohol 3:1, 0.05 mol alcohol; 3 h.

[a] Ref. [19] lower value corresponds to higher hydrophobicity.

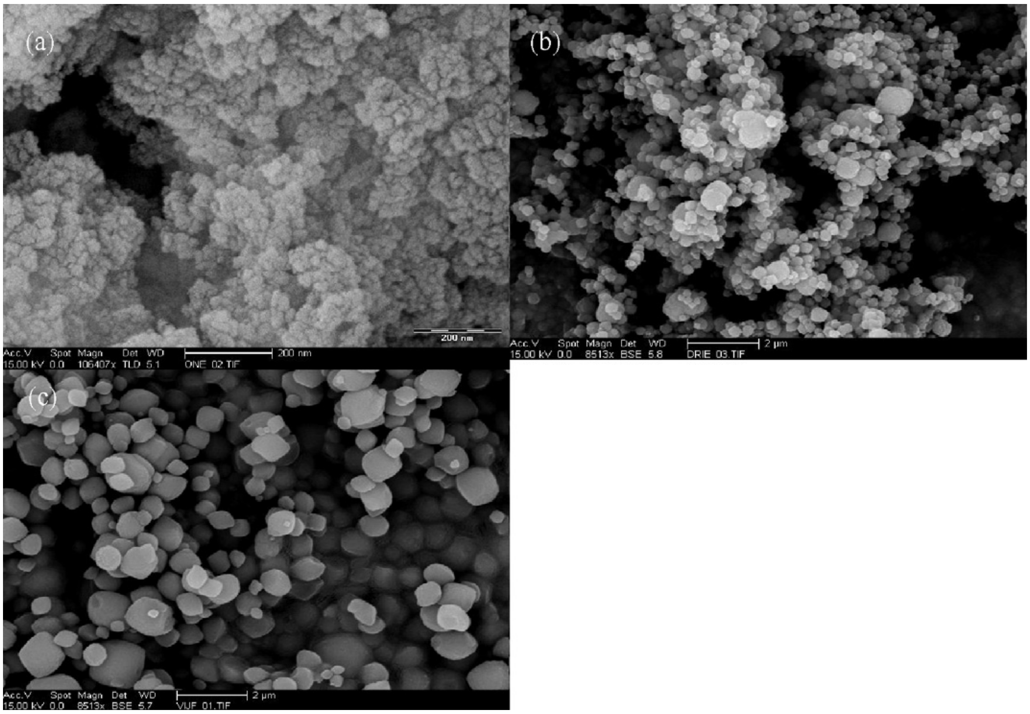


Fig. 2. SEM pictures of a selection of H-Beta zeolites: (a) H-Beta (Z-37.5), (b) H-Beta (B-75) and (c) H-Beta (E-40.5).

the Si:Al ratio the hydrophobicity of the zeolite material increases and will better adsorb a more hydrophobic reactant. This particular effect can be evidenced for the Zeolyst samples when glycols with different hydrophilicities were used as substrate. This is illustrated in Table 6. If we use the E_T^N scale [19] as a measure of their polarity, it can be concluded that the etherification activity of H-Beta (Z-12.5) is similar or slightly better than that of H-Beta (Z-37.5) for more hydrophilic substrates, such as EG and 1,3PG (Table 6) contrary to the result obtained for the etherification of 1,2PG and 1,2BG. A similar observation on the influence of hydrophilic properties of H-Beta was made by Pariente et al. for the etherification of glycerol with ethanol [24] where a specific Si:Al ratio was needed for a better product desorption.

3.2.2. Influence of the crystal size on the etherification activity

The particle size of the H-Beta was also found to have a significant influence on the etherification activity. As indicated in Table 5 the Zeolyst samples presented the smallest particle size with the most uniform particle size distribution and therefore the highest etherification activity. The particle sizes as measured by SEM for H-Beta (Z-37.5) were around 100 nm (Fig. 2a), while for H-Beta (E-40.5) and H-Beta (B-75) larger particle sizes were observed with a particle size distribution ranging from 100 nm to more than 1000 nm (Fig. 2b and c). Based on this analysis a relationship between the zeolite particle size and the etherification activity could be established (Table 5). Having smaller particle sizes H-Beta (Z-37.5) and H-Beta (Z-19) resulted in higher conversion rates as compared with the H-Beta zeolites from BASF and Exxon Mobil which have similar Si:Al ratios (Table 5, entries 8 and 9 vs. entries 4, 5, 1 and 2). H-Beta (B-75) gave a lower 1,2PG conversion compared to H-Beta (E-40.5) even though the particle size was a little bit smaller. This difference is caused by the very high Si:Al ratio and the decreased number of Brønsted acid sites. These results indicate that a combined effect is exerted by the Si:Al ratio and zeolite particle size on the etherification conversions. This also occurs for H-Beta (E-22), which gave slightly higher conversion (66%) compared to H-Beta (B-18) (62%) (Table 5 entries 1–4).

3.2.3. Extending the substrate scope

Other biomass-based glycols can be successfully used as substrates in the etherification with 1-octene. Using H-Beta (Z-37.5) as etherification catalyst very good results were obtained in the etherification of various glycols with 1-octene (Fig. 3). For all glycols the C8 ether was obtained as the main reaction product with selectivities over 70% with the C16 ether being the main reaction by-product. For 1,5-pentanediol (Fig. 3) the C8 ether was obtained with the highest selectivity (92%). The structure of the alcohol had a strong influence on the etherification activity of the H-Beta zeolites, as was previously observed in the telomerization with the Pd/TOMPP complex. The highest conversions were obtained for 1,2PG and 1,2BG (>80%), where for 1,3PG and 1,3BG conversions amounted to 51% and 53%, respectively. As already suggested, the interaction between the glycol, 1-octene and the zeolite is very important in the absence of a solvent. The influence of other properties such as steric hindrance and reactivity of the hydroxyl groups can, however, not be excluded. As observed in the telomerization the primary hydroxyl group is more reactive than the secondary hydroxyl group. The selectivity for C8 ether formed at the primary hydroxyl group was 95%, for example, in the case of 1,2PG.

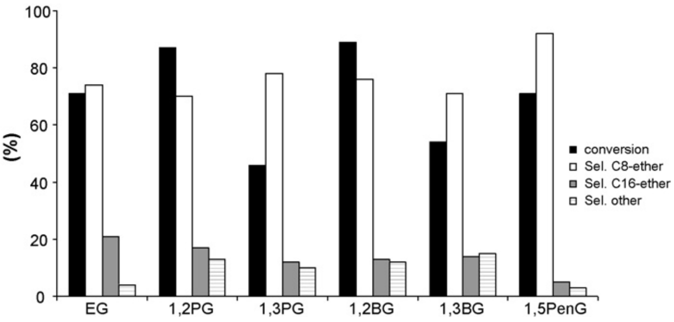


Fig. 3. Etherification of glycols with 1-octene over H-Beta (Z-37.5), 5 h, 413 K, 1-octene:glycol 3:1, 0.5 g catalyst, 10 bar Ar.

Table 7
Re-use of H-Beta zeolites in the etherification of 1,2-propylene glycol with 1-octene.

Substrate	Run		Conv.(%)	Sel.$_{C8ether}$ (%)	Sel.$_{C16ether}$ (%)	Sel.$_{other}$ (%)
Z-12.5	1	Fresh	76	82	6	9
	2	Uncalcined	57	90	3	7
	3	Uncalcined	40	91	3	6
	3	Calcined	76	83	5	9
Z-37.5	1	Fresh	87	70	17	3
	2	Uncalcined	54	88	4	8
	3	Uncalcined	42	90	3	7
E-40.5[a]	1	Fresh	71	83	8	9
	2	Uncalcined	38	91	3	6

Reaction conditions: 1 g of catalyst, 1-octene:1,2PG 3:1, 5 h, 10 bar Ar, 140 °C.
[a] 3 h.

Table 8
Short overview of the advantages and challenges related to the synthesis of C8 ethers of glycols via either a telomerization or etherification route.

	Telomerization	Etherification
Advantages	Very high TON and TOF values can be reached in the telomerization of 1,3-butadiene with glycols High selectivities for the linear mono-telomer can be obtained, in particular for branched glycols Low loadings of homogeneous catalysts can be used (200 ppm of Pd) and the reaction can proceed under greener conditions (no solvent, no base co-catalysts) A low ratio 1,3-butadiene:glycol can be used (2:1) Hydrogenation of the telomers is easily done in a consecutive reaction step without any intermediate purification step. The use of a heterogeneous hydrogenation catalyst under solvent-free conditions gave fast conversion and did not influence the ether selectivity	Commercial heterogeneous catalysts can be used. The catalyst can be easily recovered and re-used and the products can be easily separated and purified Saturated alkyl ethers can be obtained in one reaction step under solvent-free conditions 1-octene is less toxic than 1,3-butadiene
Remaining challenges	Homogeneous catalysts are used which makes the recovery and re-use very difficult. As expensive Pd is used, catalyst recovery becomes important A two step process is needed, if saturated alkyl ethers are the desired product	The zeolite catalyst gradually deactivates. The extent of deactivation can, however, be reduced by adjusting the properties of the zeolite Side products are formed with yields around 10%. Higher selectivities can be achieved by decreasing the conversion or adjusting the zeolite properties

3.2.4. *Recovery and re-use of H-Beta zeolite*

The H-Beta zeolite was recovered and re-used in the etherification of 1,2PG (Table 7). The zeolites were found to suffer from partial deactivation during the etherification reaction. This leads to a partial loss of the etherification activity after each reaction cycle. Still, after three reaction cycles more than 50% of the initial etherification activity is preserved for the H-Beta (Z-12.5) zeolite. The deactivation is related both to the Si:Al ratio and the zeolite particle size. A higher loss of activity in the second reaction cycle is observed for H-Beta (Z-37.5) and H-Beta (E-40). Already for H-Beta (E-40) in the second reaction run the conversion drops to 38% compared to 71% from the first run. Although the activity is lost, the high selectivity for the C8 ether was preserved after several reaction runs for all the H-Beta zeolites under study. Fortunately, the calcination of the H-Beta zeolites always leads to a full regeneration of the catalyst materials and the initial etherification activity and selectivity could again be obtained.

4. Conclusions

Two complementary catalytic routes have been developed for the synthesis of the octyl-ethers of biomass-based glycols. Both processes can be in principle integrated in a 100% biomass-based synthesis platform as long as butadiene and 1-octene are obtained from renewable sources. For the telomerization of 1,3-butadiene a very active Pd/TOMPP homogeneous catalyst has been developed, whereas for the direct etherification with long linear alkenes commercial H-Beta zeolites were found to be very active and selective. Depending on the desired application of the ether product, either the telomerization or etherification route can be followed (Table 8). More specifically, the telomerization of 1,3-butadiene can be used for the synthesis of linear ethers, whereas the direct etherification route affords the production of the branched isomers in high yields.

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