Influence of acid ion-exchange resins morphology in swollen state on the synthesis of ethyl octyl ether from ethanol and 1-octanol

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Abstract

Ethyl-octyl ether (EOE) liquid phase synthesis from ethanol and 1-octanol over ion-exchange resins is feasible at 423K, though di-ethyl ether and di-n-octyl ether were also formed. The influence of the catalyst morphology on the reaction was checked by testing twenty-two acidic resins. Gel-type resins of low crosslinking degree yielded the higher amounts of EOE, whereas macroreticular ones of high crosslinking degree gave mainly di-ethyl ether. Ethanol conversion highly depends on the resin acid capacity, $[H^+]$, whereas 1-octanol conversion and selectivity to EOE depends on the specific volume of swollen polymer, V_{sp}, and porosity. The variation of ethanol and 1-octanol conversion, selectivity to EOE with respect to both alcohols as well as ethers TOF as a function of $[H^+]/V_{sp}$ suggests that a part of the active sites does not take part in the EOE synthesis reaction on highly cross-linked resins. Amberlyst 70 could be interesting in industry due to its selectivity to EOE and higher thermal stability.

Keywords: ethyl octyl ether, ion-exchange resins, resin morphology, ethanol, 1-octanol

1. Introduction

In order to fulfill new European specifications (Directive 2009/30/EC), a possible option of reformulating diesel fuels may be the introduction of oxygenates in commercial blends. It is a well-known fact that linear ethers with at least 9 carbon atoms show high cetane numbers and desirable cold flow properties as light diesel fuels [1]. As shown in Table 1, ethyl octyl ether (EOE) could be an appropriate oxygenate for this purpose, among other linear ethers.

The telomerization of 1,3-butadiene with a nucleophilic compound has been widely explored to synthesize products such as ethers, lactones or terpene derivatives [2]. When the nucleophile is an alcohol, saturated linear ethers can be obtained after the hydrogenation of the intermediate unsaturated linear ethers [3]. Many papers deal with the production of methyl octyl ether (MOE) following this pathway [4-7], and a few ones report the use of ethanol to produce EOE [2,4,5]. An alternative pathway to obtain EOE could be the reaction of 1-octanol with di-ethyl carbonate [8]. In this work, the direct intermolecular dehydration of ethanol and 1-octanol is proposed as a feasible pathway to obtain EOE. From an industrial point of view it could take advantage of synthesizing EOE in only one reaction step leading accordingly to simpler process schemes. Another important point of this reaction pathway is that EOE could be labeled as bio-fuel if bio-ethanol is the raw material. In addition, it is worth noting that 1-octanol could also be obtained by ethanol oligomerization on hydroxyapatite in a process that gives place to butanol, hexanol, octanol and other linear alcohols of even carbon atoms number [9,10].

Acidic styrene-divinylbenzene (styrene-DVB) ion-exchange resins have shown to be suitable catalysts for intermolecular n-alcohol dehydration to ether [11-13], and they are considered as the best option in terms of selectivity and activity to achieve good linear ether yields [14-16]. In non-aqueous conditions, ion-exchange resins show acid strength comparable to 63-70% (w/w) H_2SO_4, similar to H-Beta zeolite [12]. The alcohol molecules would react with the $–SO_3H$ groups to form the corresponding sulfates (general acid catalysis) [17]. A subsequent attack of an alcohol molecule would form the ether. In excess of water, the acid strength of ion-exchange resins decreases and are comparable to 35% (w/w) H_2SO_4 [12]. Water competes for $–SO_3H$ groups forming hydrated protons within the resin matrix. The reaction mechanism could then involve the in situ formation of an oxonium ion (specific acid catalysis) [17]. The ether would be formed by the nucleophilic attack of alcohol on the oxonium ion.

Both gel-type and macroreticular ion-exchange resins are good options to catalyze this type of reactions, since the accessibility to inner acid centers of gel-type resins is possible due to the swelling by interaction with the reaction medium. Permanent pores of macroreticular resins make these catalysts appropriate for swelling and non-swelling media [18].

The aim of this work is to study the etherification of 1-octanol with ethanol to obtain EOE over ion-exchange resins. Particularly, the influence of the catalyst morphology on the synthesis of the ether is discussed.

2. Experimental

2.1 Materials

1-Octanol (≥ 99.5%) and ethanol (≥ 99.8%, < 0.02% water), supplied by Fluka, were used without further purification. Ethyl-octyl ether (EOE, > 99.9%; obtained and purified in our lab), di-ethyl ether (DEE, > 99%; Panreac), di-n-octyl ether (DNOE, > 97%; Fluka) and 1-octene (> 97%; Fluka) were used for analysis purposes.

Gel-type and macroreticular resins supplied by Rohm and Haas France (Amberlyst 15, Amberlyst 16, Amberlyst 31, Amberlyst 35, Amberlyst 36, Amberlyst 39, Amberlyst 46, Amberlyst 70, Amberlyst 121, Amberjet 1200H and Amberjet 1500H), Purolite (CT124, CT151, CT165, CT175, CT224, CT252, CT275 and CT276), and Aldrich Chemicals (Dowex 50Wx2-50, Dowex 50Wx4-50 and Dowex 50Wx8-50) were used as catalysts. Their main characteristics are shown in Table 2.

2.2 Apparatus

Experiments were carried out in a 100 mL stainless steel autoclave operated in batch mode. A magnetic drive turbine was used for mixing and baffles were placed inside the reactor to improve the agitation. Temperature was controlled to within ±1 K by an electric furnace. The pressure was set at 2 MPa by means of N_2 in order to maintain the reacting mixture in the liquid phase over the whole temperature range. One of the outlets was connected directly to a liquid sampling valve, which injected 0.2 μL of pressurized liquid into a gas-liquid chromatograph.

2.3 Analysis

The composition of liquid samples was determined by using a split mode operation in a HP6890A GLC apparatus equipped with TCD to measure water amounts. A methyl silicone capillary column (50m × 0.2mm × 0.5 μm) was used to determine ethanol, 1-octanol, water, DEE, EOE, DNOE, ethylene, octenes and branched octyl ethers. The column was temperature programmed with a 10 K/min ramp from 323 K up to 523 K and held for 6 min. Helium was used as carrier gas at a total flow rate of 30 mL/min. The response of TCD was calibrated by using mixtures of known composition.

2.4 Procedure

Catalysts were dried at 383 K in an oven, firstly at atmospheric pressure overnight, and then 2 h under vacuum (residual water content 1-2% by Karl Fischer titration). Fresh catalyst and 70 mL of a ethanol/1-octanol mixture (ethanol/1-octanol initial molar ratio, $R_{EtOH/OcOH} = 1$; initial water content ≤ 0.5%) were charged into the reactor and, after checking for leakages, heated to the reaction temperature, which was 423 K for all experiments. When the reaction medium reached that temperature, the time was set as the initial instant. To monitor the variation of chemicals concentration along time, liquid samples were taken out of the reactor and analyzed hourly for 6 h. The stirring speed was set at 500 rpm and catalyst mass in 1 g of dry resin with the commercial distribution of particle sizes in order to avoid external mass transfer resistance and catalyst loading effects, respectively, as seen in previous studies of alcohol dehydration to ether on this type of catalysts performed in the same setup. In addition, data are not influenced by the resins bead size at these reaction conditions [12,28].

Conversion, selectivity and yield of EOE were computed and followed along experiments. Since there were two reactants, ethanol (X_{EtOH}) and 1-octanol (X_{OcOH}) conversion, selectivity to EOE (S_{EtOH}^{EOE}) and to DEE (S_{EtOH}^{DEE}) with respect to ethanol, selectivity to EOE (S_{OcOH}^{EOE}) and to DNOE (S_{OcOH}^{DNOE}) with respect 1-octanol, and yield of EOE with respect to ethanol (Y_{EtOH}^{EOE}) and 1-octanol (Y_{OcOH}^{EOE}) were calculated by:

$$X_{EtOH\ \mathrm{or}\ OcOH} = \frac{mole\ of\ alcohol\ reacted}{initial\ mole\ of\ alcohol} \tag{1}$$

$$S_{EtOH}^{EOE\ or\ DEE} = \frac{mole\ of\ ethanol\ reacted\ to\ form\ EOE\ or\ DEE}{mole\ of\ ethanol\ reacted} \tag{2}$$

$$S_{OcOH}^{EOE\ or\ DNOE} = \frac{mole\ of\ 1\text{-}octanol\ reacted\ to\ form\ EOE\ or\ DNOE}{mole\ of\ 1\text{-}octanol\ reacted} \tag{3}$$

$$Y_{EtOH}^{EOE} = \frac{mole\ of\ ethanol\ reacted\ to\ form\ EOE}{initial\ mole\ of\ ethanol} = X_{EtOH} \cdot S_{EOE}^{EtOH} \tag{4}$$

$$Y_{OcOH}^{EOE} = \frac{mole\ of\ 1\text{-}octanol\ reacted\ to\ form\ EOE}{initial\ mole\ of\ 1\text{-}octanol} = X_{OcOH} \cdot S_{EOE}^{OcOH} \tag{5}$$

Reaction rates of EOE formation at any time were calculated from the functions of variation of n_{EOE} (number of produced EOE mole) versus time, where W is the mass of dry catalyst:

$$r_{EOE} = \frac{1}{W}\left(\frac{dn_{EOE}}{dt}\right)_{\mathrm{t}} \quad \left[\frac{mol\ EOE}{kg{\cdot}h}\right] \tag{6}$$

Reaction rates of DEE (r_{DEE}) and DNOE (r_{DNOE}) formation were calculated similarly. Finally, the turnover frequency of EOE (TOF_{EOE}), DEE (TOF_{DEE}) and DNOE (TOF_{DNOE}) formation, can be computed by dividing the reaction rate by the number of acid sites per gram of dry resin (acid capacity), $[H^+]$. For example:

$$TOF_{EOE} = \frac{r_{EOE}}{\left[H^+\right]} \quad \left[\frac{mol\ EOE}{eqH^+{\cdot}h}\right] \tag{7}$$

Experiments were replicated twice to assure reproducibility of data. Conversion, selectivity and yield data are accurate within ± 3%. Mass balance of each compound was accomplished within ± 5%. In particular, the carbon balance was also accomplished within ± 5%.

Results and discussion

3.1 Morphology of tested resins in swollen state

Tested catalysts were chosen in order to have a wide range of resins with very different morphology both in dry state and swollen in polar media. Macroreticular resins are polymers of low (Amberlyst 39 and 70), medium (Amberlyst 16 and 36, CT151 and CT152) and high crosslinking degree (Amberlyst 15 and 35, CT175, CT275 and CT276); gel-type ones contain 2 - 8 DVB%. As for sulfonation degree, they include monosulfonated (about a $–SO_3H$ group per aromatic ring [29]) and oversulfonated (partially disulfonated copolymers so that each benzene ring has an average of between 1 and 1.2 $–SO_3H$ groups [29], even though disulfonated rings are probably the gel-phase outer ones). Some resins series are especially interesting to check the influence of polymer structure. For example, Amberlyst 15, 16 and 39 are monosulfonated macroreticular resins with similar acid capacity, but different crosslinking degree. CT275 and CT276 are oversulfonated versions of CT175, and Amberlyst 35 and 36 of Amberlyst 15 and 16, respectively. Among gel-type resins, there is the series Dowex 50Wx2, 50Wx4 and 50Wx8 of monosulfonated ones with crosslinking degree increasing from 2 to 8%, as well as the pair CT124 and its oversulfonated version CT224 (4% DVB).

Amberlyst 46 and Amberlyst 70 should be highlighted. Amberlyst 46 is a macroreticular resin of high DVB% sulfonated only at the polymer surface (i.e. it has a negligible amount of acid sites in the gel phase compared to those on the surface of the micro-particles) [30]. Surface sulfonated means that functionalization is promoted from the surface inward and the depth of functionalization of catalyst beads is severely restricted to only the first few layers of styrene rings, which implies that practically all acid sites are accessible [31]. As a result, it has about a fifth of the acid sites number of most tested catalysts. Amberlyst 70 is a low-crosslinked macroreticular resin with chlorine substituting hydrogen atoms in its polymeric network as well as the aromatic rings. Chlorine substitution confers higher thermal stability to the catalyst. It is claimed that sulfonic group loss is less than 10% after 24 h at 473K, and chlorine leaching less than 0.2% [23]. However, its acid capacity is about half of Amberlyst 39, a non-chlorinated macroreticular resin with the same DVB%.

Ion exchange resins are nearly spherical beads of sulfonated styrene-DVB copolymers. Copolymerization of styrene and DVB gives place to an ensemble of entangled styrene-DVB chains with no spaces among them in dry state (gel-type resins). However, if copolymerization proceeds in the presence of a solvent (e.g. toluene), soluble in styrene-DVB mixtures but unable to react with both co-monomers, it is excluded from the polymer and the spaces filled by the solvent become pores (macroreticular resins). These resins consist of large agglomerates of gel-phase micro-spheres; each one showing smaller nodules that are more or less fused together [32]. In between the nodules there is a family of very small pores (micropores), and in between the micro-spheres a second family of intermediate pores of diameter 8-20 nm (mesopores) is observed. A third family of large pores of diameter 30-80 nm (macropores) is located between the agglomerates. Macropores are permanent and can be detected by standard techniques of pore analysis, i.e. adsorption-desorption of N_2 at 77 K. Meso- and micropores are non-permanent. They appear in polar media able to swell the polymer and can be detected by characterization techniques in aqueous media such as inverse steric exclusion chromatography (ISEC) [33].

Swelling of ion-exchange resins can be observed from the particle size distribution in water, ethanol, 1-octanol and air determined by laser diffraction (Beckman Coulter LS Particle Size Analyzer). Fig. 1 shows the particle size distribution of Amberlyst 70 in air, water, ethanol and 1-octanol. The other resins show similar distributions from a qualitative point of view. Table 3 gathers the mean laser bead diameter of some resins as well as swelling with respect to air. As seen, resin beads swell highly in water and in less extent in ethanol. In general, 1-octanol swells resins as much as water, probably by the interaction between the hydrocarbon tail of the alcohol molecule and resin matrix [34]. However, the number of ethanol mole in the swollen gel phase, estimated from the mean particle diameter relative to air, is higher than those of 1-octanol i.e. 0.067 mol of ethanol/g dry resin vs. 0.035 mol 1-octanol/g dry resin in Amberlyst 121, or 0.035 mol of ethanol/g dry resin vs. 0.016 mol 1-octanol/g dry resin in Amberlyst 39. Swelling in water and alcohols depends on the resins morphology and as a rule decrease in the order: gel-type resins with 2, 4 and 8 DVB%, macroreticular ones of low, medium and high crosslinking degree. Swelling in water and 1-octanol of gel-type resins with 2% DVB is higher than 400%, about 150% for Amberlyst 39 (macroreticular, low DVB%), and around 50% in macroreticular resins of medium and high DVB% such as CT252 or Amberlyst 15. On the contrary, linear ethers hardly swell resins as shown by Amberlyst 70 in DNPE [35] and DNHE [13].

Resin morphology changes on swelling and non-permanent pores appear. A description of their nature and characteristics can be obtained by the analysis of ISEC data. In macroreticular beads, a part of open spaces can be characterized by the cylindrical pore model by estimating surface area, S_g^{ISEC}, and pore volume, V_g^{ISEC}. These spaces, in the mesopores range, are placed between aggregates. However, such model is unable to describe the spaces between polymer chains formed in the micropores range by aggregates and nodules swelling. A good view of the three-dimensional polymer network of swollen gel phase is given by the Ogston geometrical model in which micropores are described by spaces between randomly oriented rigid rods [36]. From ISEC data, the Ogston model allows to estimate the specific volume of swollen polymer (free space volume plus that occupied by the skeleton), V_{sp}, and also to distinguish gel zones of different density or polymer chain concentration. According to Ogston model, polymer chains density is described as the total rod length per unit of volume of swollen polymer, nm^{-2}. All the spaces formed in swollen gel-type resins lay in the micropores range.

As seen in Table 4, macroreticular resins with high and medium crosslinking degree but Amberlyst 16 have permanent macropores in dry state. Amberlyst 16 and Amberlyst 39 and 70 (low crosslinking degree) show very low BET surface areas when resin samples for adsorption-desorption N_2 measurements are dried by heating at vacuum at 383K with no pretreatment to remove water. However, if water is previously removed by consecutive rinsing with methanol, toluene and hexane, macropores do not collapse and BET surface areas about 30 m^2/g are found. ISEC data analysis shows surface areas between 132 (CT152) and 176 m^2/g (CT276), and pore volumes between 0.33 (Amberlyst 36) and 0.82 cm^3/g (CT175). Both parameters are far higher than those in dry state showing that new spaces (mesopores) are open. In general, BET surface area (S_g) and pore volume (V_g), and pore volume in swollen state (V_g^{ISEC}) lessen on decreasing DVB% (e.g. Amberlyst 15, 16 and 39; or Amberlyst 35 and 36). As a rule, monosulfonated macroreticular resins show higher surface area and pores volume than their oversulfonated versions. This fact is apparent if pore diameter, in dry and swollen state, is compared. On the contrary, gel-type resins do not show mesopores neither in dry state nor in swollen state.

Typically, gel-type resins show higher V_{sp} values than macroreticular ones and, among each resins group, V_{sp} decreases as DVB% increases. For example the resins series of similar acid capacity but increasing crosslinking degree: Dowex 50Wx2, 50Wx4, 50Wx8 and CT165 (gel-type) or Amberlyst 39, 16 and 15 (macroreticular). The polymer density zones distribution of the swollen gel-phase of tested resins is shown in Fig. 2. Gel-type resins with 2-4 DVB% and macroreticular resins of 8 DVB% show chain concentrations in swollen gel-phase of 0.4-0.8 nm^{-2}, typical of slightly dense polymer mass. Gel-type resins with ≥ 8 DVB% and medium and highly macroreticular degree show densities in the range 1.5-2 nm^{-2}, typical of highly dense polymer mass. Spaces in gel phase zones of chain density 0.4 nm^{-2} are equivalent to 2.9 nm pores; 1.5 nm in density zones of 0.8 nm^{-2}; and ≤ 1 nm for chain densities higher than 1.5 nm^{-2} [37]. Porosity of swollen gel-phase, θ_{gel}, which is a function of V_{sp} and skeletal density, and V_{sp} show a similar trend. They increase with DVB%, and macroreticular resins have smaller values than gel-type ones. Finally, as seen in Table 4 and Fig.2, by comparing monosulfonated resins with their oversulfonated versions (Amberlyst 15 vs. 35, Amberlyst 16 vs. 36, CT175 vs. CT275 or CT124 vs. CT224), the introduction of additional acid sites results in stiffer morphology.

CT165 is considered as gel-type since it does not show mesopores in swollen state. In fact, it only shows micropores. Its V_{sp} value and the distribution of density zones are similar to that of high-crosslinked macroreticular resins. In addition, it is outstanding that surface area of swollen Amberlyst 46 is similar to that of the other macroreticular resins. However, the V_{sp} value is very low since $–SO_3H$ groups are located in a narrow layer of polymer near the surface, and the non-sulfonated polymer zone is impervious to polar molecules such as water or alcohol.

3.2 Description of an experiment

Fig 3 shows the evolution of ethanol and 1-octanol conversions and selectivity with time in an experiment conducted on Dowex 50Wx2. It was found that ethanol and 1-octanol amounts decreased monotonically over time giving place to water, DEE, EOE and DNOE. DEE and EOE were formed in similar quantities unlike DNOE that was formed in smaller amounts. Branched ethers, C_8 alkenes or ethylene were no detected. As expected, conversions increased with time, X_{EtOH} being always higher than X_{OcOH}. As for ethanol, S_{EtOH}^{DEE} was higher than S_{EtOH}^{EOE}, whereas for 1-octanol S_{OcOH}^{EOE} was higher than S_{OcOH}^{DNOE}. Selectivity changes after 1h are little.

Taking into account the products detected in the reaction between 1-octanol and ethanol, the reaction network of Scheme 1 can be inferred. The desired reaction between the alcohols to give place to EOE [R1] takes place in parallel with the intermolecular dehydration of two ethanol molecules to produce DEE [R3], and that of two 1-octanol molecules forming DNOE [R2]. The 1-octanol intramolecular dehydration to 1-octene [R4] and subsequent C_8 alkenes isomerization [R5,R6,R7] were detected on CT276 but in very little extent ($\leq 0.14\%$ w/w). Finally, ethylene and branched octyl ethers were no found on any resin catalyst.

3.3 Catalysts test

Fig. 4 (up) plots the products distribution after 6 h of reaction over all catalysts, in increasing order of EOE production from left to right. Although the formation of an ether molecule implies the release of a water molecule, the mole of water in the liquid phase was lower than the sum of the ethers, i.e. on Dowex 50Wx2 the liquid contained 0.056 mol/g of water and 0.087 of ethers. About 0.030 mol/g of water was retained in the resin contributing to swelling. Since in aqueous media a $-SO_3H$ group may be hydrogen-bonded to 3 water molecules on average [38] it can be assumed that up to 0.015 mol/g of water are linked to acid groups. The higher amounts of EOE were found on gel-type resins with 2 DVB% Amberlyst 121 and Dowex 50Wx2. Then, in decreasing order, gel-type with 4 DVB% (CT224, CT124, Dowex 50Wx4 and Amberlyst 31), gel-type of 8 DVB% and macroreticular of low crosslinking degree (Amberlyst 39, Dowex

50Wx8, Amberlyst 70, Amberjet 1200H and 1500H), macroreticular of medium DVB% (Amberlyst 16, CT151, Amberlyst 36 and CT252), and macroreticular of high crosslinking degree (CT175, CT276, CT275, Amberlyst 15 and 35). CT165 resin (gel-type, > 8 DVB %) gave place to EOE amounts similar to the last group. As seen, more EOE was obtained over gel-type than on macroreticular ones, and among each group, the lower the DVB% the higher EOE formation. Resins that gave higher EOE amounts have high V_{sp} values as well as low gel-phase densities which results in a flexible morphology in swollen state. It is thus assumed that flexibility of swollen polymer matrix is an important issue for the reaction to proceed. Similarly, DNOE production increased on increasing the flexibility of resins matrix. On the contrary, formation of DEE was favored in the stiffer resins. It is to be noted that the pattern observed for the EOE and DNOE simultaneous syntheses agree with that of DNOE synthesis from 1-octanol over ion-exchange resin catalysts [39].

Amberlyst 16, CT151, Amberlyst 36 and CT252 yielded the higher total amount of ethers, DEE being preferably formed (Fig. 4 down). The ethers pool contained 75-80 % mol/mol DEE. Accordingly, the C_{10} – C_{16} ethers fraction was quite low, e.g. 22% on Amberlyst 36 (40% w/w). On the contrary, similar amounts of EOE and DEE were found on Amberlyst 121 and Dowex 50Wx2 (gel-type, 2% DVB), the sum of EOE and DNOE mole fraction being about 55% (76% w/w on Amberlyst 121, 73% w/w on Dowex 50Wx2). To implement industrial processes for EOE synthesis these figures point out promising ethers yields for direct blending in commercial diesel. CT224, CT124 and Dowex 50Wx4 (gel-type, 4% DVB) could be interesting as well since the joint molar amount of EOE and DNOE yielded was of the same order as that of DEE.

Due to the low number of acid sites, Amberlyst 46 and 70 yielded smaller amount of ethers. Amberlyst 70 has the same crosslinking degree as Amberlyst 39 but its acid capacity is lower by 40% due to substitution of hydrogen by chlorine. DEE production was higher on Amberlyst 39 but ethers distribution on Amberlyst 70 is close to that found on CT124 or Dowex50Wx2. As seen, despite Amberlyst 70 swells less in both alcohols (Table 3), the swollen gel-phase is less dense (Fig. 2) and this could favor the formation of bulkier ethers. Thus the nature of open spaces on swelling is an issue to consider. On the other hand, ethers distribution on Amberlyst 46 is between those of Amberlyst 39 and Dowex 50Wx4 (Fig. 4, down). Amberlyst 46 can be considered as a catalyst model, in which permeation effects of reaction species are negligible, since all active centers are very near the polymer surface. It can thus be assumed that resins yielding ethers distribution close to Amberlyst 46, or more favorable to bulkier ethers, all they highly swell in 1-octanol, and show gel-phase zones of density 0.4 nm^{-2} (equivalent to 2.9 nm pores) by analysis of ISEC data. Such catalysts have to be flexible enough to allow the diffusion of reactants and products, as well as to accommodate reaction intermediates.

X_{EtOH} of Amberlyst 46 and 70 at 6 h was 12.7 and 33.7% at 6h, respectively. Table 5 shows 1-octanol conversion, selectivity and yield to EOE, estimated from the mole-time curves of obtained ether, at those ethanol conversions. All catalysts reach X_{EtOH} = 12.7% faster than Amberlyst 46 since they have higher $[H+]$. Generally, the faster the reaction the lower X_{OcOH}, Y_{EtOH}^{EOE} and Y_{OcOH}^{EOE}. High ether yields are shown by the resins having high X_{OcOH} and S_{EtOH}^{EOE}, but low S_{OcOH}^{EOE}. In agreement with Fig. 4 (up), higher EOE yields were found, in decreasing order, on gel-type resins with 2-4 DVB%, macroreticular of low crosslinking degree, gel-type of 8 DVB% , macroreticular of medium and high crosslinking degree. It is to be noted that Dowex 50Wx2, Amberlyst 121, CT224, Dowex 50Wx4, CT124 and Amberlyst 70, have higher yields than Amberlyst 46. At X_{EtOH} = 33.6%, 1-octanol conversion, selectivity and yield to EOE follow similar trend to that described at X_{EtOH} = 12.7%. Amberlyst 121, Dowex 50Wx2 and Amberlyst 70 show the best behavior; activity of Dowex 50Wx4, CT124 and CT224 being a bit less. All of them have simultaneously higher X_{OcOH} and S_{EtOH}^{EOE} at both conversion levels. They highly swell and the swollen gel-phase morphology is slightly dense.

Table 6 shows 1-octanol and ethanol conversions, and selectivity and yield to EOE with respect to both alcohols at the same time of reaction (6h). The higher ethanol conversions were found in the less swollen resins. It is seen that on increasing DVB%, X_{EtOH} decreases and X_{EtOH} increases. In addition, S_{EtOH}^{EOE} also decreases whereas S_{OcOH}^{EOE} show higher values on gel-type resins with 8 DVB% and medium cosslinked resins. As a result, Y_{EtOH}^{EOE} and Y_{OcOH}^{EOE} increased as a whole on lowering the DVB% of catalysts. As seen, the decrease in X_{EtOH} is balanced by higher S_{EtOH}^{EOE} values whereas the rise in Y_{OcOH}^{EOE} can be explained by the increase in X_{OcOH} observed on decreasing DVB%. Amberlyst 121, Dowex 50Wx2 and CT224 gave the higher EOE yields. Yields on Amberlyst 39 and 70 are close to those of gel-type resins of 4 DVB%. The smallest EOE yields were found on Amberlyst 46.

By comparing resins having the same number of acid sites but different crosslinking degree (Amberlyst 15, 16 and 39; Amberlyst 35 and 36; Dowex50Wx2, 50Wx4, 50Wx8) it is seen that X_{EtOH} increased whereas X_{OcOH} and S_{EtOH}^{EOE} decreased on increasing crosslinking degree. S_{OcOH}^{EOE} shows an smooth maximum on gel-type resins with 8% and medium crosslinked macroreticular ones. On the other hand, on comparing monosulfonated resins with oversulfonated versions (Amberlyst 15 vs. 35, Amberlyst 16 vs. 36, CT151 vs. CT252, CT124 vs. CT224 or CT175 vs. CT275), the first resins showed more X_{OcOH} and as a consequence less X_{EtOH} and S_{EtOH}^{EOE}. S_{OcOH}^{EOE} is higher on oversulfonated macroreticular resins and less oin gel-type ones.

Macroreticular ion-exchange resins of medium and high DVB% showed the higher initial reaction rates for DEE formation, whereas the higher EOE and DNOE initial reaction rates were found on gel-type resins of low crosslinking degree. For each single catalyst, the following pattern was observed: $r^0_{DEE} > r^0_{EOE} >> r^0_{DNOE}$. The lowest initial reaction rates were obtained on Amberlyst 46 due to its very low acid capacity. However, as for initial *TOF* values, Amberlyst 70 appeared as the best catalyst for EOE formation (Fig. 5). As a whole, initial *TOF* values for EOE and DNOE formation are higher on gel-type resins with 2 - 4 DVB% and Amberlyst 70. They are similar to that of the surface sulfonated Amberlyst 46. It is to be noted that generally these catalyst are highly selective to EOE

3.4 Influence of [H^+], acid strength, and swollen morphology on resins catalytic activity

The influence of acid capacity and acid strength, besides V_{sp} and θ_{gel} (gel-phase porosity), on conversion and selectivity was checked. These structural parameters are relevant since describe the morphology of swollen resins in aqueous media which is probably close to the real state of the resins over the reaction seeing that water is formed in the reactions [11].

X_{EtOH} and X_{OcOH} at 6 h are plotted versus *[H+]* in Fig. 6 (up). As seen, X_{EtOH} increased almost linearly with *[H+]* and X_{OcOH} increased up to values of 2.65 meq H^+/g, but it hardly increased at higher *[H+]* values. However, a great dispersion is observed for resins containing from 4.8 to 5.4 meq H^+/g, suggesting the concurrent influence of other issues such as swollen morphology. Similar trends were observed in conversions vs. θ_{gel} or V_{sp} plots. As seen in Fig. 6 (down) X_{OcOH} increased with V_{sp}. High crosslinking macroreticular resins with $V_{sp} \approx 0.8$ cm^3/g (e.g. Amberlyst 15), showed the lowest 1-octanol conversion whereas the higher values were obtained over gel-type resins Amberlyst 121 or Dowex 50Wx2 having $V_{sp} \geq 2$ cm^3/g, e.g.. As for X_{EtOH}, a smooth maximum at $V_{sp} \approx 1$ cm^3/g ($30 \leq \theta_{gel} \leq 35\%$) is seen on CT151 or Amberlyst 36. Conversions of ethanol on Amberlyst 46 and 70 were clearly lower than on the other resins due to their lower acid capacity. However, their X_{OcOH} follows the general trend.

Selectivity to EOE and DEE with respect to ethanol or to EOE and DNOE with respect to 1-octanol was little influenced by *[H^+]* (Fig. 7 up). Again, selectivity plots against V_{sp} and θ_{gel} are quite similar. As shown in Fig. 7 (down), the selectivity to EOE with respect to ethanol clearly increased with V_{sp}. Accordingly, selectivity to DEE decreased. As for selectivity to EOE with respect to 1-octanol, a smooth maximum (82 -83%) is seen at $1 \leq V_{sp} \leq 1.6$ cm^3/g ($30 \leq \theta_{gel} \leq 60\%$) on Dowex 50Wx8, CT165 and Amberlyst 36 and, accordingly, a minimum in selectivity to DNOE with respect to 1-octanol. Dowex 50Wx2 and Amberlyst 121 gave the higher EOE yield, S_{OcOH}^{EOE} being of 67-68%. Flexibility of swollen gel-phase influences to a great extent the selectivity. Catalysts with stiff matrix favored DEE formation, whereas resins with highly swollen and flexible polymer matrix favored EOE synthesis. In the latter, DNOE synthesis competed actively with that of EOE diminishing selectivity to EOE with respect to 1-octanol.

As for Amberlyst 70 and 46, both follow the general trend showing similar selectivity as gel-type ones with 4 DVB%.

Acid strength data of acidic resins are scarce in the open literature [40-42]. The Hammett acidity functions ($-H_0$) of Amberlyst 15 (2.2) and Amberlyst 35 (2.65) are equivalent to a H_2SO_4 solution of 35 -48 % (w/w). However, in non aqueous solution Amberlyst 35 has ($-H_0$) ≈ 5.6, of the same order as common zeolites, and equivalent to a H_2SO_4 solution of 70 % (w/w) [40]. The enthalpy of ammonia adsorption ($-\Delta H_{ads}$) measured by flow ammonia adsorption calorimetry has been used to compare differences in acid strength of acid resins. As for tested catalysts, the following ($-\Delta H_{ads}$) values are found: 111 ± 2 kJ/mol (Amberlyst 15), 114.2 ± 1 kJ/mol (CT175), 117 ± 2 kJ/mol (Amberlyst 35, 36 and 70) and 119.2 ± 1 kJ/mol (CT275) [41,42]. Amberlyst 15 and CT175 (monosulfonated resins) have less acid strength than Amberlyst 35, 36 and CT275 (oversulfonated resins), therefore it is inferred that acid strength of oversulfonated is usually higher. Amberlyst 70 and oversulfonated resins have similar ($-\Delta H_{ads}$) possibly as a consequence of the activating halogen substitution on the benzene rings. Amberlyst 35, 36, and CT275 show X_{EtOH}, S_{EtOH}^{DEE} and S_{OcOH}^{EOE} higher than Amberlyst 15, 16, and CT175 (monosulfonated versions). As a result, X_{OcOH}, S_{EtOH}^{EOE} and S_{OcOH}^{DNOE} were lower (Table 5), and the latter gave higher amounts of EOE and DNOE (Fig. 4, up). Oversulfonated resins do not take advantage of the higher number of acid sites and acid strength to produce EOE since the excess of acid sites gives place to less swollen polymers (with the same gel-phase density) so that the fact that gel-phase was stiffer constrained the effects of higher acidity. Conversely, Amberlyst 70 gives a similar amount of EOE and DNOE as Amberlyst 39 despite the higher $[H^+]$ of the latter. These could be due to the combined effect of higher acid strength and less dense gel-phase (Fig. 2).

It is assumed from conversion and selectivity data that the reaction between ethanol and 1-octanol takes place mainly in the pores of the swollen resins. Alcohols compete for the acid sites and the distribution of ethers can be explained by the nature of the spaces open in the gel-phase which is related to the chains density in the different polymer zones. In the gel-type resins with

2 DVB% (i.e. Dowex 50Wx2) open spaces on swelling are wide, it is likely that liquid inside pores contain more 1-octanol than ethanol, and spatial requirements for transition state can be fulfilled for EOE and DNOE synthesis. As spaces open are increasingly narrow, despite both alcohols can reach sulfonic groups spatial restrictions are increasingly higher and selectivity to EOE decreases. As macroreticular of medium DVB% showed the higher X_{EtOH}, it is likely that in swollen gel-phase pores of those of high crosslinking DEE formation was also hindered.

ChemBioOffice 2010 software allows drawing molecules in the conformation of minimum energy and from the distances and angles of bond between atoms estimating length, height, and width of molecules. Estimation of molecular size of reactants and products by ChemBioOffice 2012 show that alcohols and ethers are almost linear (0.33 nm height x 0.18 nm width) with length ranging from 0.41 nm (ethanol) to 2.16 nm (DNOE) as Table 7 shows.

An indication of which part of the porous system is accessible to spherical molecules having the diameter d_m is given by the Ogston distribution coefficient, K_0, estimated by [37,43]:

$$K_0 = \exp\left(-0.25\pi C\left(d_m^2 + d_c^2\right)\right) \quad (8)$$

K_0 indicates the relative quantity of compound present in a zone of a given density as compared to the quantity in the free solution. As defined by eq. 8 K_0 ranges from 1 (the amount of a given compound is the same as outside gel-phase) to 0 (the compound is totally excluded from that gel-phase zone). The diameter of rigid rods representing polymer chains is d_c (0.4 nm) and C is the polymer chain density (nm^{-2}). As Eq. 8 considers spherical molecules, length is a good approximation of the effective size, d_m [43]. From K_0 values (Table 7) it is seen that ethanol and 1-octanol can penetrate easily to the little dense swollen gel-phase zones of gel-type resins with 2% DVB (0.4 nm^{-2}, Fig 2), and the three ethers can be readily formed in their pores. Accordingly, ethanol and 1-octanol compete for the acid sites and the amount of EOE is comparable to that of DEE (Fig 4). On the contrary, macroreticular resins of high crosslinking degree have a very dense swollen polymer zone. According to K_0 only ethanol would have a significant presence in such zone, and consequently DEE is preferably formed. The very low K_0

of 1-octanol, EOE and DNOE suggest that they are practically excluded from that polymer region in agreement with the small amounts of EOE and DNOE are formed.

Similar conclusions are obtained by comparing the random coil diameter to the equivalent pore diameter of the distinct density zones of swollen polymer. The random coil diameter, Φ_d (nm) is a measure of the space filled by a molecule of molecular weight, $\overline{M_w}$ (g/mol). It can be computed by the empirical equation [44]

$$\Phi_d = 0.02457\left(\overline{M}_w\right)^{0.5882} \qquad (9)$$

It is accepted that spaces between polymers chains had to be at least 2.5 times higher than Φ_d to assure that there is no permeation problems into gel phase. As seen by comparing data of Table 7 with the equivalent pore diameters, ethanol, 1-octanol and all ethers permeate easily in 2.6 nm pores, but only ethanol and, perhaps, DEE have mobility in pores of diameter less than 1 nm. Therefore, the access of 1-octanol to this stiff zone could be hindered and as a result EOE and DNOE syntheses.

Alcohol dehydration to ether was found to occur by Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal mechanisms [45-48]. The first involve the reaction between two alcohol molecules adsorbed onto the resin and from a molecular standpoint it requires an state of transition on two adjacent sites, so that proton transfer takes place by concerted mechanisms (Scheme 2) [45,46]. In Eley-Rideal ones, an alcohol molecule reacts from the liquid phase with a second alcohol molecule adsorbed on the resin. The transition state would require a single acid site (Scheme 3, up), or the cooperation of a second site (down) to stabilize the intermediate of reaction and facilitate the proton transfer [47]. On the other hand, by studying the dehydration of deuterated secondary alcohols it was found that the reaction can be depicted as the attack of an alcohol molecule acting as a nucleophile over a second one acting as an electrophile, and that during the ether formation the carbon atom bond to oxygen of alcohol acting as a nucleophile underwent the inversion of its configuration [49]. The surface of resins is quite flexible and adaptable to the spatial requirements of transition state for the reaction of EOE synthesis takes place. Considering that the hydrocarbon counterpart of adsorbed ethanol or 1-octanol molecules moves freely on the surface, and the spatial needs for the inversion of configuration, it can be reasonably assumed that the likelihood of formation of the transition state is maximum if all molecules have the lowest energy configuration. Thus 1-octanol and ethanol would be mobile in a hemisphere of 1.2 and 0.4 nm, respectively. Gel-zone resins with density 0.4 nm^{-2} met such requirements and production of EOE and DNOE is significant. In zones of density ≤ 1 nm^{-2} it is unlikely that adsorbed 1-octanol could adapt the lowest energy configuration. As a consequence to find the appropriate molecular arrangement of the transition state for EOE synthesis would be largely hindered.

3.5The influence of H^+ concentration in the gel phase on the catalytic behavior

As section 3.3 shows, the number of acid sites and morphology greatly influenced the catalytic behavior of resins. Still, the effect of *[H+]* and V_{sp} on activity is partially overlapped i.e. oversulfonation is accompanied by an increase of the stiffness of swollen resins. The ratio between [*H+]* and V_{sp} (Eq. 10) reports the average concentration of active sites per volume unit of swollen polymer. Despite assuming a uniform distribution of acid centers, it could be a useful global parameter to explain the catalytic behavior of resins. Oversulfonated highly crosslinked macroreticular resins (e.g. Amberlyst 35) have the higher $[H^+]/V_{\mathrm{sp}}$ values whereas monosulfonated gel-type ones with 2 DVB% (e.g. Amberlyst 121) have the lower ones.

$$\left[H^+\right]/V_{sp} \quad \left[\mathrm{meq\ H^+ / cm^3\ of\ swollen\ polymer}\right] \qquad (10)$$

Fig. 8 shows the variation of alcohols conversion (up) and selectivity to ethers (down) as a function of $[H^+]/V_{sp}$. As seen, X_{EtOH}, S_{EtOH}^{DEE} and S_{OcOH}^{EOE} increased for $[H^+]/V_{sp} \leq 4$ meq H$^+$/cm^3, whereas X_{OcOH}, S_{EtOH}^{EOE} and S_{OcOH}^{DNOE} decreased. Still, for $[H^+]/V_{sp} \geq 5$ meq H$^+$/cm^3 ethanol and octanol conversions and selectivity to ethers remained almost constant, even though an smooth maximum in X_{EtOH} is seen at $[H^+]/V_{sp} \approx 6$ meq H$^+$/g. Therefore, ethanol conversion was favored on resins showing high acid sites concentration in the swollen gel phase. Conversely, 1-octanol conversion increases in resins with low $[H^+]/V_{sp}$ values. As for selectivity, the ether of smaller molecular size is favored on increasing $[H^+]/V_{sp}$ for the two alcohols. Gel-type resins with 2 DVB% have the lower $[H^+]/V_{sp}$ values. They greatly swelled in the reaction medium showing large zones of polymer density 0.4 nm^{-2} in which ethanol and 1-octanol easily access and spaces are wide enough so that DEE, EOE and DNOE are obtained in significant amount. Increasing $[H^+]/V_{sp}$ values correspond to resins of higher polymer density; therefore the formation of bulkier ethers EOE and DNOE is increasingly hindered. Finally, the resins with $[H^+]/V_{sp} \geq 5$ meq H^+/cm^3 are CT165 (gel-type, ≥ 8 DVB %) and macroreticular with medium and high crosslinking degree but Amberlyst 16. They have zones of polymer density ≥ 1.5 nm^{-2} (Fig. 2) and low swelling degree and as a result, EOE (and DNOE) synthesis are more limited than that of DEE. Therefore, high $[H^+]/V_{sp}$ values are not profitable since a fraction of the active sites is located in high density zones and EOE and DNOE syntheses is significantly hindered. Ethanol conversion over Amberlyst 46 and 70 was lower than those of resins with similar $[H^+]/V_{sp}$ due to their very low acid capacity. However, 1-octanol conversion and selectivity followed well the trends shown for the other resin catalysts.

Initial TOF values for DEE synthesis are plotted as a function of $[H^+]/V_{sp}$ in Fig.9 (up). As seen initial TOF values rose with $[H^+]/V_{sp}$. Acid sites concentration in the swollen gel-phase has therefore a positive effect on DEE formation. TOF^0_{DEE} values can be grouped along two straight lines. Initial TOF of CT124, CT224, Amberjet 1200H and 1500H ($2.6 \leq [H^+]/V_{sp} \leq 3.3$ meq H^+/cm^3), as well as Amberlyst 15, CT165, CT151, CT275 and CT276 ($6 \leq [H^+]/V_{sp} \leq 6.4$ meq H^+/cm^3) are found in the line of lower slope. In all these resins the zone of polymer density 2 nm^{-2} has a significant volume in swollen state. The other resins have zones of density 0.4 – 1.5 nm^{-2} and show higher sensitivity to acid site concentration what suggests that in the first group (stiffer resins) actually DEE formation is limited in some extent. Unexpectedly, TOF^0_{DEE} of Amberlyst 46 is far less than those of resins with $[H^+]/V_{sp} \approx 5.5$ meq H^+/cm^3, seeing that ethanol access to acid sites of the surface sulfonated resin the likelihood is not hindered.

Initial TOF values for DNOE formation decreased noticeably with $[H^+]/V_{sp}$ (Fig. 9, down). Amberlyst 121, Dowex 50Wx2, CT124 and Amberlyst 46 showed higher TOF^0_{DNOE} values. Since acid groups in Amberlyst 46 are located in a very shallow polymer layer near the surface it can be assumed that all acid sites are able to participate in DNOE synthesis. Swollen polymer volume of Amberlyst 121, Dowex 50Wx2 and CT124 is high and polymer density low (0.4 - 0.8 nm^{-2}, Fig. 2) so that DNOE is readily formed. As $[H^+]/V_{sp}$ rises the spaces open on swelling are narrower and the synthesis of DNOE is greatly hindered. Macroreticular resins of medium and high crosslinking degree, and gel-type resins with ≥ 8 DVB% show TOF values between a half and a tenth of that of Amberlyst 46.

As for EOE formation, TOF values decreased moderately as a whole on increasing $[H^+]/V_{sp}$ (Fig. 9, medium). The highest initial TOF was found on Amberlyst 70. Besides, a resins series (gel-type with 2-8 DVB%, Amberlyst 39, medium crosslinked macroreticular but CT252; $1.5 \leq [H^+]/V_{sp} \leq 5.6$ meq H^+/cm^3) showing $1.7 \geq TOF^0_{EOE} \geq 1.3$ mol/h·meq H^+, and a second series (CT165, CT252, highly crosslinked macroreticular resins; $5.0 \leq [H^+]/V_{sp} \leq 6.9$ meq H^+/cm^3) with TOF^0_{EOE} values ranging from 1 to 1.5 mol/h·meq H^+ can be distinguished. As seen, the second series is composed by catalysts with a swollen polymer gel-phase very dense. Initial TOF values in the first series are close to that of Amberlyst 46; thus it can be assumed that in the swollen gel-phase of these resins ethanol and 1-octanol actually compete for the active sites and it is to ne noted that initial TOF^0_{EOE} appear to be nearly independent on $[H^+]/V_{sp}$ unlike TOF^0_{DEE} and TOF^0_{DNOE}. Amberlyst 70 TOF^0_{EOE} is higher than that of Amberlyst 46 by 59%. Morphology of swollen Amberlyst 70 is accordingly suitable for the reaction of EOE synthesis. It could be favored as well by its acid strength, a bit higher than that of monosulfonated resins.

On swelling Amberlyst 46 shows mean pore diameter of 10.3 nm (macropores, Table 4) and the functionalized gel-phase has similar density to medium cross linked macroreticular resins (1.5 nm^{-2}). As compared with Amberlyst 36, CT151 or CT252 (that have a similar $[H^+]/V_{sp}$), Amberlyst 46 shows lower TOF^0_{DEE}. However, it shows very higher TOF^0_{DNOE} and in general higher TOF^0_{EOE} (Fig. 9). These facts suggest that despite swollen gel-phase is quite dense, as the swollen region has only a few polymer layers it is likely that liquid surrounding acid groups and outside resin has the same composition. Amberlyst 46 can thus be considered as a reference since all actives sites are accessible to reactants. For EOE and DNOE syntheses Amberlyst 46 TOF was as high as those of gel-type resins with 2 DVB% that highly swell and composition of the liquid inside gel-phase allows the alcohols to compete for acid sites. However, TOF values for EOE and DNOE synthesis decrease as resins have a more impervious morphology. Some causes could be: 1) swelling degree highly decreases on increasing DVB% and simultaneously gel-phase is increasingly denser; 2) despite that 1-octanol probably predominates in the swollen polymer, the spatial requirements for transition estate hinders the synthesis of bulkier ethers in impervious environments; 3) EOE and DNOE are excluded from pores ≤ 1 nm due to molecular size. A rough estimation of the fraction of acid sites taking part in EOE and DNOE synthesis can be performed from the ratio of resins initial TOF to that of Amberlyst 46 ratio (Table 8). As seen, the ratio ranges from ≈ 1 to 0.5 for EOE synthesis, and from 1 to 0.17 for that of DNOE. For EOE synthesis they are similar to those estimated for 1-octanol dehydration to DNOE in the absence of other alcohols [39]. In the presence of ethanol the fraction of accessible sites giving place to DNOE, particularly for medium and highly crosslinked macroreticular resins, is clearly smaller. This fact could be ascribed to competition with ethanol for acid sites. The high values for Amberlyst 70 can be ascribed to the combined effect of suitable swollen morphology and a bit higher acid strength of acid sites by the presence of chlorine in this resin.

The concentration of acid sites in the swollen resin, $[H^+]/V_{sp}$, could be used as a guide for selecting a suitable resin to catalyze the formation EOE from ethanol and 1-octanol. Since high $[H^+]/V_{sp}$ values are characteristic of resins with low $\mathrm{V_{sp}}$ and very dense polymer zones, the two parameters could be used jointly to select the proper catalyst. In this way, resins with $V_{sp} \geq 2$ cm^3/g and $1.5 \leq [H^+]/V_{sp} \leq 1.5$ meq $H^+ \cdot cm^{-3}$ (Amberlyst 121 and Dowex 50Wx2) showed the best behavior for EOE synthesis and that of DNOE byproduct. Amberlyst 70 ($[H^+]/V_{sp} = 2.2$ meq $H^+ \cdot cm^{-3}$ and $V_{sp} = 1.2$ cm^3/g) shows a very good activity to EOE. On the contrary, good yields to DEE byproduct are obtained by using resins with $V_{sp} \approx 1$ cm^3/g and $[H^+]/V_{sp} \approx 5.5$ meq

$H^+\cdot cm^{-3}$ (Amberlyst 36 and CT252). However, data scattering of Figs. 6, 7, 8 and 9 suggest that the influence of V_{sp}, $[H^+]$ and $[H^+]/V_{sp}$ on the resins activity cannot be analyzed separately. Therefore, the study their combined effect on conversion, selectivity to EOE and reaction rate deserves further work.

4. Conclusions

The formation of EOE over ion-exchange resins is feasible, though DEE and in less extent DNOE were also formed. EOE is the ether of intermediate molecular size and morphology of resins in the reaction medium is a very important factor for the reaction to take place selectively to EOE. The resins able to largely swell in the reaction medium gave the better yields in EOE, and DNOE byproduct. In this way, gel-type resins with 2 DVB % Amberlyst 121 and Dowex 50Wx2 yielded the maximum amount of EOE, whereas highly crosslinked macroreticular resins (e.g. Amberlyst 35 or CT275) produced mainly DEE. Resins acid capacity was found to be the most relevant property for ethanol conversion. In addition, 1-octanol conversion and selectivity to EOE were greatly influenced by V_{sp} and porosity. The ratio $[H^+]/V_{sp}$ could be used as a guide for selecting a proper catalyst for EOE synthesis. The variation of initial reaction rate of ethers syntheses with regard to $[H^+]/V_{sp}$ showed that EOE formation (and that DNOE) is enhanced in resins with low concentration of acid sites in the swollen polymer. It suggests that a fraction of the active sites of highly crosslinked resins does not take part in EOE synthesis.

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6. Nomenclature

C	polymer chain density (nm^{-2})

d_c	diameter of polymer chains (nm)
d_m	molecule diameter assumed spherical (nm)
d_p	particle diameter (μm)
d_{pore}	pore diameter (nm)
$[H^+]$	number of acid sites per unit mass of dry resin (meq H^+ g^{-1})
K_0	Ogston distribution coefficient
$\overline{M}_w$	molecular weight (g/mol)
n_j	mole of compound j (mol)
r_j	reaction rate of synthesis of compound *j* (mol h^{-1} kg^{-1})
r^0_j	initial reaction rate of synthesis of compound *j* (mol h^{-1} kg^{-1})
$R_{EtOH/OcOH}$	initial molar ratio ethanol/1-octanol
S_j^k	selectivity to k (product) with respect to j (reactant) (%)
S_g	surface area estimated by BET method (m^2 g^{-1})
S_g^{ISEC}	surface area of swollen polymer estimated from ISEC data (m^2 g^{-1})
t	time (h)
T	temperature (K)
T_b	boiling point (K)
TOF_j	turnover frequency of reaction of synthesis of compound *j* (mol h^{-1} $(eqH^+)^{-1}$)
V_g	pore volume from N_2 adsorption-desorption at 77 K (cm^3 g^{-1})
V_g^{ISEC}	pore volume of swollen polymer estimated from ISEC data (cm^3 g^{-1})
V_{sp}	specific volume of the swollen polymer phase (cm^3 g^{-1})
W	weight of dry catalyst (g)

X_j	conversion of reactant j (%)
Y_j^k	yield to k (product) with respect to j (reactant) (%)

Acronyms

DEE	diethyl ether
DNHE	di-n-hexyl ether
DNOE	di-n-octyl ether
DNPE	di-n-pentyl ether
DNPM	di-n-pentoxy methane
DVB	divinylbenzene
EtOH	ethanol
EOE	ethyl octyl ether
MOE	methyl octyl ether
OcOH	1-octanol

Greek letters

Φ_d	random coil diameter, nm
ρ_s	skeletal density (g/cm^3)
θ_{gel}	porosity of gel phase

7. Literature

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Figure captions

Figure 1. Bead size distribution of Amberlyst 70 in air (—), 1-octanol (—), ethanol (····) and water (----)

Figure 2. ISEC pattern for gel-type (up) and macroreticular (down) resins

Figure 3. Evolution of ethanol (■) and 1-octanol (♦) conversions (right y-axis), selectivity to DEE (■) and EOE (♦) with respect to ethanol and selectivity to EOE (x) and DNOE (○) with respect to 1-octanol (left y-axis) over time (1g Dowex 50Wx2, T=423 K, $R_{EtOH/OcOH}$ = 1).

Figure 4. Products molar distribution: (up) water (▒), DEE (□), EOE (▒) and DNOE (█) formed and (down) DEE (□), EOE (▒) and DNOE (█) fraction in the ether mixture (t= 6 h, T=423 K, 1 g of catalyst, $R_{EtOH/OcOH}$ = 1).

Figure 5. Initial TOF of EOE (▒), DEE (□) and DNOE (█) syntheses on tested catalysts (T = 423K, W_{cat} = 1g, $R_{EtOH/OcOH}$ = 1)

Figure 6. Influence of resin morphology on ethanol (♦) and 1-octanol (▲) conversion versus acid capacity (up) and V_{sp} (down) (T = 423K, W_{cat} = 1g, $R_{EtOH/OcOH}$ = 1, t = 6h). Open Square (□) and Circle (○) correspond to Amberlyst 46 and 70, respectively.

Figure 7. Influence of resin morphology on selectivity to DEE (♦) and EOE (♦) with respect to ethanol and selectivity to EOE (▲) and DNOE (x) with respect to 1-octanol versus acid capacity (up) and V_{sp} (down) (t = 6h,T = 423K, W_{cat} = 1g, $R_{EtOH/OcOH}$ = 1). Squares and Circles correspond to Amberlyst 46 and 70, respectively.

Figure 8. Ethanol (♦) and 1-octanol (▲) conversion (up), selectivity to DEE (♦) and EOE (♦) with respect to ethanol and selectivity to EOE (▲) and DNOE (x) with respect to 1-octanol (down) as a function of $[H^+]/V_{sp}$ (t = 6h,T = 423K, W_{cat} = 1g, $R_{EtOH/OcOH}$ = 1). Squares and circles correspond to Amberlyst 46 and 70, respectively.

Figure 9. Initial TOF values of DEE (up), EOE (middle) and DNOE (down) formation vs. $[H^+]/V_{sp}$ ($T = 423K$, $W_{cat} = 1g$, $R_{EtOH/OcOH} = 1$). High crosslinked macroreticular resins (◆), medium crosslinked macroreticular resins (■), CT165 (▲), low crosslinked macroreticular resins (X), microporous resins with 8% DVB (○), microporous resins with 4% DVB (●), microporous resins with 2% DVB (+), A46 (◇).

Scheme captions

Scheme 1. Reaction network for EOE synthesis from ethanol and 1-octanol

Scheme 2. Suggested dual-site mechanisms (Langmuir-Hinselwood-Hougen-Watson) for ether formation

Scheme 3. Suggested single site mechanisms (Eley-Rideal) for ether formation