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Thermal stability and water effect on ion-exchange resins in ethyl octyl ether production at high temperature

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ABSTRACT

Thermal stability and water inhibition effects were studied at 150 and 190 °C on the chlorinated acidic polystyrene-divinylbenzene resins Amberlyst 70, Amberlyst XE804 and Purolite CT482, and the non-chlorinated one Dowex 50Wx2. Catalytic activity in the reaction between ethanol and 1-octanol to form ethyl octyl ether (EOE) was monitored for 70 h in a continuous fixed-bed reactor. Leaching of sulfonic groups at 190 °C was found to be negligible for Purolite CT482 and Amberlyst 70, but it was significant for Amberlyst XE804 and Dowex 50Wx2. The activity decay to a steady EOE reaction rate on Purolite CT482 and Amberlyst 70 has been ascribed to the reaction rate inhibition by the formed water. However, water adsorption on the catalyst also modified the resin morphology during the course of the reaction. Adsorbed water swelled the gel-phase and more acid sites became accessible for 1-octanol molecules. As a result, the activity decay of EOE and the longer byproduct di-n-octyl ether syntheses was smaller than that of the shorter one diethyl ether.

1. Introduction

Sulfonic polystyrene-divinylbenzene (PS-DVB) resins are used as catalysts in many industrial applications [1,2]. As a drawback, they present a low thermal stability as, at high temperature, sulfonic groups, the actual catalytic species, undergo deactivation by leaching [3,4]. Many PS-DVB resins are stable up to 150 °C, but the maximum operating temperature of some resins such as Amberlyst 15 is even lower (120 °C) [1]. In contrast, fluorinated polystyrene sulfonic resins like Nafion® can operate up to 210 °C, because fluorine atoms increase the thermal stability. In addition, fluorine atoms confer a higher acid strength which contributes positively to the catalytic activity [5]. Nevertheless, compared to PS-DVB resins, Nafion® has lower acid capacity and it is more expensive, which are important drawbacks for industrial use [6,7].

New thermally stable PS-DVB resins Amberlyst 70 and Purolite CT482 have been recently commercialized to catalyze processes such as esterification, aromatic alkylation and olefin hydration at temperatures higher than 150 °C [3,4]. In these resins, some hydrogen atoms have been substituted by chlorine. These additional electron withdrawing atoms increase the acid strength of ion exchangers and minimize the cleavage of the sulphur bond to aromatic carbon atoms up to 190 °C [8–10]. Thus, in some reactions taking place over acidic ion-exchange resins, the operating temperature can be raised to obtain higher reaction rates and, therefore, to have a more economically feasible reaction units.

Besides, it is well-known that acidic resins suffer different morphological changes, and therefore catalytic performance varies, depending on the nature of reaction medium. Consequently, their catalytic activity is highly related to the properties of the reaction mixture [11]. In the presence of polar substances such as alcohols and water, non-permanent pores appear and diffusion of reactants towards the acid centres is enhanced [12]. However, in some reaction systems interactions between water and PS-DVB resin matrix have opposite effects: on one hand, water competes with reactants as it adsorbs strongly on the sulfonic groups [13–17]; on the other hand, as water is a polar compound, it contributes to open the resin backbone, what enhances the accessibility of reactants to acid centres. In addition, depending on the water amount, the catalytic mechanism can change from concerted to ionic which are slower. In industrial reaction units, the best resin performance takes place at low water contents (0.1–3 mol water/L) where sulfonic groups are partially dissociated [18].

A reaction particularly sensitive to the aforementioned water effects is the dehydration of linear alcohol to ether, in which water is a reaction product [19]. This reaction is of industrial interest since long linear ethers have excellent properties for blending with commercial diesel. They raise the cetane number of blends and reduce the environmental impact of engine exhaust emissions [20–23]. Additionally, the use of renewable alcohols to produce synthetic fuels can enhance the bio-fuel percentage in the diesel pool without a reduction of diesel fuel quality.

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Nomenclature

a_i	activity of reaction i, dimensionless
$a_{\infty,i}$	terminal activity of reaction i, dimensionless
DEE	diethyl ether
DNOE	di-n-octyl ether
d_p	particle diameter (μm)
d_{pore}	pore diameter (nm)
DVB	divinylbenzene
E_d	activation energy of activity decay, kJ/mol
EOE	ethyl octyl ether
EtOH	ethanol
F_j	molar flow rate (mol/h)
G	gel-type resin
$[H^+]$	acid capacity (meq H^+/g)
k_d	rate decay constant (h^{-1})
ISEC	inverse steric exclusion chromatography
M	macroreticular resin
OcOH	1-octanol
P	pressure
PS-DVB	polystyrene-divinylbenzene
q	volumetric liquid flow rate (mL/min)
r_i	reaction rate of reaction i at time t (mol/(h kg_{cat}))
r_i^0	reaction rate of reaction *i* with fresh catalyst (mol/(h kg_{cat}))
$R_{\mathrm{OcOH/EtOH}}$	1-octanol/ethanol molar ratio (mol/mol)
S_j^k	selectivity to k with respect to *j* (mol/mol)
S_{BET}	BET surface area (m^2/g)
S_{ISEC}	surface area from ISEC data (m^2/g)
SEM	Scanning Electron Microscopy
t	time, h
t_0	time when decay begins (h)
T	temperature (°C)
$T_{\max}$	maximum operating temperature (°C)
X_j	relative conversion of compound *j* (mol/mol)
V_{ISEC}	pore volume from ISEC data (cm^3/g)
V_j	resin volume in solvent *j* (cm^3)
V_0	resin volume in air (cm^3)
V_{sp}	specific volume of the swollen polymer phase (cm^3/g)
W_{cat}	dry catalyst mass (g)
ρ_s	skeletal density (g/cm^3)

In this work, the reaction of ethanol (EtOH) with 1-octanol (OcOH) to produce ethyl octyl ether (EOE) is studied. EtOH has been chosen because it allows introducing bio-fuels to the fuel market, and OcOH in order to obtain long chain ethers, which are preferred as diesel fuels. Fig. 1 shows the reaction scheme. In parallel with EOE formation (1), dehydration reactions of EtOH to give diethyl ether (DEE) (2) and that of OcOH to di-n-octyl ether (DNOE) (3) take place. The chlorinated PS-DVB resins Amberlyst 70, Amberlyst XE804, and Purolite CT482 have been used as catalysts. The PS-DVB resin Dowex 50Wx2 has also been used for the sake of comparison. The aim of this paper is to evaluate the thermal stability of chlorinated resins, as well as the effect of water on their catalytic performance, in the temperature range 150–190 °C. Besides, their properties are examined and compared to those of conventional ones.

2. Material and methods

2.1. Chemicals

OcOH (≥99%, Acros) and EtOH (≥99.8%, Panreac) were used as the reactants. 1-octene and DNOE (≥97%, Fluka), and DEE (≥99%, Panreac) were used for analysis purposes. EOE was obtained and purified in our lab by rectification to 99% purity (GC). Bidistilled water was also used.

2.2. Catalysts and catalyst characterization

Tested catalysts were supplied by Purolite (CT482), Rohm and Haas (Amberlyst 70 and XE804) and Aldrich (Dowex 50Wx2). They were used with the commercial particle sizes distribution to approach the industrial reactor. Skeletal density (ρ_s) was measured by helium displacement in an Accupyc 1330 apparatus (Micromeritics). BET surface area, S_{BET}, was estimated from N_2 adsorption-desorption isotherm at 77 K (krypton for $S_{\mathrm{BET}} < 1\ m^2/g$). Surface of fresh dried resins was observed by using an H-2300 Scanning Electron Microscope (Hitachi). Acid capacity was measured by titration against standard base. Water content in the catalysts was determined by Karl-Fisher titration (Orion AF8) in dry samples prior to their use in the reactor, and after separation from the reaction liquid by filtration at atmospheric pressure.

The particle size distribution of commercial catalysts was determined with a LS 13320 Laser Diffraction Particle Size Analyzer in different environments: air, water, and a mixture of 1-octanol and ethanol (molar ratio $R_{\mathrm{OcOH/EtOH}} = 10$); the latter was considered to be representative of the feed composition in catalytic tests. Prior to particle size analysis dry samples were submerged in the selected solvent for 2 days to ensure a fully swollen state of the resin. Swelling degree was calculated by Eq. (1), as the quotient of the resin volume increase with respect to the resin volume in air. V_j is the mean particle volume in water or in the alcohol mixture, and V_o is the volume of dry resin in air. Volumes were computed by assuming that particles are spherical.

$$\{\text{Swelling degree}\} = \frac{V_j}{V_0} - 1 \tag{1}$$

The nature and characteristics of the non-permanent pores of resins were determined by the inverse steric exclusion chromatography (ISEC) technique as described elsewhere [24,25].

2.3. Catalytic tests

The experiments were performed in a 20-mL continuous fixed-bed reactor (PID Eng & Tech) fed by a HPLC pump (Gilson 307). The reactor bed consisted of resin homogeneously diluted with

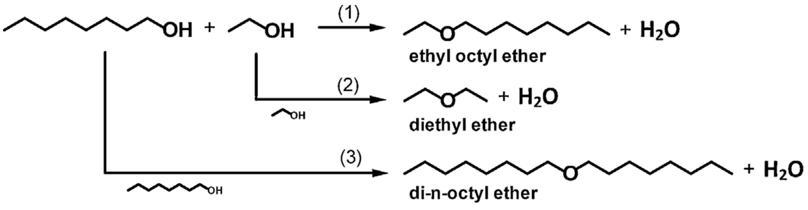

Fig. 1. Reaction scheme of EOE synthesis from 1-octanol and ethanol.

inert quartz. Quartz was used to keep the bed isothermal and to ensure good contact between reactants and catalyst. Back-mixing and channelling effects were avoided by using a resin to inert mass ratio large enough accordingly to previous studies in our lab. During the experiment liquid samples were taken on-line from the reactor inlet and outlet. Their composition was determined in an HP6890A GLC equipped with TCD detector. A 50 m × 0.2 mm × 0.5 µm capillary column HP-Pona (Agilent) was used to separate and quantify the compounds present in the reaction medium. The column was temperature programmed to start at 50 °C with a 25 °C/min ramp up to 250 °C and held for 6 min. Helium (≥99.998%, Linde) was the carrier gas. Chemical species were identified by a second GLC apparatus equipped with mass spectrometer GC/MS 5973 (Agilent) assisted by a chemical database software.

Catalysts were dried overnight at 110 °C under vacuum (0.01 bar). Dry samples (0.1–0.7 g) were diluted in quartz (12–15 g). Reactor feed consisted of an OcOH–EtOH mixture ($R_{\mathrm{OcOH/EtOH}} = 10$). The large excess of 1-octanol was selected to enhance the formation of EOE and DNOE in front of DEE, and also to promote the formation of 1-octenes, and in this way, to study the possible catalyst deactivation by carbon deposition. Water (1 wt%) was added to the reactant mixture in some runs to stress its effect on the reaction rate without the liquid splitting off in two phases. The feed was preheated in a hot box at 80 °C and then fed to reactor at a flow rate of 0.25 mL/min. The reactor operated isothermally at 25 bars in the temperature range 150–190 °C to assure that the reaction took place in the liquid phase.

An additional series of experiments was performed to test the catalyst reusability. After 48 h on-stream, the reactor was cooled at room temperature. EtOH was fed at a flow rate of 2 mL/min for 1 h to remove water and OcOH present in the resins. Subsequently, the catalysts were dried for 2 h in a 50 mL/min N_2 stream to remove EtOH. Catalysts dried in this way in the reactor were reused two times. It is to be noted that water content of fresh catalysts (2–4 wt%) was some higher than the residual water content after the reactivating process (<1 wt % [26]).

Due to the small catalyst mass in the reactor bed, conversions were low ($X_{\mathrm{OcOH}} < 10\%$, $X_{\mathrm{EtOH}} < 25\%$). Reaction rates to form EOE, DEE and DNOE were calculated by means of the following equations where it is assumed that the reactor operated in the differential regime:

$$r_1 = r_{\mathrm{EOE}} = \frac{F_{\mathrm{OcOH}} X_{\mathrm{OcOH}}}{W_{\mathrm{cat}}} S_{\mathrm{OcOH}}^{\mathrm{EOE}} = \frac{F_{\mathrm{EtOH}} X_{\mathrm{EtOH}}}{W_{\mathrm{cat}}} S_{\mathrm{EtOH}}^{\mathrm{EOE}} \tag{2}$$

$$r_2 = r_{\mathrm{DEE}} = \frac{F_{\mathrm{EtOH}} X_{\mathrm{EtOH}}}{2 W_{\mathrm{cat}}} S_{\mathrm{EtOH}}^{\mathrm{DEE}} \tag{3}$$

$$r_3 = r_{\mathrm{DNOE}} = \frac{F_{\mathrm{OcOH}} X_{\mathrm{OcOH}}}{2 W_{\mathrm{cat}}} S_{\mathrm{OcOH}}^{\mathrm{DNOE}} \tag{4}$$

$$S_j^k = \frac{\{\text{mole of } j \text{ reacted to form } k\}}{\{\text{mole of } j \text{ reacted}\}} \tag{5}$$

In these equations, W_{cat} is the dry catalyst mass, F_j the molar flow rate of species j fed into the reactor, X_j the conversion of species j, and S_j^k the selectivity of reactant j towards product k at the reactor outlet. The relative error by assuming differential behaviour of the fixed-bed reactor in Eq. (2) was estimated to be lower than 5%, within the limits of the experimental analysis error.

Catalyst activity, a_i, for reaction i was defined as the ratio of the reaction rate at time t to the reaction rate for fresh catalyst, r_i^0, by means of Eq. (6).

$$a_i = \frac{r_i}{r_i^0}. \tag{6}$$

3. Results and discussion

3.1. Properties and structural parameters of tested resins

The main properties of tested catalysts are shown in Table 1. Used catalysts are acidic PS-DVB resins of two different classes: macroreticular and gel-type. In the manufacture of macroreticular resins (Amberlyst 70, Amberlyst XE804 and Purolite CT482), styrene and DVB copolymerization is carried out in the presence of a solvent, called porogen. The formed polymer is not soluble in the porogen, which is excluded from the resin backbone after polymerization. After porogen removal large agglomerates of gel micro-spheres interspersed by a three-dimensional network of permanent pores appear inside of the resin bead. The reaction rates of the formation of bulky ethers are not typically affected by the particle size of the resin used. However they proved to be mass transfer limited within the densest gel-phase fractions of the gel micro-spheres [6,12,27,28]. Purolite CT482 photomicrographs under different magnifications are shown in Fig. 2 as an example of typical macroreticular resins. On the contrary, in gel-type resins as Dowex 50Wx2 copolymerization takes place in the absence of any porogen, and no permanent pores are formed. As seen in Table 1, chlorinated resins tested in this work are macroreticular. To the best of our knowledge, gel-type chlorinated resins have not been commercialized up-to-date.

In dry state, Purolite CT482 showed the highest BET surface area, typical of medium cross-linked macroreticular resins with 12% DVB, such as Amberlyst 16 or 36 [27], whereas Dowex 50Wx2, Amberlyst 70 and XE804 showed extremely low BET surface areas, typical of low crosslinked resins (macroreticular with 8% DVB and gel-type ones [27]).

In order to characterize the resin morphology in an environment similar to the reaction medium, particle size distribution was determined in a mixture of 1-octanol and ethanol ($R_{\mathrm{OcOH/EtOH}} = 10$) and in water, and related to dry state in air. Table 2 shows that all resins swelled noticeably at the ambient temperature as compared with dry state. The highest swelling with regard to air was observed for Dowex 50Wx2 (swelling degree from 282% in the OcOH–EtOH mixture to 473% in water). This catalyst is a gel-type resin with 2% DVB, and therefore its polymeric gel-phase is highly flexible. In polar media, gel-phase micropores are open and accessibility to active centres is highly improved. It is also observed that the three macroreticular resins greatly swell in water, with swelling degrees from 150 to 206%. In this case, besides micropores in the gel-phase, intermediate pores in the mesopore range appear among gel-type aggregates. Purolite CT482 showed the lowest swelling degree among chlorinated resins, probably as a consequence of having the highest crosslinking degree. Amberlyst 70 and XE804 also are highly expanded in water and in the alcohol mixture.

To describe the resin morphology in swollen state, the distribution of non-permanent pores was determined in water by ISEC technique. This description is assumed to be representative of the morphology of swollen PS-DVB resins in aqueous alcohol solution. Table 2 shows the main morphological parameters obtained from analysis of ISEC data. As seen, chlorinated macroreticular resins develop wide spaces in the mesopore range with pore diameter ranging from 8.5 nm (Amberlyst XE804) to 19.6 nm (Purolite CT486), which allow reactants to get easily to internal gel-phase surface. No mesopores were detected in gel-type resin Dowex 50Wx2. From ISEC data it is possible to obtain a rough space distribution within the swollen gel-phase (not detectable by standard techniques of pore analysis, i.e. N_2 adsorption-desorption at 77 K) and, correspondingly, a distribution of zones of different chain density [24,25,29,30].

As Table 2 shows, Dowex 50Wx2 exhibits the highest specific volume of the swollen gel-phase, V_{sp}. Then, in decreasing order:

Table 1
Properties of tested catalysts.

Catalyst	Structure[a]	DVB%	Chlorinated	ρ_s [b] (g/cm^3)	S_{BET} [c] (m^2/g)	Acid capacity (meq H$^+$/g)		T_{max} (°C)
						This work[d]	literature	
Dowex 50Wx2	G	2	No	1.426	1.32	5.06	4.83 [19]	150 [3]
Amberlyst 70	M	8	Yes	1.514	0.02	2.65	2.55 [8]–3.01 [6]	190 [3]
XE804	M		Yes	1.475	0.27	3.17		
CT482	M		Yes	1.538	8.70	4.25		190 [4]

[a] G = gel-type; M = macroreticular.
[b] ρ_s = skeletal density.
[c] BET surface area in dry state (N_2 for $S_{BET} \geq 1$ m^2/g; Kr for $S_{BET} < 1$ m^2/g).
[d] Titration against standard base.

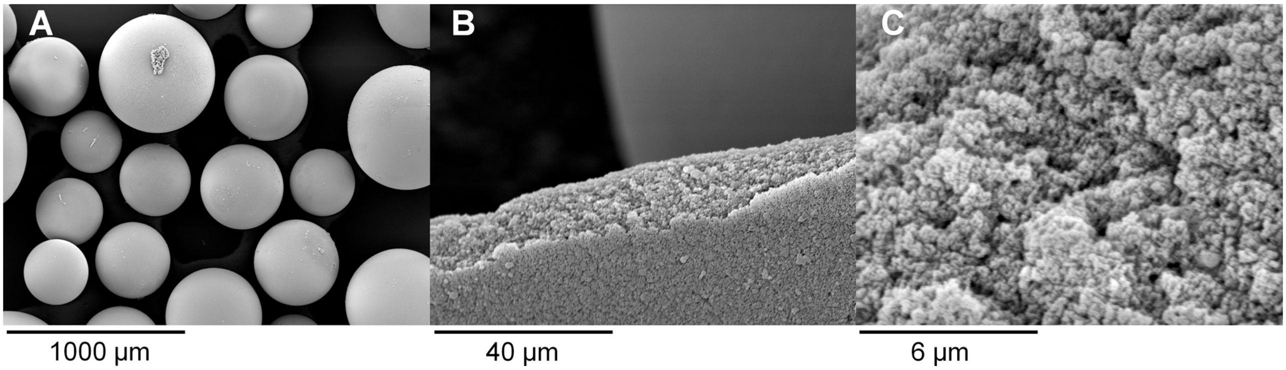

Fig. 2. Microphotography of CT482. Magnifications: 25 (A), 600 (B) and 4000 (C).

Table 2
Morphological parameters from analysis of ISEC data and particle diameter of resins in air and fully swollen in water and an alcohols mixture.

Catalyst	ISEC analysis				d_p (µm)			Swelling degree (%)	
	S_{ISEC} (m^2/g)	V_{ISEC} (cm^3/g)	d_{pore} (nm)	V_{sp} (cm^3/g)	Air[a]	Water	OcOH/EtOH[b]	Water	OcOH/EtOH[b]
Dowex 50Wx2	–	–	–	2.68	252	451	394	473	282
Amberlyst 70	66	0.22	13.2	1.15	590	857	843	206	192
XE804	243	0.52	8.5	0.83	505	710	697	178	163
CT482	214	1.05	19.6	1.08	527	715	675	150	110

[a] Dried at vacuum overnight (T = 110 °C).
[b] $R_{OcOH/EtOH}$ = 10.

Amberlyst 70, Purolite CT482 and Amberlyst XE804. Therefore, the lower the DVB% the higher V_{sp}. Fig. 3 shows the space distribution in the swollen gel-phase. Among chlorinated resins, Amberlyst 70 has wider spaces between chains (polymer density 0.4 nm^{-2}, equivalent to pores of 2.6 nm diameter [28]), similarly to low cross-linked gel-type resin Dowex 50Wx2. In resins with such low polymer density, gel-phase is highly expanded in polar media and the accessibility of large molecules, such as OcOH, to a higher number of acid sites is favoured [27,30,31]. Amberlyst XE804 showed a slightly denser polymer (0.8 nm^{-2}, equivalent to pores of 1.5 nm diameter), similarly to the macroreticular Amberlyst 39 (8% DVB) and gel-type with 4% DVB Purolite CT124 [30]. Finally, in line with swelling data, Purolite CT482 showed the densest swollen gel-phase (1.5 nm^{-2}, equivalent to pores of 1.0 nm diameter), typical of medium cross-linked macroreticular resins [27]. BET surface area, swelling degree and ISEC data suggest that Purolite CT482 morphology is similar to conventional medium cross-linked macroreticular resins.

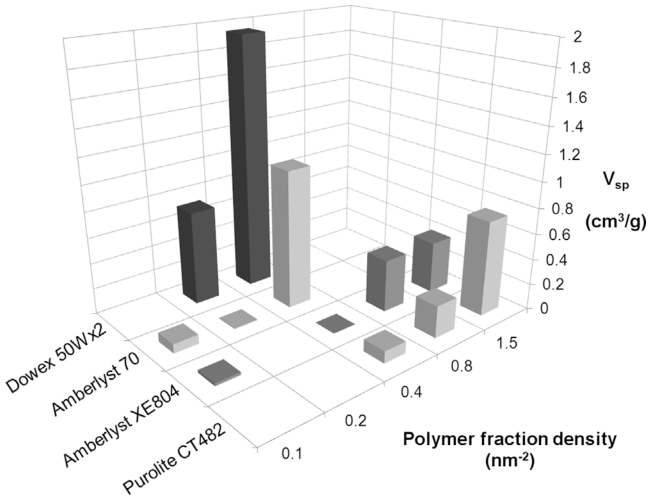

Fig. 3. ISEC pattern in water for used acidic ion-exchange resins.

The acid capacity of tested chlorinated resins ranges from 2.55 to 4.25 meq H$^+$/g (Table 1). These values are lower than those of non-chlorinated monosulfonated (typically 4.8–5 meq H$^+$/g) and oversulfonated (5.3–5.6 meq H$^+$/g) resins [27]. The substitution of hydrogen by chlorine atoms lessens the acid capacity, because there are less available phenyl rings for the further process of sulfonation in the resin synthesis on a weight basis [8]. Concerning tested chlorinated resins, it is observed that the higher acid capacity (Purolite CT482 > Amberlyst XE804 > Amberlyst 70), the higher resin stiffness. This behaviour is usual in non-chlorinated PS-DVB resins, in which oversulfonated resins show higher acid capacity and

Table 3
Reaction rates, activity and selectivity at $t = 0$ (fresh catalyst) and after 70 h on-stream ($R_{OcOH/EtOH} = 10$, $q = 0.25$ mL/min, $P = 25$ bar).

Catalyst	t (h)	$r_1 = r_{EOE}$ (mol/h kg)	$r_2 = r_{DEE}$ (mol/h kg)	$r_3 = r_{DNOE}$ (mol/h kg)	a_1	a_2	a_3	S^{EOE}_{EtOH}	S^{DEE}_{EtOH}	S^{EOE}_{OcOH}	S^{DNOE}_{OcOH}	S^{Octene}_{OcOH}
$T = 150\,°C$												
CT 482	0	2.89	0.442	3.08				0.767	0.234	0.304	0.647	0.049
	70	2.55	0.328	2.88	0.882	0.743	0.937	0.794	0.205	0.294	0.664	0.042
XE804	0	2.11	0.380	2.50				0.735	0.265	0.286	0.678	0.036
	70	1.78	0.285	2.12	0.844	0.670	0.846	0.758	0.242	0.288	0.683	0.029
Amberlyst 70	0	1.88	0.228	2.89				0.804	0.196	0.240	0.739	0.021
	70	1.54	0.155	2.50	0.819	0.678	0.864	0.832	0.168	0.232	0.752	0.016
Dowex 50Wx2	0	2.60	0.251	6.40				0.839	0.162	0.168	0.815	0.023
	70	2.30	0.200	5.90	0.885	0.743	0.922	0.852	0.148	0.159	0.819	0.022
$T = 190\,°C$												
CT 482	0	28.2	4.58	35.8				0.755	0.245	0.250	0.635	0.115
	70	23.0	3.31	33.0	0.816	0.728	0.891	0.777	0.223	0.236	0.676	0.088
XE804	0	24.8	3.60	26.1				0.775	0.225	0.257	0.541	0.202
	70	17.5	2.53	20.2	0.706	0.703	0.774	0.776	0.224	0.236	0.546	0.218
Amberlyst 70	0	18.5	2.20	32.0				0.808	0.192	0.213	0.737	0.050
	70	15.2	1.77	28.4	0.822	0.802	0.887	0.812	0.188	0.203	0.758	0.039
Dowex 50Wx2	0	24.0	1.83	49.1				0.867	0.133	0.189	0.774	0.037
	70	15.9	0.865	33.4	0.662	0.717	0.680	0.858	0.142	0.186	0.784	0.030

rigidity than their monosulfonated analogues [27]. However, their acid capacity decreases as DVB% increases unlike the non-chlorinated ones. Finally, acid strength of chlorinated resins is higher than that of non-chlorinated monosulfonated analogues [8].

As a result of their morphology, Amberlyst 70 is a suitable catalyst in hydrophilic liquid systems [6,8,10,16,19,27], whereas the permanent porosity of Purolite CT482 allows its use in lipophilic reaction media too.

3.2. Catalytic tests

The catalytic performance has been studied in the liquid-phase reaction between 1-octanol and ethanol. Experiments were carried out at 150 °C and 190 °C in the fixed bed reactor at a flow rate of 0.25 mL/min (WHSV = 17–120 h^{-1}), representative of the industrial case. They lasted 70 h to evaluate possible catalytic activity variation. Besides EOE, DEE and DNOE were formed. C_8 alkenes from 1-octanol dehydration were also detected, but in very small amounts (<1%, w/w, at 190 °C; <0.25%, w/w, at 150 °C). Results are gathered in Table 3. The evolution of reaction rates vs. time at 150 °C and 190 °C is shown respectively in Figs. S1 and S2 (Supporting Information).

As Table 3 shows, reaction rates of EOE and DNOE syntheses were of the same order of magnitude on the macroreticular resins at 150 °C, whereas that of DEE was much lower, since 1-octanol was in large excess in the reactor feed ($R_{OcOH/EtOH} = 10$). On gel-type resin Dowex 50Wx2, results are qualitatively similar, but the reaction rate of DNOE synthesis was about 3-fold higher than that of EOE, which is about 10-fold higher than reaction rate of DEE synthesis. As for EOE synthesis, Purolite CT482 showed the highest reaction rate, followed by Dowex 50Wx2, Amberlyst XE804 and 70. Reaction rate of EOE synthesis decreased continuously with time and the same effect was observed for DNOE and DEE formation reactions (See Fig S1, supporting information). Activity decay for EOE synthesis was of the same order on all resins, by 12–18% with regard to the fresh catalyst. Decay for DNOE synthesis was of 6–15%, and for DEE synthesis it was of 25–35%. Selectivity to ethers changed slowly with time, showing that EOE and DNOE are more favoured with time on-stream with regard to DEE. The fact that the more bulky ethers are preferably formed from each alcohol can be explained by the large excess of OcOH in the reaction medium and the very important effect of the resin morphology in EOE synthesis [32].

At 190 °C, Purolite CT482 was the most active resin for both EOE and DEE formation, followed by Amberlyst XE804, Dowex 50Wx2 and Amberlyst 70. Dowex 50Wx2 was the most active to DNOE formation. Among macroreticular resins, reaction rate of DNOE synthesis decreased in the order CT482, Amberlyst 70 and Amberlyst XE804. It is to be noted that a short period of constant activity was observed before the activity decay for the three reactions starts, being more noticeable on Amberlyst XE804 and Dowex 50Wx2 (Fig. S2, Supporting information). As shown in Table 3, activity decay of EOE synthesis ranges from 18 to 34%, from 10 to 32% in DNOE formation and from 20 to 30% in DEE synthesis. In general, selectivity hardly changes with time.

Apparent activation energies can be estimated by Arrhenius relationship from reaction rates at the two temperatures both on fresh catalysts and after 70 h on-stream (Table S1). Apparent activation energies for the three reactions of ether formation are in the range 90–100 kJ/mol, what shows a high sensitivity to temperature. Apparent activation energies obtained for CT482 and Amberlyst 70 do not change with time, that of Amberlyst XE482 decreased moderately, and for Dowex 50Wx2 decreased by 10–15% with respect to the values found over fresh catalysts.

Observed activity decays could be ascribed to several causes: (1) thermal instability of resins, (2) changes of activity caused by the interaction of the polymeric matrix with the water formed as byproduct, and/or (3) deposition of alkene oligomers on the resin surface.

3.3. Hydrothermal stability

Hydrothermal stability tests were carried out by adding bidistilled water to the reactor feed for 24 h at the selected temperature. Afterwards, acid capacity was measured by titration and compared to that of fresh catalyst. The difference correspond to the lost of acid sites (Table S2, Supporting Information). The conventional PS-DVB resin Dowex 50Wx2 retained acid capacity fully at 150 °C, but it greatly decreased at 190 °C, which is far above its maximum operating temperature. Amberlyst 70 and Purolite CT482 showed negligible desulfonation at 150 °C and 190 °C, in agreement with the manufacturer's tests [3,4]. These data confirm that introduction of chlorine atoms into the resin backbone improves its thermal stability. Finally, Amberlyst XE804 lost sulfonic groups at both temperatures, what indicates that it is not as suitable as the other two chlorinated resins for catalyzing high temperature processes.

Since hydrothermal tests showed that resins retained the acid capacity at 150 °C, except for the slight desulfonation of Amberlyst XE804, the activity decay observed at this temperature cannot be ascribed to the loss of sulfonic groups by thermal instability. As a result, interaction with the reaction medium has to be considered.

Activity drop at 190 °C after 70 h on-stream agrees well with the higher leaching of acid groups found in hydrothermal experiments (Table 3). Some differences in the activity decay of catalysts have been observed at this temperature which could be partly ascribed to their thermal stability. After 70 h on-stream, the non-chlorinated resin Dowex 50Wx2 showed higher activity decay at 190 °C (34%) than at 150 °C (12%) for EOE synthesis. Similar decays have been found in DNOE synthesis (32% at 190 °C, and 8% at 150 °C). The decay found at 190 °C is is of the same order as sulfonic group leaching and could be explained because its low maximum operating temperature is 150 °C. Similarly, activity decay of Amberlyst XE804 at 190 °C (29%) was almost twice that observed at 150 °C (16%) for EOE synthesis, whereas for DNOE synthesis decays are 23% at 190 °C and 15% at 150 °C. For both catalysts, activity decay in DEE synthesis is of the same order at both temperatures.

Some inferences about the water influence on the leaching of sulfonic groups can be drawn by comparing acid capacity loss in hydrothermal experiments and activity decay. Sulfonic group leaching rate in PS-DVB resins is not uniform; the most active sites are lost faster [33]. As a result, the early loss of a small number of acid sites should cause a high drop on the catalytic activity. Data show that the active sites loss after 24 h in water stream was equivalent to the activity drop after 70 h in the alcohol stream for Dowex 50Wx2 and Amberlyst XE804. As a result, sulfonic group hydrolysis seems to be faster in water than in alcohols, in agreement with the open literature [34]. However, since activity decay is much higher than acid sites leaching on the two catalysts at the low temperature of explored range, other causes than desulfonation have to be taken into account to explain activity drop.

Over Purolite CT482 and Amberlyst 70, catalytic activity decay at 150 °C and 190 °C is similar for the three reactions, especially on Amberlyst 70. As desulfonation was not observed in the hydrothermal stability experiments with these resins, activity decay cannot be accounted for sulfonic groups leaching. Instead, it could be attributed to carbon deposition by chemical species present in the reaction medium, particularly C_8-alkene oligomers. C_8 alkenes formation rose by 6-fold from 150 °C to 190 °C, but the catalytic activity decay was of the same order at both temperatures, what excludes such relationship. On the other hand, it can be assumed that the formed ethers (DEE, EOE and DNOE) do not deactivate the catalyst as their effect on the reaction rate was found to be negligible in ether syntheses as in that of di-n-pentyl ether from 1-pentanol previously studied [19].

3.4. Reusability tests

Accordingly to literature, activity decay of thermally stable resins in alcohol dehydration reactions can be ascribed to the preferred adsorption of the water formed in the reaction on active sites [9,13,14,16,18]. In order to confirm the inhibitory effect of water, Purolite CT482 and Amberlyst 70 were washed and dried in the reactor at room temperature after 48 h on-stream and reused twice. Reaction rate of formation of the three ethers, and selectivity and activity of catalysts at 48 h for fresh and reused catalysts follows a similar evolution with time (Table S3, Supporting Information). As example, Fig. 4A and B display the activity evolution of Purolite CT482 and Amberlyst 70, respectively, in EOE synthesis during the three cycles at 190 °C. Fresh (1st cycle) and reused catalyst (2nd and 3rd cycle) showed the same pattern. After two cycles using reused catalyst, both resins show a very similar behaviour to the fresh catalyst. So, it can be concluded that Purolite CT482 and Amberlyst 70 could be recovered after 48 h on-stream and reused without any noticeable activity loss. This fact confirmed that catalyst decay on these two resins was caused mainly by the inhibitory effect of water formed in the EOE formation.

3.5. Catalytic tests with alcohol–water feed

A set of experiments was performed on Amberlyst 70 and Purolite CT482 by adding water to the alcohol mixture feed. As an example, Fig. 5 shows the activity of Amberlyst 70 with ethanol–octanol and ethanol–octanol–water feeds (that of Purolite CT482 can be found in Fig. S3, Supporting Information). The reaction rate of fresh catalyst in ethanol–octanol mixtures was taken as the reference for catalysts activity. As seen, activity to EOE was lower in the presence of water. Unlike experiments with ethanol–octanol feed, the activity to EOE formation was almost constant along time on Purolite CT482 but it decreased slightly on Amberlyst 70. The water content of resins was determined after each experiment by titration. As Table 4 shows, water content within the resin increased with time-on-stream, which could be related to the continuous decrease of the catalytic activity to EOE with ethanol–octanol feed. It is also seen that higher water contents were found in resins when feeds contained water. Purolite CT482 retained higher water amounts than Amberlyst 70. However, the number of water molecules per sulfonic group is similar on the two resins (2.78–2.98 mol H_2O/mol sulfonic group). These water

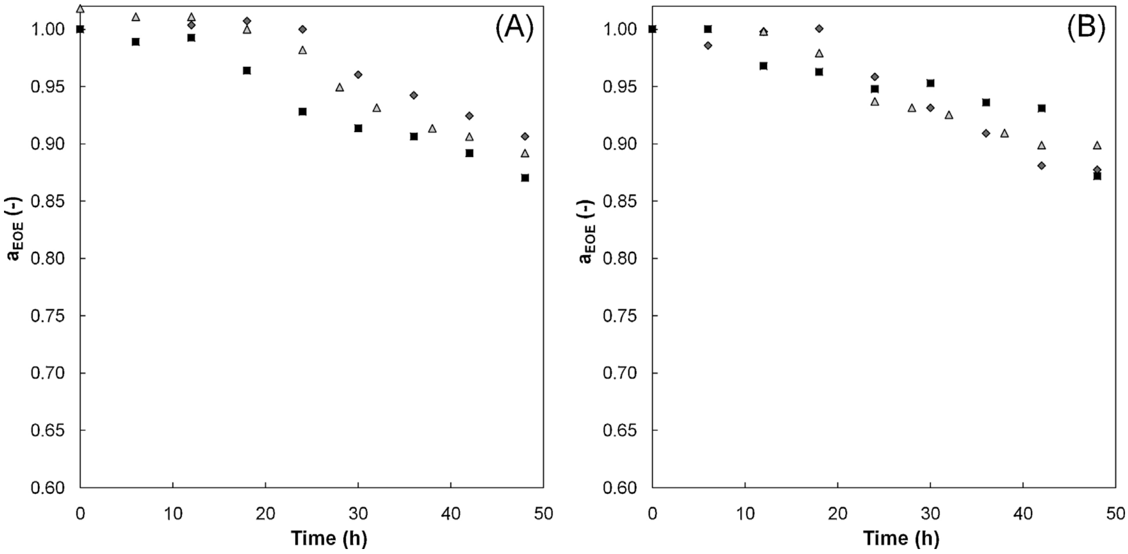

Fig. 4. Evolution of activity to EOE formation along the time on CT482 (A) and on Amberlyst 70 (B) at $T = 190$ °C, $R_{OcOH/EtOH} = 10$, $q = 0.25$ mL/min, $P = 25$ bar (■, 1st cycle; ♦, 2nd cycle; ▲, 3rd cycle).

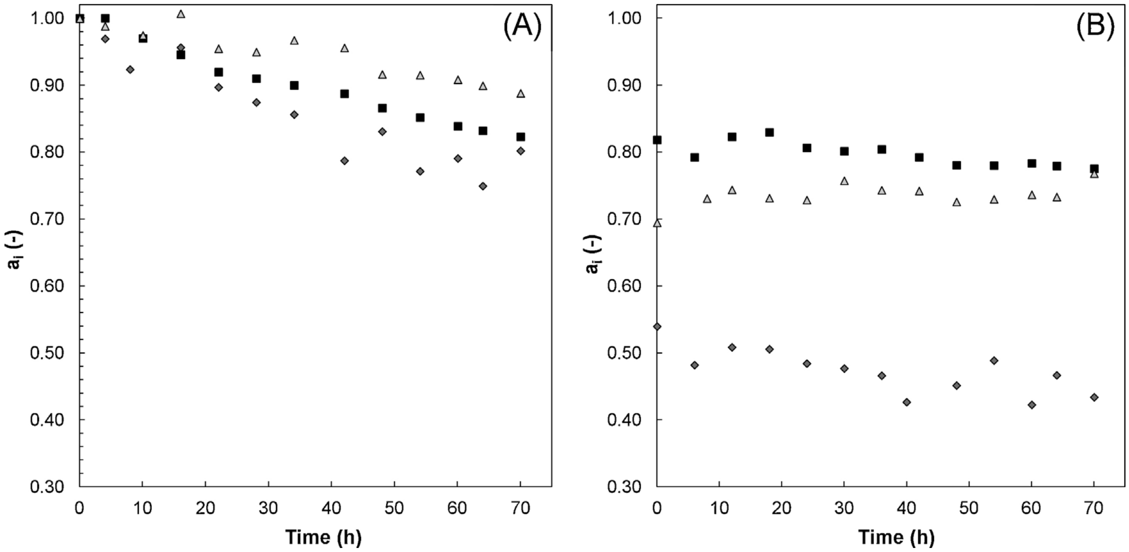

Fig. 5. Activity to DEE (◆), EOE (■) and DNOE (▲) formation vs. time on Amberlyst 70 at T = 190 °C, q = 0.25 mL/min, P = 25 bar, $R_{OcOH/EtOH}$ = 10. (A) Pure alcohols fed and (B) 1% (w/w) water fed.

contents are far from those of a resin saturated by water (4.2 mol H_2O/mol sulfonic group) [26]. This fact can be due to the high affinity of alcohols, which compete with water, for the acid sites.

As Table 4 shows, turnover frequency (TOF) is similar at the beginning of ethanol-octanol fed experiments on the two catalysts; however TOF of Purolite 482 is a bit lower after 70 h, and with ethanol–octanol–water feed it is lower by 20% than activity at the same time on stream with ethanol-octanol feed. Thus, the effect of water on the activity drop of Purolite CT482 was stronger than on Amberlyst 70. This pattern can be attributed to the higher acid site density in the gel-phase of Purolite CT482. With respect to activity of Amberlyst 70, a short initial flat period is observed (4 h) and afterwards a continuous decay, whereas for CT482 the flat period is longer (16 h) and the decay rate is higher, so that after 70 h the activity level of Amberlyst 70 is slightly higher than that of CT482. In experiments where water was fed, the activity level of CT482 is always clearly lower.

Without water in the feed, both OcOH and EtOH swell the resins and compete for adsorbing on acid centres and the highest reaction rate is achieved with fresh catalyst. Then, a part of formed water adsorbs gradually on the resin and the reaction rate starts to decrease. The phase-equilibrium between water in the liquid phase and adsorbed on acid sites is not likely to be reached during the experiments without feeding water. On the contrary, when water was fed, the water amount in the liquid phase was enough to reach water-resin quasi-equilibrium, and the reaction rate to form EOE is nearly independent on time on-stream. As Table 4 shows, the amount of adsorbed water is similar in both resins. The different TOF could be explained by the fact that water probably acts as a solvent inside pores even at small quantities, and a transition takes place from concerted to ionic catalytic mechanism (slower) where the hydrated proton is the true catalytic agent takes place [14]. The effect of the mechanism change on the rate would be more noticeable on the three dimensional networks of sulfonic groups in the denser gel-phase of Purolite CT482 as a result of their proximity [35].

Table 4
Water content inside resin and TOFs as a function of time on stream. T = 190 °C, $R_{OcOH/EtOH}$ = 10, q = 0.25 mL/min, P = 25 bar.

Catalyst	Time on-stream (h)	Water content (w/w, %)	Mol H_2O per sulfonic group	TOF (h^{-1})
Amberlyst 70	0	2.1	0.45	6.98
	24	7.2	1.62	
	70	9.5	2.19	5.74
	70[a]	12.5	2.98	5.40
CT482	0	3.6	0.49	6.94
	24	10.6	1.55	
	70	13.2	1.98	5.41
	70[a]	17.5	2.78	4.71

[a] 1% (w/w) water in the feed.

3.6. Catalytic activity for DEE, EOE and DNOE syntheses

Morphological changes that take place in the resins with time-on-stream by the action of water can modify their catalytic behaviour. As the amount of water adsorbed on resins increases with time-on-stream, accessibility of OcOH and EtOH to acid sites is also modified. Fig. 5 displays the activity to DEE, EOE and DNOE along time for Amberlyst 70 (that for CT 482 can be found in Fig. S3, Supporting Information). Reaction rates, activity and selectivity can be found in Table S4. It is observed that activity drop shows different pattern depending on the ether. As a rule, activity decay was higher as the ether is less bulky: DEE > EOE > DNOE. When water is fed together with the alcohol mixture, it is seen that EOE and DNOE syntheses tend to similar activity levels, but DEE formation continues decreasing.

In ethanol–octanol feed, fresh ion-exchange resins were not fully swollen and the accessibility to acid centres was in some extent hindered. It is expected that steric restrictions play a major role for larger ether formation (DNOE > EOE > DEE). Resins swelled progressively with reaction time and the void spaces appearing between polymer chains favoured the diffusion of OcOH and bulky ethers EOE and DNOE. Thus, activity drop was less pronounced as the size of the ether increased. The effect of water was especially stressed in ethanol–octanol–water experiments. The adsorption of water caused remarkable activity decay for DEE synthesis, but in the case of EOE and DNOE it was partially balanced by the higher accessibility to acid centres of 1-octanol. Accordingly, the activity after 70 h time-on-stream was reduced by 30–35% in EOE and DNOE syntheses, and 57% in DEE formation, in relation to activity of fresh catalysts in ethanol–octanol feed.

Table 5
Parameters of first-order activity decay function for Amberlyst 70 and CT482. $R_{\mathrm{OcOH/EtOH}} = 10$, $q = 0.25$ mL/min, $P = 25$ bar.

Reaction	T (°C)	$k_{d,i}$ (h^{-1})	a_∞	t_0 (h)	$E_{d,i}$ (kJ/mol)
Amberlyst 70					
EOE synthesis	150	5.17×10^{-2}	0.710	4	3.0
	190	5.56×10^{-2}	0.721	6	
DEE synthesis	150	3.38×10^{-2}	0.496	0	20
	190	5.31×10^{-2}	0.651	0	
DNOE synthesis	150	2.53×10^{-2}	0.674	6	4.6
	190	2.81×10^{-2}	0.688	12	
CT482					
EOE synthesis	150	1.89×10^{-1}	0.865	2	6.4
	190	2.21×10^{-1}	0.810	14	
DEE synthesis	150	5.22×10^{-2}	0.626	0	28
	190	1.04×10^{-1}	0.696	0	
DNOE synthesis	150	4.90×10^{-1}	0.927	0	7.8
	190	5.95×10^{-1}	0.914	12	

Summarizing, water effects on the reaction between OcOH and EtOH are complex as this study shows. It is seen that the period of time necessary to get a steady activity in this case is extremely long. On Purolite CT482 and Amberlyst 70, which show very good hydrothermal stability at 190 °C, released water acts as a solvent and increased the accessibility of bulky molecules to the active centres. Consequently, catalytic activity to produce long chain ethers is less hindered in the presence of water than to short ones. In the particular case of Dowex 50Wx2 and Amberlyst XE804 the presence of significant desulfonation at 190 °C makes the situation more complicated.

Finally, activity decay patterns were modelled for Amberlyst 70 and Purolite CT482 in runs with ethanol–octanol feed. Activity drop in Dowex 50Wx2 and Amberlyst 804 was not modelled since it was partly due to leaching of sulfonic groups. Literature supplies relationships between resin activity and the amount of water in the liquid-phase. Some are essentially empirical, but equations based on exponential, or Langmuir and Freundlich equilibrium approaches have been also used [36,37]. Still, in our experiments the water amount in the liquid phase was always small and often around the threshold of chromatographic detection. So that, activity as a function of time was fitted to first and second order activation decays functions. Best results were found by assuming a first order decay with terminal activity. In this way, for the reaction i:

$$-\frac{da_i}{dt} = k_{d,i}(a - a_\infty) \tag{7}$$

whose integrated form is

$$a_i = a_{\infty,i} + (1 - a_{\infty,i})\exp(-k_{d,i}(t - t_0)) \tag{8}$$

where $a_{\infty,i}$ is the terminal activity, $k_{d,i}$ is the rate constant of decay, and t_0 the time when decay starts. The parameters of Eq. (8) for EOE, DNOE and DEE syntheses on both catalysts are shown in Table 5. As seen, terminal activities roughly agree with the values found at large time-on-stream in alcohol–water experiments. Therefore, it can be assumed that activity stabilizes after a long period of time at lower reaction rates than fresh catalyst. Rate decay constants are of the same order of magnitude on both resins and increase in the order DEE, EOE, DNOE syntheses on Purolite CT482, and DNOE, DEE, EOE syntheses on Amberlyst 70. As apparent activation energies show, temperature dependence of rate decay constant is low except for DEE synthesis. Finally, it is to be noted that t_0 appear for EOE and DNOE syntheses, being higher at 190 °C. On the contrary for DEE synthesis decay starts as soon as the reaction begins.

4. Conclusions

The thermal stability study of acidic PS-DVB resins shows that Dowex 50Wx2 and XE804 lose a relevant quantity of acid centres at 190 °C. Leaching of active sites appears to be enhanced by the action of the water formed in the reaction between OcOH and EtOH to form EOE.

On the contrary, desulfonation is not significant for Amberlyst 70 and Purolite CT482 at 190 °C. As a consequence of the adsorption of water which competes with ethanol and 1-octanol for sulfonic groups, reaction rate on thermally stable resins Amberlyst 70 and Purolite CT482 decreases with time-on stream up to a constant activity level lower than that of fresh resins. Both resins recover completely their activity as soon as water is removed from the reaction medium and therefore they could be reused. Reused resins showed a similar kinetic behaviour in the reaction system of EOE formation.

Ion-exchange resins are not completely swollen in the absence of water. As a consequence, diffusion of OcOH and bulky ethers are hindered. However, with time on-stream, released water acts as solvent and swells partially the resin. Thus, the catalytic activity drop is less pronounced for the ethers with more steric restrictions (EOE and DNOE) than for the smallest one (DEE).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.07.024.

References

[1] M.A. Harmer, Q. Sun, Appl. Catal. A: Gen. 221 (2001) 45–62.
[2] K. Tanabe, W.F. Hölderich, Appl. Catal. A: Gen. 181 (1999) 399–434.
[3] Dow Chemical website, www.dow.com (10/2012).
[4] Purolite website, www.purolite.com (10/2012).
[5] S.R. Samms, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1498–1504.
[6] R. Bringué, M. Iborra, J. Tejero, J.F. Izquierdo, F. Cunill, C. Fité, V.J. Cruz, J. Catal. 244 (2006) 33–42.
[7] J. Zhang, L. Zhang, H. Liu, A. Sun, R. Liu, Wiley-VCH, Singapore, Weinheim (Germany), 2012, pp. 293.

[8] P.F. Siril, H.E. Cross, D.R. Brown, J. Mol. Catal. A: Chem. 279 (2008) 63–68.
[9] D.M. Alonso, J.Q. Bond, J.C. Serrano-Ruiz, J.A. Dumesic, Green Chem. 12 (2010) 992–999.
[10] D.M. Alonso, J.Q. Bond, D. Wang, J.A. Dumesic, Top. Catal. 54 (2011) 447–457.
[11] G.V. Samsonov, V.A. Pasechnik, Chem. Rev. 38 (1969) 547.
[12] J. Guilera, R. Bringue, E. Ramírez, M. Iborra, J. Tejero, Ind. Eng. Chem. Res. 51 (2012) 16525–16530.
[13] B.C. Gates, J.S. Wisnouskas, H.W. Heath, J. Catal. 24 (1972) 320–327.
[14] B.C. Gates, W. Rodriguez, J. Catal. 31 (1973) 27–31.
[15] R. Thornton, B.C. Gates, J. Catal. 34 (1974) 275–287.
[16] R. Bringué, J. Tejero, M. Iborra, J.F. Izquierdo, C. Fité, F. Cunill, Top. Catal. 45 (2007) 181–186.
[17] A.A. Kiss, F. Omota, A.C. Dimian, G. Rothenberg, Top. Catal. 40 (2006) 141–150.
[18] J.M. Aragon, J.M.R. Begas, L.G. Jodra, Ind. Eng. Chem. Res. 32 (1993) 2555–2562.
[19] R. Bringué, E. Ramírez, C. Fité, M. Iborra, J. Tejero, Ind. Eng. Chem. Res. 50 (2011) 7911–7919.
[20] G.C. Pecci, M.G. Clerici, F. Giavazzi, F. Ancillotti, M. Marchiona, R. Patrini, Proceedings IX Int. Symp. Alcohol Fuels 1 (1991) 321–335.
[21] G. A. Olah, Cleaner and cetane enhancing diesel fuel supplements. US Patent US005520710A (1996).
[22] J. Song, Z. Huang, X. Qiao, W. Wang, Energy Convers. Manage. 45 (2004) 2223–2232.
[23] T. Dogu, D. Varisli, Turk. J. Chem. 31 (2007) 551–567.
[24] K. Jerabek, Anal. Chem. 57 (1985) 1595–1597.
[25] K. Jerabek, Anal. Chem. 57 (1985) 1598–1602.
[26] M. Iborra, J. Tejero, F. Cunill, J.F. Izquierdo, C. Fité, Ind. Eng. Chem. Res. 39 (2000) 1416–1422.
[27] J. Guilera, R. Bringué, E. Ramírez, M. Iborra, J. Tejero, Appl. Catal. A: Gen. 413-14 (2012) 21–29.
[28] C. Casas, R. Bringué, E. Ramírez, M. Iborra, J. Tejero, Appl. Catal. A: Gen. 396 (2011) 129–139.
[29] B. Corain, K. Jerabek, P. Centomo, P. Canton, Angew. Chem. 116 (2004) 977–980.
[30] J. Tejero, F. Cunill, M. Iborra, J.F. Izquierdo, C. Fité, J. Mol. Catal. A: Chem. 182–183 (2002) 541–554.
[31] K. Jerabek, L. Holub, 13th International IUPAC Conference on Polymers and Organic Chemistry, Montreal, 2009.
[32] R. Bringué, E. Ramírez, M. Iborra, J. Tejero, F. Cunill, J. Catal. 304 (2013) 7–21.
[33] L. Petrus, E.J. Stamhuls, G.E.H. Joosten, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 366–371.
[34] N. Bothe, F. Döscher, J. Klein, H. Widdecke, Polymer 20 (1979) 850–854.
[35] B.L. Yang, S.B. Yang, R.Q. Yao, React. Funct. Polym. 44 (2000) 167–175.
[36] B.L. Yang, M. Maeda, S. Goto, Int. J.Chem. Kinet. 30 (1998) 137–143.
[37] U. Limbeck, C. Altwicker, U. Kunz, U. Hoffmann, Chem. Eng. Sci. 56 (2001) 2171–2178.