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# Conversion of 1-hexanol to di-n-hexyl ether on acidic catalysts

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#### 1. Introduction

After sweeting diesel streams in order to decrease its sulfur content, formulation of future diesel fuels will be characterized by a higher cetane number and a lower density and aromatic content [1]. Due to the huge oil demand, heavy crude amounts processed in refineries are increasing and total quantity of such compounds increases. Refineries have made an effort introducing hydrocracking units in order to decrease sulfur content and obtain high added value products from heavy streams. In addition, legislation is in continuous evolution, and a hypothetical change in cetane number specifications would help to decrease particle matter emissions as well as CO, NO<sub>x</sub>, unburned hydrocarbons and smoke [2,3].

In order to fulfill new European specifications, a possible option of reformulating diesel blends may be the introduction of oxygenates in commercial blends. Previous studies concluded that linear ethers with at least 9 carbon atoms showed high cetane numbers and desirable cold flow properties [4].

Di-n-hexyl ether (DNHE) has been selected to carry out the present study since it behaves itself as a light diesel fuel. Boiling point of DNHE is about 220 °C, close to light end of commercial boiling point of diesel fuels (200–380 °C). Density and viscosity of DNHE are actually lower than that of standard diesel fuels. Furthermore, since DNHE cetane number is as high as 118, its introduction in commercial blends would contribute to upgrade diesel properties particularly in the light end of the boiling point curve [5].

## ABSTRACT

Conversion, selectivity and yield of 1-hexanol liquid phase dehydration to di-n-hexyl ether (DNHE) were determined at 150–190 °C on three acidic catalysts, the thermally stable resin Amberlyst 70, the perfluoroalkanesulfonic Nafion NR50 and the zeolite H-BEA-25, in a batch reactor. The highest conversion and yield were achieved on Amberlyst 70 at 190 °C, but the most selective catalyst was Nafion NR50. Good results were obtained at 190 °C on the zeolite. Apparent activation energies for the three catalysts were in the range 108–140 kJ/mol. Unlike H-BEA-25, the reaction of DNHE synthesis on Amberlyst 70 and NR50 was a bit more active but less selective than the analogous 1-pentanol dehydration to di-n-pentyl ether (DNPE).

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Oil industry is interested in increasing the cetane number of low quality diesel streams, e.g. linear  $C_5$  olefins. The production of high cetane ethers from linear olefins could be a promising way, since it offers a solution for species with a very high ozone formation potential, such as pentenes, which should be removed from gasolines. With this aim, 1-hexanol may be synthesized by hydroformylation of 1-pentene, a feedstock of  $C_5$  olefin streams. The industrial synthesis consists of selective hydroformylation and hydrogenation of 1-pentene in the presence of Rh and Co phosphines [6]. Afterwards, the molecular dehydration reaction of the alcohol gives DNHE. The alcohol dehydration reaction needs an acidic catalyst to proceed. Ion exchange resins are today the best option in terms of selectivity and activity to achieve good linear ether yields [7–9].

Literature on dehydration of 1-hexanol to ether is rather scarce. Dehydration in the gas phase of some  $C_6$  alcohols on a Nafion/SiO<sub>2</sub> composite and Y zeolites was studied at 200 °C < T < 300 °C [10]. It was found that the formation of alkenes was the main reaction (2hexene was the predominant isomer) and DNHE synthesis was a secondary reaction. Also in the gas phase, the dehydration of C<sub>5</sub>-C12 linear 1-alcohols over n-alumina was studied in a fixed bed flow reactor at 250–350 °C, 0–4 MPa, and WHSV of 1–4  $h^{-1}$ . The highest ether yield was 54% at 300 °C, 1 MPa and WSHV of 1 h<sup>-1</sup> [11]. The dehydration of some alcohols (including 1-hexanol) in the liquid phase at 200 °C over montmorillonite showed that primary alcohols underwent preferential intermolecular dehydration to ethers while secondary alcohols favored the formation of alkenes via intramolecular dehydration [12]. Finally, in the liquid phase synthesis of DNHE over Nafion-H yields of 95% in overnight experiments at 145-150 °C were found [13].

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#### Nomenclature

d <sub>pore</sub> E <sub>ap</sub>	pore diameter (nm) apparent activation energy (kJ/mol)
$n_{\rm DNHE}$	number DNHE moles
r <sub>DNHE</sub>	reaction rate of DNHE synthesis (mol h <sup>-1</sup> kg <sup>-1</sup> )
$r^{o}_{\rm DNHE}$	initial reaction rate of DNHE synthesis
	$(\text{mol } h^{-1} \text{ kg}^{-1})$
S	selectivity (%)
Sg	surface area $(m^2 g^{-1})$
t	time (h)
Т	temperature (K)
$V_{ m g}$	pore volume (cm <sup>3</sup> g <sup>-1</sup> )
$V_{\rm sp}$	specific volume of the swollen polymer phase
	$(cm^3 g^{-1})$
W	weight of dry catalyst (g)
X <sub>HeOH</sub>	conversion of 1-hexanol (%)
Y <sub>DNHE</sub>	DNHE yield
Greek le	tters
$\rho_{\rm s}$	skeletal density (g/cm <sup>3</sup> )
$\theta$	porosity
-	r

On the other hand, acidic ion exchange resins have shown to be highly selective to the ether formation from 1-alkanol, avoiding secondary reactions, e.g. dehydration to olefin. Recently, the thermally stable ion exchange resin Amberlyst 70 based on a styrene-divinylbenzene copolymer has been commercialized. It has shown to be an effective catalyst in 1-pentanol dehydration to di-n-pentyl ether (DNPE) [14,15]. Actually, compared to Nafion NR50, Amberlyst 70 was more active than Nafion catalyst, but only a bit less selective.

We have studied recently the chemical equilibrium of liquid phase dehydration of 1-hexanol to di-n-hexyl ether on Amberlyst 70 [16]. The present work is devoted to study the catalyst activity of Amberlyst 70 in the 1-hexanol conversion to DNHE. In addition, experiments on Nafion NR50 and H-BEA-25 zeolite have been also performed in order to compare the behavior of the three catalysts. Finally, the syntheses of DNHE and DNPE on these solids, in the same experimental set-up, are compared.

### 2. Experimental

#### 2.1. Materials

Table 1

1-Hexanol (99.5% pure, <0.3% 2-methyl-1-pentanol, 0.1% water) was used after purification in a distillation column of the

		Particle size ()	μ <b>m</b> )
	10	100	1000 10000
	0		
	5 -	i	
-	-		HeOH
Volu	10 -		DNHE
ıme			! — Air
(%)	15 -		Water
	20 -	M	â.

Fig. 1. Distribution of bead size of Amberlyst 70 in air, 1-hexanol, DNHE and water.

alcohol supplied by Fluka ( $\geq$ 98%). Di-n-hexyl ether was obtained in our lab and purified to  $\geq$ 98%. 1-Hexene ( $\geq$ 99%) from Aldrich, *trans*-2-hexene ( $\geq$ 98%), *cis*-2-hexene ( $\geq$ 95%), *trans*-3-hexene ( $\geq$ 97%), *cis*-3-hexene ( $\geq$ 95%), and 2-methyl-1-pentanol ( $\geq$ 99%) were supplied by Fluka and used for analysis purposes.

Three acidic catalysts were tested. Amberlyst 70 (A70), a chlorinated low crosslinked polystyrene-divinylbenzene (PS-DVB) copolymer from Rohm and Haas France, with an acidic capacity of 3.01 meq H<sup>+</sup>/g, and skeletal density of  $1.52 \text{ g/cm}^3$ , mean bead diameter of 570  $\mu$ m, and a maximum operating temperature of 200 °C [17]. Some structural properties are given in Table 1. Amberlyst 70 is a macroporous resin flexible enough to accommodate to aqueous media because of its low crosslinking degree. This fact is stated in the determination of bead size made in water, DNHE, 1-hexanol and air by a laser technique with a Microtrack SRA analyzer. As Fig. 1 shows, beads swell clearly in water, but hardly swell in alcohol and ether. The same fact is observed by Inverse Steric Exclusion Chromatography (ISEC) structural measurements in water (Table 1) [18].

Nafion NR50 (NR50) is a perfluoroalkane sulfonic resin well described in the literature [14,15,19], with an acidic capacity of 0.81 meq H<sup>+</sup>/g, and skeletal density of 2.042 g/cm<sup>3</sup>, mean bead diameter of 2350  $\mu$ m and a maximum operating temperature of 220 °C.

Finally, the zeolite H-BEA-25 (BEA25) with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 25.1, an acidic capacity of 1.2 meq H<sup>+</sup>/g, and skeletal density of 2.237 g/cm<sup>3</sup> and a mean bead diameter of 8.1  $\mu$ m. An exhaustive report of H-BEA-25 properties as well as the pore distribution curve is available elsewhere [15,20].

#### 2.2. Experimental set-up

Experiments were carried out in a 100 mL stainless steel autoclave which operated in batch mode, stirred by means of a

$V_{\rm g}^{\rm c}$ (cm <sup>3</sup> /g)		$d_{\rm pore}^{\ \ d}$ (nm)	$\theta^{e}$ (%)	
0.153		19,3		
$V_{\rm g}~({\rm cm}^3/{\rm g})$	$V_{\rm sp}~({\rm cm}^3/{\rm g})$	d <sub>pore</sub> <sup>d</sup> (nm)	$\theta^{e}$ (%)	
0.355	1.189	1.19	57.4	
	Vg <sup>c</sup> (cm <sup>3</sup> /g) 0.153 Vg (cm <sup>3</sup> /g) 0.355	Vg <sup>c</sup> (cm <sup>3</sup> /g)           0.153           Vg (cm <sup>3</sup> /g)           Vg (cm <sup>3</sup> /g)           Vsp (cm <sup>3</sup> /g)           1.189	Vg c (cm³/g)         dpore <sup>d</sup> (nm)           0.153         19,3           Vg (cm³/g)         Vsp (cm³/g)           Vg (cm³/g)         Vsp (cm³/g)           1189         1.19	

<sup>a</sup> Dried by successive percolation with methanol, toluene and isooctane.

<sup>b</sup> BET method.

<sup>c</sup> Determined by adsorption-desorption of  $N_2$  at 77 K.

<sup>d</sup> Assuming pore cylindrical model.

Structural properties of Amberlyst 70.

<sup>e</sup> In dry state  $\theta = 100 V_g/(V_g + (1/\rho_s))$ . Swollen in water,  $\theta = 100(V_g + V_{sp} - (1/\rho_s))/(V_g + V_{sp})$ .

magnetic drive turbine. Temperature was controlled to within  $\pm 1~^\circ\text{C}$  by an electric furnace. To carry out the reaction in the liquid phase pressure was set at 2.1 MPa using N<sub>2</sub> as inert gas. 0.2  $\mu\text{l}$  samples were taken from the reactor through a liquid sampling valve directly connected to a GLC apparatus.

## 2.3. Analysis

The composition of liquid mixtures was analyzed by using a split-mode operation in a HP6890A GLC apparatus equipped with TCD, which allowed quantifying also water as a reaction product. A 50 m × 0.2 mm × 0.5  $\mu$ m methyl silicone capillary column was temperature programmed with a 6 min initial hold at 45 °C, followed by a 30 °C/min ramp up to 180 °C and holding for 10 min. Helium was used as a carrier gas at a total flow rate of 30 ml/min. It allowed to separate 1-hexanol, DNHE, water and by-products: C<sub>6</sub> olefins (1-hexene, 2-hexene and 3-hexene) and branched ethers (2,2-oxybis hexane and 1,2-oxybis hexane). Identification of by-products was carried out with an additional GLC apparatus equipped with a MS detector, where samples were injected manually.

#### 2.4. Methodology

Amberlyst 70 and NR50 were dried at  $110 \,^{\circ}$ C in an oven, firstly at atmospheric pressure during 15 h, and then 2 h under vacuum. H-BEA-25 was activated by calcination at 500  $\,^{\circ}$ C for 3 h under air stream in a muffle furnace and kept under vacuum overnight. Dried catalyst (1 g) and 70 ml of 1-hexanol were charged into the reactor and when pressure achieved 2.1 MPa leaking problems were checked. Then, the reactor was heated until the desired reaction temperature was reached. This moment was considered as the zero time of experiment. For 6 h, liquid samples were analyzed hourly to



**Fig. 2.** Variation of composition of the reaction medium with time at 190 °C on 1 g of Amberlyst 70 and 500 rpm (70 ml 1-hexanol). Up: 1-pentanol, DNHE, and water; down: by-products.

obtain the variation in concentration over time of all compounds. The assayed temperatures were selected in the range 150-190 °C.

In each experiment, 1-hexanol conversion ( $X_{HeOH}$ ), selectivity to DNHE ( $S_{DNHE}$ ), and similarly to alkenes ( $S_{alkenes}$ ) and to branched ethers ( $S_{ethers}$ ), and yield of DNHE with respect 1-hexanol ( $Y_{DNHE}$ ) were calculated by the expressions:

$$X_{\text{HeOH}} = \frac{\text{mole of 1-hexanol reacted}}{\text{initial mole of 1-hexanol}}$$
(1)

$$S_{\text{DNHE}} = \frac{\text{mole of 1-hexanol reacted to form DNHE}}{\text{mole of 1-hexanol reacted}}$$
(2)

$$Y_{\text{DNHE}} = \frac{\text{mole of 1-hexanol reacted to form DNHE}}{\text{initial mole of 1-hexanol}}$$
$$= X_{\text{HeOH}}S_{\text{DNPE}}$$
(3)

Reaction rates of DNHE formation at any time were calculated from the function of variation of  $n_{\text{DNHE}}$  (number of DNHE moles produced) versus time:

$$r_{\rm DNHE} = \frac{1}{W} \left( \frac{dn_{\rm DNHE}}{dt} \right)_t \left[ \frac{\rm mol \ DNHE}{\rm kg \ h} \right]$$
(4)

Finally, the turnover frequency (TOF) can be computed by dividing the reaction rate by the acidic capacity:

$$\text{TOF} = \frac{r_{\text{DNHE}}}{\text{eq } \text{H}^+/\text{kg}} \left[ \frac{\text{mol } \text{DNHE}}{\text{eq } \text{H}^+ \text{ h}} \right]$$
(5)

#### 3. Results and discussion

#### 3.1. Description of an experiment

Fig. 2 shows a typical plot of DNHE and by-products mole evolution on Amberlyst 70 over an experiment conducted at 190 °C. After a heating period of about 20 min, the alcohol conversion was about 3.5%. From this time, the reaction proceeds smoothly, DNHE being the main product. By-products appeared as soon as the reaction begins, and their amount increased continuously through the experiment. Detected byproducts were C<sub>6</sub> olefins (1-hexene, trans- and cis-2-hexene, cis/ trans-3-hexene), C<sub>6</sub> alcohols (2- and 3-hexanol) and C<sub>12</sub> branched ethers (1,2-oxybis hexane and 2,2-oxybis hexane). It is to be noted that the amount of water in the liquid phase was lower than that of DNHE despite that reactions of dehydration to DNHE and olefins release water. This can be explained by the preferential adsorption of water on the resin, as seen in Fig. 1, and by the formation of by-products such as C<sub>6</sub> alcohols other than 1-hexanol. As for by-products, olefins are the main ones. As Fig. 2 shows, 2-hexene is the most favored olefin, the quantities of 3-hexene and 1-hexene being much smaller. Branched ethers and, especially, 2- and 3-hexanols appear in a much lesser quantity.

Fig. 3 shows the evolution of 1-hexanol conversion and selectivity with time over the experiment.  $X_{\text{HeOH}}$  increased with time as expected, with a slow rise in the experiment ending by the influence of the reverse reaction.  $S_{\text{DNHE}}$  decreased with time, whereas selectivity to olefins and branched ethers increased but very slowly. Selectivity to alcohols other than 1-hexanol was very low, and it is not shown in Fig. 3.

Based on the evolution of the liquid phase composition, the following reaction scheme could be proposed:

(1) Dehydration of 1-hexanol to DNHE is the main reaction.

$$^{2}$$
  $^{0}$   $^{0}$   $^{0}$   $^{0}$   $^{0}$   $^{1}$   $^{1}$   $^{1}$ 

(2) Dehydration to 1-hexene is the main side-reaction,

(3) 1-Hexene isomerizes to 2-hexene (*cis* and *trans*), and 3-hexene (*cis* and *trans*).



- (4) Alkenes may react with water giving place to C<sub>6</sub> alcohols (2and 3-hexanol).
- (5) The reaction between the appropriate pair of alcohols yields branched ethers: 2-hexanol originates 2,2-oxybis hexane; 2hexanol and 1-hexanol react to give 1,2-oxybis hexane.

50–80 °C with methanol [22]. Consequently, reaction between 1-hexene and 1-hexanol could contribute to the formation of 1,2 oxybis hexane since: (1) working temperature is substantially higher in our study, and (2) hexenes concentration in the liquid phase is much higher than that of 2-hexanol. It is to be considered that, in the same way that 2-pentanol dehydration on acidic resins yields preferably olefins to the corresponding ether [23], it is likely that 2-hexanol gives place to hexenes as liquid phase composition suggests.

# 3.2. Synthesis of DNHE: effect of temperature

Preliminary experiments were performed to check whether measured reaction rates were free of mass transfer effects over Amberlyst 70 at 190  $^{\circ}$ C [24], the higher temperature of the range



(6) Finally, the reaction between the corresponding pair of  $C_6$  olefin and alcohol could also give branched ethers, i.e. 1-hexene reacting with 1-hexanol to give 1,2-oxybis hexane.



Literature on etherification of  $\alpha$ -olefins with shorter alcohols shows that they hardly react on acidic resins as compared to tertiary olefins. Still, literature also shows that on specially favorable conditions  $\alpha$ -olefins can be etherified, i.e. de Klerk [21] reported that treating a C<sub>6</sub> cut containing 86.6% of 1hexene at 69 °C with a methanol/tert-olefin initial molar ratio of 0.3 a 1-hexene conversion of 8% was observed. *sec*-Butyl methyl ether formation as by-product of MTBE synthesis has been also reported when a C<sub>4</sub> cut containing isobutene (40– 55 wt %), 1-butene (20–30), 2-butene (8–18) was etherified at



**Fig. 3.** Hexanol conversion ( $X_{\text{Hexanol}}$ ) and selectivity to DNHE ( $S_{\text{DNHE}}$ ), branched ethers ( $S_{\text{ethers}}$ ) and  $C_6$  olefins ( $S_{\text{alkenes}}$ ) at 190 °C (1 g Amberlyst 70, 500 rpm, 70 ml 1-hexanol).

explored. In this way, the effect of the amount of catalyst was checked by changing the mass of dried resin from 0.5 to 5 g. It was observed that the initial reaction rate did not change when the



catalyst load was lower than 4 g. Next, the influence of the external mass transfer was tested in a series of experiments with stirring speeds of 50–800 rpm. It was found that over 200 rpm initial reaction rates were the same within the limits of the experimental error. Finally, to evaluate the effect of the catalyst size on the reaction rate, experiments were performed over sieved batches of Amberlyst 70. No effect of diffusion was observed with batches between 450 and 670  $\mu$ m. Thus, further experiments were performed by using 1 g of dried catalyst with commercial distribution of particle sizes, and stirring speed of 500 rpm. It was assumed that obtained results on NR50 and H-BEA-25 were free of mass transfer influence as it was shown in the study of 1-pentanol dehydration to di-n-pentyl ether conducted in the same set-up [15].

To test the effect of temperature, a series of experiments was performed on Amberlyst 70 and NR50 at the temperature range of 150–190 °C, and on H-BEA-25 at 160–190 °C. Table 2 shows 1hexanol conversions, selectivities to DNHE and by-products, yields to DNHE after 6 h of reaction, as well as initial reaction rates of ether synthesis. As expected, 1-hexanol conversion increased with temperature for all tested catalysts, Amberlyst 70 being the most active due to its higher acidic capacity. Despite acid capacity of NR50 is lower than that of H-BEA-25, NR50 was more active because of its higher acid strength [15]. Although the high conversion achieved after 6 h at 190 °C with Amberlyst 70 ( $\approx$ 71%), reaction system was still far from chemical equilibrium, as seen in preliminary experiments with 5 g of resin where 1-hexanol

#### Table 2

Conversion, selectivity, ether yield after 6 h of reaction and initial reaction rate of dehydration of 1-hexanol to DNHE on Amberlyst 70, NR50 and H-BEA-25 ( $W_{cat}$  = 1 g, 70 mL 1-hexanol, 500 rpm).

<i>T</i> (°C)	C) X <sub>HeOH</sub> (%)		S <sub>DNHE</sub> (%)		Y <sub>DNHE</sub> (%)		S <sub>alkenes</sub> (%)		S <sub>ethers</sub> (%)		$r^{0}_{\text{DNHE}}$ (mol/h kg)							
	A-70	NR50	BEA25	A-70	NR50	BEA25	A-70	NR50	BEA25	A-70	NR50	BEA25	A-70	NR50	BEA25	A-70	NR50	BEA25
150	16.5	10.3		97.7	97.9		16.1	10.0		1.5	1.5		0.8	0.6		10.7	4.7	
160	29.7	18.4	6.7	96.2	98.0	92.2	28.6	18.0	6.1	2.4	1.2	2.8	1.4	0.8	5.0	18.7	9.4	$1.9\pm0.1$
170	47.6	35.6	15.1	94.3	97.9	93.0	44.9	34.8	14.0	3.5	1.2	0.3	2.1	0.9	6.7	32.3	19.2	$\textbf{5.3} \pm \textbf{0.3}$
180	63.7	53.9	31.2	91.1	96.9	90.0	58.0	52.2	28.0	5.9	1.9	4.8	3.0	1.2	5.2	73.3	36.1	$15\pm3$
190	70.9	66.1	53.8	86.9	93.4	88.8	61.7	61.7	47.8	9.4	4.7	6.8	3.6	2.0	4.4	151	89.7	$26\pm1$

conversions above 90% were found. Moreover, from liquid phase equilibrium constants of synthesis of DNHE [16] an equilibrium conversion of 1-hexanol of about 93% has been estimated at 190  $^{\circ}$ C.

On the other hand,  $S_{\text{DNHE}}$  decreased on increasing temperature due to the formation of C<sub>6</sub> alkenes, which was the main sidereaction; although some branched ethers were also detected. It is likely that branched ethers were formed by reaction between olefins and alcohols, since the detected amounts of C<sub>6</sub> alcohols other than 1-hexanol were very low. Moreover,  $S_{\text{alkenes}}$  and  $S_{\text{ethers}}$ increased on decreasing  $S_{\text{DNHE}}$ . The decrease in  $S_{\text{DNHE}}$  on rising the temperature was a bit higher on Amberlyst 70 than on NR50 and H-BEA-25, in particular at 190 °C. NR50 was the most selective catalyst in the whole temperature range, followed by Amberlyst 70 at 150–180 °C, and H-BEA-25 at 190 °C.

Despite the decrease on the  $S_{\text{DNHE}}$ , DNHE yields increased with temperature, reaching a value of 61.7% after 6 h on Amberlyst 70 and NR50 at 190 °C. In the entire range of temperature, the highest DNHE yields were obtained on Amberlyst 70, but at 190 °C DNHE yields on NR50 and Amberlyst 70 are the same. At present working conditions, the upgrade in ether yield observed on increasing the temperature is due to higher 1-hexanol conversions which balance the slight decrease in selectivity. Thus NR50 could be a good option for industrial operation at 190 °C, whereas Amberlyst 70 is the best option when the whole temperature range is considered.

As Table 2 shows, initial reaction rates of DNHE synthesis strongly increase with temperature and, again, the highest value was achieved at 190 °C with Amberlyst 70, followed by NR50. Fig. 4 plots the reaction rate versus 1-hexanol conversion for the three catalysts at 190 °C. Amberlyst 70 was the more active at  $X_{\text{HeOH}} \leq 40\%$ . At higher conversions, rates on Amberlyst 70 and NR50 were the same within the limits of the experimental error. At low  $X_{\text{HeOH}}$  values, reaction rate on Amberlyst 70 is the highest since it has the highest acid capacity, followed by NR50 since it has by far the highest acid strength, and finally H-BEA-25. A sharp decrease in the



Fig. 4. Reaction rate versus 1-hexanol conversion for the assayed catalysts at 190  $^\circ\text{C}$  (1 g of dried catalyst, 500 rpm, 70 ml 1-hexanol).

reaction rate was observed for Amberlyst 70 and in lower extent for NR50 on increasing  $X_{\text{HeOH}}$ . This decrease can be ascribed primarily to the effect of reverse reaction, since the formation DNHE and water decreases the driving force of the reaction. The presence of increasing amounts of water as reaction proceeds can also play a role: water is preferably adsorbed on the resin and swells the catalyst (Fig. 1), favoring diffusion of 1-hexanol and accessibility to HSO<sub>3</sub><sup>-</sup> groups. Nevertheless, some inhibiting effect because of preferential adsorption of water on sulfonic groups diminishing the actual number of active sites [25], and even by a reaction mechanism change from a concerted one (the true catalytic species is the  $HSO_3^-$  group) to an ionic one (the true catalytic species is the solvated H<sup>+</sup>) could take place [26]. NR50 shows a similar behavior. Instead, reaction rates decrease slightly on H-BEA-25 with X<sub>HeOH</sub>, maintaining the activity level during the whole experiment, probably because this catalyst does not swell on adsorbing water, in such a way that the observed rate decrease is only due to the effect of reverse reaction.

Fig. 5 shows the variation of turnover frequency (TOF) with  $X_{\text{HeOH}}$  at 190 °C. NR50 showed the highest TOF values. This behavior was expected since fluorine atoms confer NR50 superacid characteristics, with a Hammett acidity function  $(-H_0)$  of 11 (Table 3). Table 3 also shows the Hammett acidity functions of Amberlyst 35 and H-BEA-25. The acid strength of Amberlyst 70 is assumed to be the same as Amberlyst 35, as shown by ammonia adsorption flow calorimetry tests carried out by Siril et al. [27]. At low X<sub>HeOH</sub> values, TOFs of Amberlyst 70 are higher than those of H-BEA-25, which correlates with its slightly higher values of  $(-H_0)$ . But as reaction pass by TOFs of NR50 and Amberlyst 70 decrease dramatically whereas those of H-BEA-25 only decreases slightly. TOF decrease of NR50 and Amberlyst 70 can be explained by the influence of reverse reaction and the inhibitor effect of water. Moreover, the fact that acid strength of both catalysts decreases when the content of water of the liquid phase increases (Table 3) could additionally contribute to TOF decrease. On the other hand,



Fig. 5. TOF versus 1-hexanol conversion for the assayed catalysts at 190  $^\circ C$  (1 g of dried catalyst, 500 rpm, 70 ml 1-hexanol).

# **Table 3** Hammett acidity function $(-H_0)$ in aqueous and non-aqueous conditions [14,15].

Catalyst	Aqueous	Non-aqueous
A35ª NR50 BEA 25	2.65 8.4	5.6 11 $4.4 \le -H_0 \le 5.7$

<sup>a</sup> Amberlyst 35 and Amberlyst 70 have similar acid strength [27].



Fig. 6. Arrhenius plot of initial reaction rates for the assayed catalysts.

#### Table 4

Apparent activation energies (kJ/mol) for DNHE (this work) and DNPE [15] synthesis reactions.

Catalyst	$E_{\rm ap,DNHE}$	$E_{\rm ap,DNPE}$
A70 NR50 BEA 25	$\begin{array}{c} 108\pm7\\ 118\pm6\\ 148\pm11 \end{array}$	$\begin{array}{c} 115\pm5\\ 109\pm3\\ 121\pm2 \end{array}$

the slight decrease of TOF for H-BEA-25 suggests that only the reverse reaction has a significant role. Finally, the fact that at low  $X_{\text{HeOH}}$  values TOF of H-BEA-25 was nearly a 40% of that of Amberlyst 70, despite that in non-aqueous media their acid strengths are similar, agrees with the assumption that only mesopore surface (about a 40% of total surface area) is accessible to 1-pentanol and larger alcohols [15].

Arrhenius plots of initial reaction rates are straight lines for the three catalysts (Fig. 6). Thus, neither NR50 nor H-BEA-25 show diffusion concerns in the temperature range studied. From Arrhenius plots apparent activation energies for DNHE synthesis,  $E_{\rm ap}$ , were estimated (Table 4). Similar values were obtained for Amberlyst 70 and NR50, while a slightly higher value was computed for H-BEA-25, showing that the reaction is a bit more sensitive to temperature on the zeolite.

## 3.3. Comparison of DNPE and DNHE formation reactions

It is interesting to compare the behavior of the tested catalysts in the related synthesis of DNPE and DNHE, since both ethers have been proposed as options to reformulate diesel fuels. Experiments concerning the dehydration of 1-pentanol to DNPE and water were performed in the same set-up, using the same amount and type of catalysts and under the same conditions of operation free of mass transfer influence [15].

The dehydration of 1-hexanol to DNHE on Amberlyst 70 and NR50 is slightly faster than the dehydration of 1-pentanol to DNPE. On both catalysts, 1-hexanol conversions are higher than those of 1-pentanol, so that despite that selectivity to DNHE is slightly lower that selectivity to DNPE measured DNHE yields are slightly better. Moreover, selectivity to alkenes and branched ethers was a

bit higher in the hexanol/DNHE system. Instead, on H-BEA-25 higher ether yields are observed in the pentanol/DNPE system. In this case, both alcohol conversions and selectivities to ether were slightly higher in DNPE synthesis. Accordingly, selectivities to olefins and branched ethers are slightly lower in the dehydration reaction of 1-pentanol to DNPE.

Initial reaction rates show the same trend as conversions so that they were higher in the 1-hexanol/DNHE system on Amberlyst 70 and NR50 in the whole temperature range. On the contrary, higher initial reaction rates were observed in the 1-pentanol/DNHE system on H-BEA-25. It seems that swelling of both polymeric resins due to water released allows accommodate both reaction intermediates reasonably well. The fact that the longest chain alcohol, 1-hexanol, is more acid than 1-pentanol could also help to explain the higher dehydration reaction for DNHE synthesis on resins [28,29]. As for H-BEA-25, observed activity data could result from the fact that 1-hexanol is slightly bulkier than 1-pentanol.

In Table 4 the activation energies for both reaction systems are shown. It should be noted that  $E_{ap,DNHE}$  values were estimated directly from initial reaction rates, whereas  $E_{ap,DNPE}$  were computed from a kinetic model in which adsorption–desorption processes were taken into account. Notwithstanding that, activation energies for both systems are similar, particularly, for Amberlyst 70 and NR50. However, the highest value for H-BEA-25 in DNHE synthesis suggests that this reaction is a bit more sensitive to temperature on the zeolite than DNPE synthesis.

#### 4. Conclusions

The thermally stable catalysts Amberlyst 70, Nafion NR50 and zeolite H-BEA-25 have proven to be good catalysts to obtain di-n-hexyl ether. The best results were obtained with Amberlyst 70, but the most selective catalyst was Nafion NR50. In the reaction conditions, the best ether yields were obtained at the highest temperature because the gain in alcohol conversions outweighs the decrease in selectivity to ether. Apparent activation energies for DNHE synthesis were in the range 108–148 kJ/mol, showing a moderate temperature dependence of reaction rate. Compared with the related synthesis of DNPE it is seen that DNHE yields on Amberlyst 70 and NR50 are slightly better than DNPE ones, despite that selectivity to DNHE is a bit lesser than that to DNPE. On the contrary, on H-BEA-25 slightly better yields in DNPE are found.

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#### References

- [1] A. Douaud, Hydrocarb. Process. 74 (2) (1995) 55–58.
- [2] F. Giavazzi, D. Terna, D. Patrini, F. Ancillotti, G.C. Pecci, R. Trerè, M. Benelli, IX International Symposium on Alcohol Fuels, vol. 1, 1991, 327–335.
- [3] J. Van Heerden, J.J. Botha, P.N.J. Roets, XII International Symposium on Alcohol Fuels, vol. 1, Tsinghua Univ. Press, Beijing, 1998, pp. 188–199.
- [4] G.C. Pecci, M.G. Clerici, M.G. Giavazzi, F. Ancillotti, M. Marchionna, R. Patrini, X International Symposium on Alcohol Fuels, vol. 1, 1991, 321–335.
- [5] O.A. Olah, US Patent 5.520.710 (1996).
- [6] J. Hagen, Industrial Catalysis: A Practical Approach, 1st ed., Wiley-VCH, 1999.
- [7] R. Patrini, M. Marchionna, UK Patent GB 2.323.844 A (1998).
- [8] O.N. Karpov, R.M. Bistroya, L.G. Fedoysuk, Zh. Prikl. Khim. 40 (1967) 219-223.
- [9] E. Swistak, P. Mastagli, Comptes Rend. 239 (1954) 709–711.
- [10] C. Park, M.A. Keane, J. Mol. Catal. A: Chem. 166 (2001) 303-322.
- [11] R.J.J. Nel, A. de Klerk, Ind. Eng. Chem. Res. 48 (2009) 5230-5238.
- [12] J.A. Ballantine, M. Davies, I. Patel, J.H. Purnell, M. Rayanakorn, K.J. Williams, J. Mol. Catal. 26 (1984) 37-56.
- [13] G.A. Olah, T. Shamma, G.K. Surya Prakash, Catal. Lett. 46 (1997) 1-4.

- [14] J. Tejero, F. Cunill, M. Iborra, J.F. Izquierdo, C. Fité, J. Mol. Catal. A: Chem. 182–183 (2002) 541–554.
- [15] R. Bringué, J. Tejero, M. Iborra, J.F. Izquierdo, C. Fité, F. Cunill, J. Catal. 244 (2006) 33-42.
- [16] R. Bringué, J. Tejero, M. Iborra, C. Fité, J.F. Izquierdo, F. Cunill, J. Chem. Eng. Data 53 (2008) 2854–2860.
- [17] J.R. Collin, D. Ramprasad, European Patent EP 1 479 665 (2004).

77-91.

- [18] K. Jerabek, ACS Symp. Ser. 635 (1996) 211–220.
   [19] Q. Deng, Y. Hu, R.B. Moore, C.L. McCormick, K.A. Mauritz, Chem. Mater. 9 (1997)
- 36-44. [20] M. Iborra, J. Tejero, C. Fité, J.F. Izquierdo, F. Cunill, J. Catal. 231 (2005)
- [21] A. de Klerk, Ind. Eng. Chem. Res. 43 (2004) 6349-6354.
- [22] M. Vila, F. Cunill, J.F. Izquierdo, J. González, A. Hernández, Appl. Catal. A: Gen. 117 (1994) L99–L108.
- [23] R. Bringué, Ph.D. Thesis, University of Barcelona, 2006.
- [24] E. Medina, MS Chemical Engineering Thesis, University of Barcelona, 2007.
- [25] R. Bringué, J. Tejero, M. Iborra, J.F. Izquierdo, C. Fité, F. Cunill, Top. Catal. 45 (2007) 181–186.
- [26] B.C. Gates, W. Rodríguez, J. Catal. 31 (1973) 27.
- [27] P.F. Siril, H.E. Cross, D.R. Brown, J. Mol. Catal. A: Chem. 279 (2008) 63-68.
- [28] F. Ancillotti, M. Massi Mauri, E. Pescarollo, J. Catal. 46 (1977) 49-57.
- [29] F. Ancillotti, M. Massi mauri, E. Pescarollo, L. Romagnoni, J. Mol. Catal. 4 (1978) 37-48.