

Dehydration of 1-pentanol to di-*n*-pentyl ether over ion-exchange resin catalysts

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Abstract

The dehydration reaction of 1-pentanol to di-*n*-pentyl ether (DNPE) and water in the liquid phase was studied at 110–180 °C and 1 MPa on sulfonic styrene–divinylbenzene (S/DVB) copolymers and the perfluoroalkanesulfonic resin NR50. S/DVB-based catalysts were macroreticular and gel-type resins both sulfonated conventionally and oversulfonated. Macroreticular resins tested include resins whose working phase in catalysis is gel phase (i.e. Amberlyst-15 and Amberlyst-35) and XN1010 whose working phase in catalysis is macropores surface. By comparing 1-pentanol conversion, selectivity to DNPE and initial reaction rates at 150 °C it is concluded that gel-type S/DVB resins that swell moderately in the reaction medium, as CT-224, are the more suitable catalysts for the reaction. NR50, which is thermally stable up to 200 °C, is the most selective catalyst tested but it is too much expensive for industrial use. Selectivity to DNPE decreases as temperature increases showing that side reaction of dehydration to 1-pentene is more sensitive to temperature. Apparent activation energies for the dehydration reaction of 1-pentanol to DNPE were found to be about 100 kJ/mol. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1-Pentanol; DNPE; Ion-exchangers; Amberlyst-15; Nafion

1. Introduction

In the last decade, great importance was attached to the impact of diesel exhaust gases on the environment and human health. Among the factors controlling it, the design of the engine and the fuel quality are of the utmost importance. The use of low quality fuels causes greater gaseous and smokes emissions, higher noise levels and more difficult cold starting [1]. According to engine manufacturers, an improvement of the quality of diesel fuels would result in a further development of current engines, including emission

after-treatment devices. So, a cost-effective means to improve the quality of diesel fuels is an important issue for oil companies. Several options such as selective blending, upgrading refining processes and use of cetane improver additives are possible from technical and economics standpoint [2].

Diesel fuel specifications are becoming increasingly stringent as legislation is adopted to improve air quality by reducing emissions. It is expected that coming diesel fuels will be characterized by a higher cetane number, lower density, and lower aromatics, polyaromatics and sulfur contents with respect to the current ones. A good chance to meet such limits might be the use of reformulated diesel fuels containing appropriate high quality components [3]. In the case of spark-ignition engines, high-octane ethers play an

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Nomenclature

BET	Brunauer–Emmet–Teller
d_b	mean diameter of beads (mm)
d_{pore}	mean pore diameter (Å)
E_{app}	apparent activation energy (kJ/mol)
H_0	Hammett acidity function
ISEC	inverse steric exclusion chromatography
n_j	mole number of component j (mol)
r_{DNPE}^0	initial reaction rate on a dry weight catalyst basis (mol/h kg)
r_{DNPE}^0	initial reaction rate per equivalent of sulfonic groups (mol/h equiv.)
S	selectivity (dimensionless)
S/DVB	styrene–divinylbenzene
S_g	surface area (m ² /g)
t	time (h)
V_g	pore volume (cm ³ /g)
V_{sp}	specific volume of the swollen polymer phase (cm ³ /g)
W	weight of dry catalyst (g)
X	conversion of 1-pentanol (dimensionless)
Y	yield to DNPE (dimensionless)

Greek letters

ρ_s	skeletal density (g/cm ³)
θ	porosity (volume of pores/particle volume)

important role in improving exhausts and in avoiding large modifications in the engine and distribution systems. Hence the application of the same approach to diesel fuels seems interesting.

A few years ago, in a comprehensive study on the blending properties of oxygenates in diesel fuels [4], it was observed that linear ethers with ≥ 9 carbon atoms showed the best balance among blending cetane number and cold flow properties. Di-*n*-pentyl ether (DNPE) was selected because of its blending properties and the availability of potential feedstocks. DNPE has a blending cetane number as high as 109, and because of its density and viscosity (a bit lower than those of commercial fuels) it behaves as a light diesel fuel. Moreover, DNPE was shown to be very effective in reducing diesel exhaust emissions such as CO, NO_x, unburned hydrocarbons, particulates, smokes,

and aldehydes emissions [5,6]. On the other hand, 1-butene from C₄ cuts is an appropriate feedstock for the industrial manufacture of DNPE. The synthesis route consists of selective hydroformylation of 1-butene to 1-pentanol, followed by the dehydration reaction of alcohol to di-alkyl ether.

In industrial application, linear symmetrical ethers are generally produced by means of the bimolecular dehydration of primary alcohols on acid catalysts:



However, if the catalyst is not selective, the monomolecular dehydration to alkene can take place, and large amounts of the alkene byproduct can be produced [7]



In addition, the alcohol can be added to the alkene byproduct to give branched ethers. Therefore, if high selectivities to linear ethers are desired, it is necessary to minimize the production of olefins.

So far in industrial practice, alcohols dehydration has been catalyzed by sulfuric acid. This catalyst generally offers quite high selectivities to ether (>80–85%) but has various problems: it is generally used in high concentrations, it is corrosive and in addition, whereas the selectivity to olefins is rather low, heavy products are generally formed (i.e. alkyl sulfates) which tend to blacken the product and complicate the recovery of the spent acid catalyst.

To overcome those problems close bound to the use of soluble acid catalysts, the use of acid cationic resins was proposed in the sixties. However, literature on the dehydration of 1-butanol and higher alcohols to di-alkyl ether is scarce. With these alcohols, high yields in ether are obtained by using reactors equipped with Dean and Stark apparatus to remove the water as it is formed by azeotropic distillation, thus shifting the chemical equilibrium towards the synthesis of the ether. In the case of 1-pentanol, conversions to DNPE on KU-25 of about 80% [8], and of 67% on XN1010 [5], were reported. However, since working temperature is the boiling point of the alcohol–ether mixture, thermal deactivation of acid ion-exchangers could be a serious drawback for continuous industrial processes. It should be quoted that DNPE has been also prepared on Nafion H (an acid polymeric catalyst much

more thermally stable than resins) with a selectivity to DNPE of 97% [9].

Nowadays, sulfonic ion-exchange resins with an ever-increased thermal stability are available, i.e. the oversulfonated ones [10]. The aim of the paper is to study the liquid phase synthesis of DNPE on sulfonic resins without water removal. This is an important matter since the morphology of ion-exchangers, and the microenvironment of acid centers in the course of the reaction, depends on the water amount in the reaction medium. Tested resins include gel and macroreticular styrene–divinylbenzene (S/DVB) polymers, both sulfonated conventionally and oversulfonated, and a perfluoroalkane one. The role of the morphology of S/DVB resins in the reaction medium is also stressed.

2. Experimental

2.1. Chemicals

1-Pentanol (99% pure; <1% 2-methyl-1-butanol) was supplied by Fluka (Buchs, Switzerland), and used without further purification. DNPE ($\approx 99\%$), 2-pentanol (98%), 2-methyl-1-butanol ($\approx 98\%$), 1-pentene ($\approx 97\%$), *cis*-2-pentene ($\approx 98\%$), *trans*-2-pentene ($\approx 99\%$), and 2-methyl-1-butene ($>97\%$), supplied by Fluka, and water were used for analysis.

2.2. Catalysts

The perfluoroalkanesulfonic resin Nafion NR50 (Aldrich, Milwaukee, WI), and 12 sulfonic S/DVB resins were used as catalysts. S/DVB resins were XN1010, Amberlyst-15, Amberlyst-35, Amberjet 1200H, and Amberjet 1500H (Rohm and Haas, Philadelphia, USA); CT-224, CT-165, and CT-151 (Purolite, Bala Cynwyd, USA); K-2621E (Bayer, Leverkusen, Germany); and Dowex 50Wx2, 50Wx4, and 50Wx8 supplied by Fluka. Characteristics and short names of catalysts are shown in Table 1.

Some S/DVB resins are sulfonated conventionally, i.e. the concentration of $-\text{HSO}_3$ groups is at (or a bit lower) the limit of one group per benzene ring. The rest are oversulfonated. They have been sulfonated by a special procedure increasing (at least in some polymer domains) the concentration of $-\text{HSO}_3$ groups beyond the usual limit of one group per benzene ring [11]. Acid capacity was measured by titration against standard base [12].

Table 2 shows the structural and textural parameters both in dry state and swollen in water of tested S/DVB resins. Macroreticular resins are large agglomerates of gel micro-spheres, and each micro-sphere shows smaller nodules more or less fused together [13]. In between the nodules there is a family of very small pores (micropores). In between the micro-spheres a

Table 1
Characteristics of tested catalysts

Catalyst	Short name	Structure ^a	Acidity (equiv./kg)	Sulfonation type ^b	Working phase	d_b (mm) ^c	T_{\max} (°C)	Percentage of DVB
XN1010	XN1010	MR	3.43	C	Surface	0.50	150	85
Amberlyst-35	A-35	MR	5.32	O	Gel phase	0.51	130	20
Amberlyst-35	A-15	MR	4.81	C	Gel phase	0.74	120	20
K-2621E	K-2621E	MR	5.24	O	Gel phase	0.56	120	16–25
CT-151	CT-151	MR	5.54	O	Gel phase	0.43	145	
CT-165	CT-165	GT	4.94	C	Gel phase	0.43	145	
Amberjet 1500H	A-1500	GT	5.20	O	Gel phase	0.65		
Amberjet 1200H	A-1200	GT	5.56	O	Gel phase	0.63		
Dowex 50Wx8	Dx8	GT	4.83	C	Gel phase	0.10	150	8
CT-224	CT-224	GT	5.34	O	Gel phase	0.50	150	4
Dowex 50Wx4	Dx4	GT	5.16	C	Gel phase	0.10	150	4
Dowex 50Wx2	Dx2	GT	4.83	C	Gel phase	0.10	150	2
Nafion NR50	NR50	GT	0.81		Gel phase	2.4	210	

^a MR: macroreticular or macroporous; GT: gel-type or microporous.

^b O: oversulfonated; C: conventionally sulfonated.

^c Determined by sieving dry industrial samples.

Table 2
Structural parameters of tested catalyst in dry state and swollen in water

Catalyst	ρ_s (g/cm ³) ^a	Dry state				Swollen in water (ISEC method [15])				
		S_g (m ² /g) ^b	V_g (cm ³ /g) ^c	d_{pore} (Å)	θ (%)	S_g (m ² /g)	V_g (cm ³ /g)	d_{pore} (Å)	V_{sp} (cm ³ /g)	θ (%)
XN1010	1.3319	386	0.275	28.5	26.8	752	0.775	41		50.8
A-35	1.5419	34	0.28	329	30.2	166	0.623	150	0.736	52.3
A-15	1.4164	42	0.36	343	33.8	157	0.632	161	0.823	51.5
K-2621E	1.4283	35	0.27	316	27.8	132	0.426	129	0.908	47.5
CT-151	1.5592	25	0.30	480	31.9	151	0.556	147	0.932	56.9
CT-165	1.4328	2.4	0.017	288	2.4				0.846	17.5
A-1500	1.4155	0.15							1.411	49.9
A-1200	1.4183	0.16							1.618	56.4
Dx8	1.4295	0.23							1.627	57.0
CT-224	1.4236	0.92							1.811	61.2
Dx4	1.4171	1.06							2.309	69.4
Dx2	1.4259	1.32							2.655	73.6
NR50	2.084	0.35								

^a Measured by helium displacement.

^b BET method.

^c Determined by adsorption–desorption of N₂ at 77 K.

second family of intermediate pores with diameter 8–20 nm (mesopores) is observed. A third family of large pores with diameter 60–30 nm is located between the agglomerates (macropores). Macropores are permanent and can be detected by standard techniques of pore analysis, i.e. adsorption–desorption of N₂ at 77 K. Meso- and micropores that appear in polar liquid media able to swell the polymer, are non-permanent, and can be detected by characterization techniques in aqueous media, such as ISEC (inverse steric exclusion chromatography) [14].

As can be seen in Table 2, macroreticular resins A-15, A-35, CT-151 and K-2631E (with DVB contents ranging from 15 to 20%) show BET surface areas between 30 and 40 m²/g, which correspond to a permanent family of large pores. ISEC surface areas ranging from 150 to 170 m²/g reveal that a family of small pores with diameter 8–20 nm is open in the presence of polar solvents. The values of pore volume, and mean pore diameter of Table 2 agree with this fact. ISEC analysis of CT-165 shows the presence of mesopores. So, it was considered as a gel resin. BET and ISEC methods show that the macroporous resin XN1010 has a very high surface area, suggesting that even smaller pores are permanent. As a result of its high DVB content the gel phase is very stiff, and all the sulfonic groups lie within the two monolayers

bordering the polymer surface. Accordingly, its working phase for catalysis is the pore surface [16].

ISEC also provides information on the volume distribution of the differently dense gel fractions in the swollen polymer mass. A good view of the three-dimensional polymer network of swollen polymer is given by the geometrical model developed by Ogston [17], in which micropores are described by spaces between randomly oriented rigid rods. The parameter characteristic of this model is the specific volume of the swollen polymer (volume of the free space plus that occupied by the skeleton), V_{sp} . The Ogston model also allows distinguishing zones of swollen gel phase of different density or polymer chain concentration (total rod length per unit of volume of swollen polymer, nm⁻²). According to this model, the pore size is described as the total rod length per unit of volume. Fig. 1 shows the pore distribution of the swollen gel phase, probably quite representative of the morphology of swollen ion-exchangers in aqueous solution of alcohol. As can be seen, macroreticular and most of gel-type resins show polymer concentrations of 2 nm/nm³, typical of a very dense polymer mass, poorly accessible. Gel-type resins with 2–4% DVB show a fraction of polymer concentration of 0.4–0.8 nm/nm³ that corresponds to a moderately expanded gel.

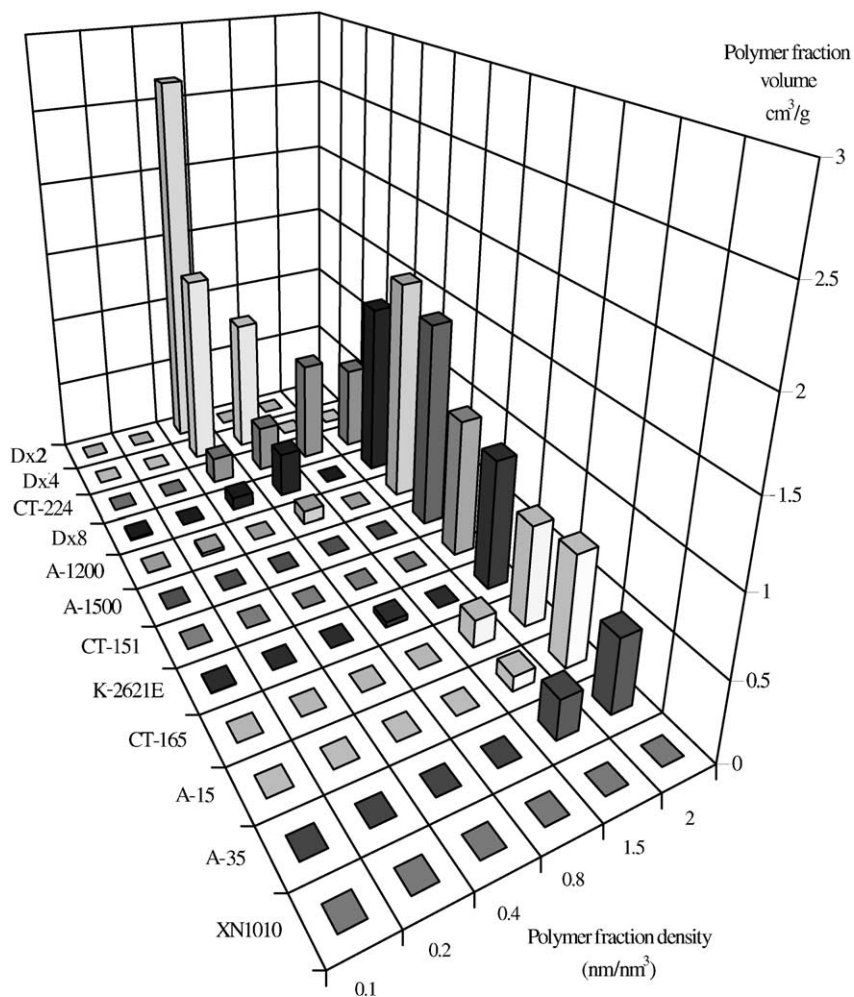


Fig. 1. ISEC pattern displayed by resins in water. Resins are plotted in increasing order of V_{sp} .

2.3. Apparatus

The experiments were carried out in a stainless steel jacketed 100 ml autoclave operating in batch mode. The reaction medium was agitated at 500 rpm by a magnetic drive turbine and mixing baffles on the reactor walls were used to improve the mixing. Temperature was controlled to within ± 1 K by thermostated oil that flowed to the jacket. To maintain the reacting mixture in the liquid phase over the whole temperature range the pressure was set at 1 MPa by means of N_2 . One of the outlets of the reactor was connected directly to a liquid sampling valve, which

injected 0.2 μ l of pressurized liquid into a gas-liquid chromatograph.

2.4. Analysis

The composition of liquid mixtures was analyzed by using a split mode operation in a HP6890A GLC apparatus equipped with a TCD detector to measure the presence of water. A 50 m \times 0.2 mm \times 0.5 μ m methyl silicone capillary column was used to separate and determine 1-pentanol, DNPE, water, and byproducts: C_5 olefins (1-pentene, 2-pentene and methyl butenes), branched ethers (di-2-pentyl ether,

1-(1-methylbutoxy)-pentane, 1-(2-methylbutoxy)-pentane and 2-(2-methylbutoxy)-pentane), 2-methyl-1-butanol, and 2-pentanol. The column was temperature programmed with a 6 min initial hold at 318 K followed by a 30 K min⁻¹ ramp up to 453 K and held for 5 min. Helium was used as the carrier gas at a total flow rate of 30 ml min⁻¹.

2.5. Procedure

Resin samples of 5 g (catalyst loading of 8%) with the commercial distribution of bead sizes were washed with water to remove impurities, and dried at vacuum for 3 h at 120 °C. 1-Pentanol and the dry catalyst were charged into the reactor and, after looking for leakages, heated to the desired temperature. The time when reaction medium reached that temperature was taken as the starting point of the reaction. To follow the concentration variation of chemicals with time liquid samples were periodically taken out the reactor, and analyzed as mentioned above. Total length of the experiments was 6 h.

In each experiment, 1-pentanol conversion (X), selectivity to DNPE, and DNPE yield were computed. The overall fractional yield of DNPE with respect to 1-pentanol was selected as a measure of how selective 1-pentanol is in forming DNPE. It is defined as [18]

$$S_{\text{DNPE}} = \frac{\text{mole of 1-pentanol reacted to form DNPE}}{\text{mole of 1-pentanol reacted}}$$

Likewise, selectivity to alkenes, S_{ALKENES} , branched ethers, S_{ETHERS} , and amyl alcohols different from 1-pentanol, S_{ALCOHOLS} , were defined.

Yield of DNPE with respect to 1-pentanol is defined as [18]

$$Y_{\text{DNPE}} = \frac{XS_{\text{DNPE}}}{\text{mole of 1-pentanol reacted to form DNPE}} = \frac{\text{mole of 1-pentanol reacted to form DNPE}}{\text{mole of 1-pentanol initially}}$$

Initial reaction rates were measured from the curves of the composition of liquid phase vs. time at $t = 0$ according to

$$r_{\text{DNPE}}^0 = \frac{1}{W} \left(\frac{dn_{\text{DNPE}}}{dt} \right)_{t=0}$$

Conversion of 1-pentanol, selectivity to DNPE, and DNPE yield were accurate within $\pm 2\%$. On the other hand, initial reaction rates were accurate within $\pm 5\%$.

3. Results and discussion

3.1. Description of an experiment

Runs on S/DVB resins were performed at 110–150 °C. Since at working temperatures thermal stability is a question for prolonged operations, it was firstly assessed the chance that experimental results were influenced by thermal deactivation. It is known that in aqueous liquid media, thermal deactivation takes place by two mechanisms: hydrolysis of sulfonic groups with liberation of H₂SO₄ and formation of sulfone bridges between adjacent polymer chains [19,20]. However, it was found that half-life of gel-type resins (i.e. Dx8), was higher than 800 h at 120–150 °C [19] what shows that thermal deactivation is rather slow in aqueous liquid phase. Moreover, kinetic runs on CT-224, A-15 and A-35 heated in vacuum show that it is necessary to maintain them a long time at high temperature for resins to be deactivated (Table 3). Therefore, since our experiments were short (6 h) it is unlikely that the results be influenced by thermal deactivation. Experiments on NR50 were carried out at 130–180 °C. In this case, working temperatures lie below the maximum operating temperature recommended by the manufacturer. So, thermal stability is not a question with NR50.

Since commercial bead sizes were used, it was firstly checked that experimental data were free of external mass transfer effects [23]. However, internal mass transfer influence cannot be excluded. In spite of that, since resins swell sizeably in polar liquid media, accessibility of 1-pentanol to sulfonic groups would not be seriously hindered at the reaction conditions [24,25]. Fig. 2 shows typical plots of DNPE, and byproducts mole evolution on CT-165 throughout an experiment. Since the reaction is rather slow and the heating period short, the extent of the reaction was very small when the working temperature was reached: 1-pentanol conversions were always <1%. As can be seen, the composition of the reaction medium changes smoothly with time, and byproducts appear as early as the reaction begins. Detected

Table 3
Summary of kinetic studies conducted on ion-exchange resins heated in vacuum for a long time

Resin catalyst	Heating conditions	Fraction of lost HSO ₃ groups (%)	Reaction	Kinetic results	Reference
CT-224	170 °C for 77 h	2	Dehydration of 1-pentanol to DNPE	Comparing with fresh resin, reaction rate decreased by 2%	[21]
A-15	164 °C for 88.5 h	6	Addition of 2-propanol to isobutene to give isopropyl <i>tert</i> -butyl ether	No significant decrease in reaction rate was observed	[22]
A-35	167 °C for 164 h	15	Addition of 2-propanol to isobutene to give isopropyl <i>tert</i> -butyl ether	Comparing with fresh resin, reaction rate decreased by 10%	[22]

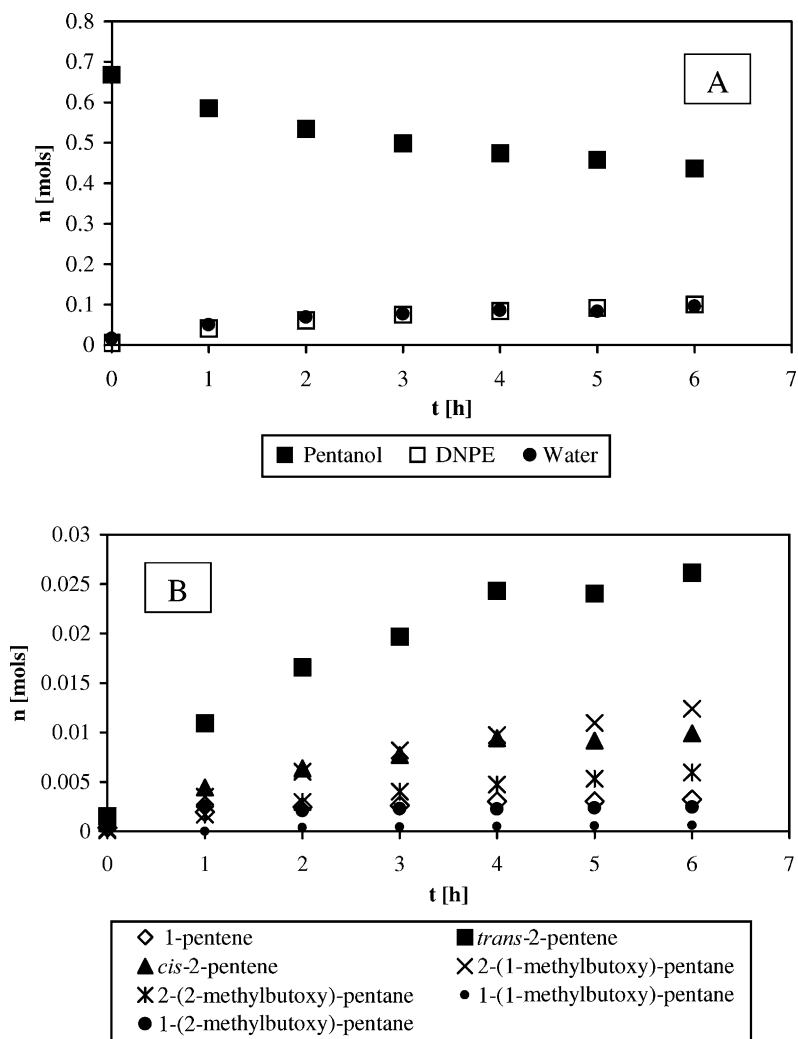


Fig. 2. Variation of composition of the reaction medium with time (catalyst CT-165, $T = 150\text{ }^{\circ}\text{C}$): (A) 1-pentanol, DNPE, and water; (B) byproducts.

byproducts were 1-pentene, *cis*-2-pentene, *trans*-2-pentene, and the branched ethers 2-(1-methylbutoxy)-pentane, 1-(1-methylbutoxy)-pentane, 1-(2-methylbutoxy)-pentane, and 2-(2-methylbutoxy)-pentane. Very small amounts of 2-methyl-1-butanol and 2-pentanol were also detected. Branched ethers were identified by means of a GLC apparatus equipped with an MS detector, after concentrating the ether fraction from the liquid mixture by distillation.

Distribution of byproducts suggests the reaction scheme of Fig. 3. Dehydration of 1-pentanol to DNPE

(1-pentoxy-pentane) is the main reaction. Dehydration to 1-pentene is the main side reaction. 1-Pentene isomerizes to 2-pentene (*cis* and *trans*), and to 2-methyl-1-butene. Pentenes react with water giving place to amyl alcohols. Finally, inter-molecular dehydration of the appropriate pair of alcohols gives branched ethers: 2-pentanol gives place to 2-(1-methylbutoxy)-pentane; 2-pentanol and 1-pentanol react with 2-methyl-1-butanol to give 2-(2-methylbutoxy)-pentane, and 1-(2-methylbutoxy)-pentane, respectively; finally, 2-pentanol and 1-pentanol give

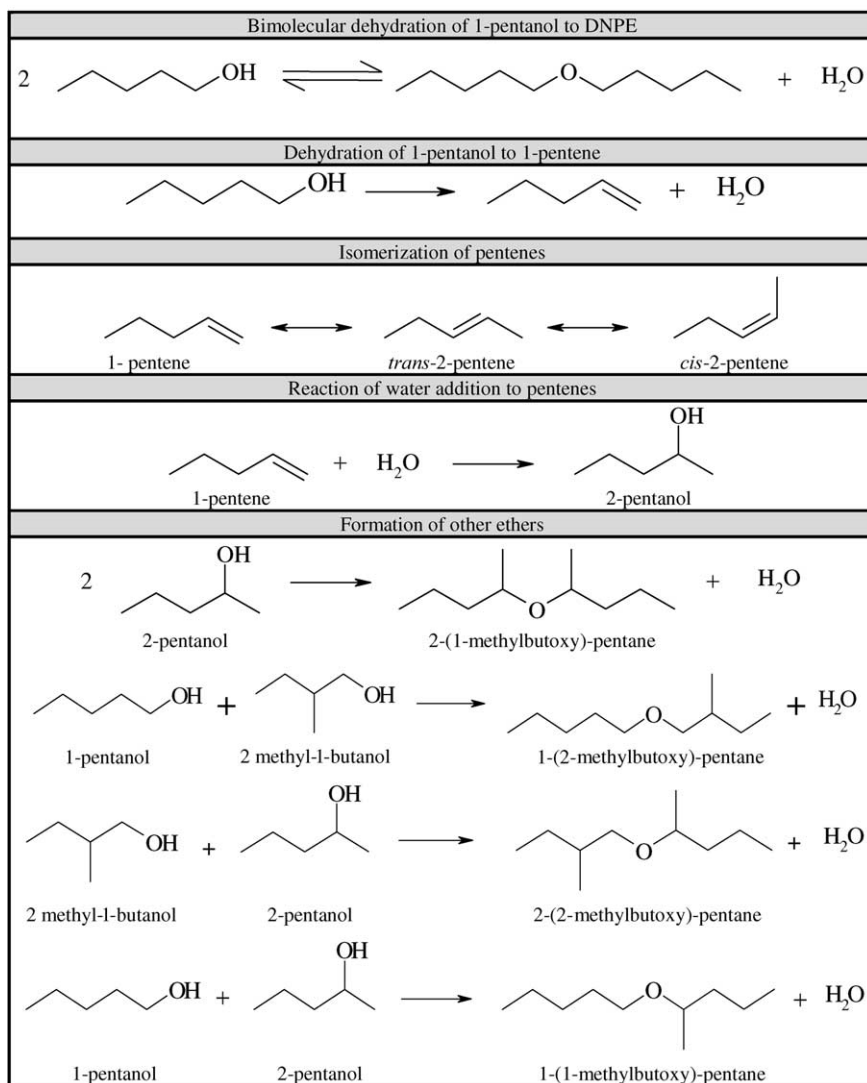


Fig. 3. Scheme reaction.

Table 4

Conversion of 1-pentanol, selectivity to DNPE, yield to DNPE, initial reaction rate of DNPE synthesis on tested catalysts at 150 °C

Catalyst	X (%)	S _{DNPE} (%)	S _{ALKENES} (%)	S _{ETHERS} (%)	S _{ALCOHOLS} (%)	Y (%)	r _{DNPE} ⁰ (mol/h kg)	r _{DNPE} ⁰ (mol/h equiv.)
XN1010	29.2	86.4	7.72	5.28	0.59	25.2	4.38	1.28
A-35	34.2	63.4	22.7	12.4	1.53	21.7	6.16	1.16
A-15	39.8	70.5	16.8	11.54	1.21	28.0	6.91	1.44
K-2621-E	38.4	73.5	14.7	10.8	1.08	28.3	6.54	1.25
CT-151	46.9	80.2	10.1	8.87	0.87	37.6	8.78	1.58
CT-165	38.8	73.0	14.4	11.5	1.15	28.3	6.34	1.28
A-1500	43.3	89.2	6.20	3.93	0.66	38.6	9.06	1.74
A-1200	45.3	91.0	4.84	3.72	0.41	41.2	9.85	1.77
Dx8	43.9	89.1	7.27	3.26	0.39	39.0	7.29	1.51
CT-224	47.6	95.5	2.43	1.9	0.21	45.4	9.61	1.80
Dx4	46.9	94.1	3.62	1.61	0.22	44.1	9.56	1.85
Dx2	38.1	95.9	2.65	1.48	0.0	36.5	6.04	1.20
NR50	22.6	98.8	0.44	0.74	0.0	22.3	3.80	4.39

1-(1-methylbutoxy)-pentane. However, it should be pointed out that branched ethers could also be synthesized by the reaction between an alcohol and the appropriate olefin.

3.2. Conversion of 1-pentanol, selectivity to DNPE, and DNPE yield at 150 °C

Table 4 shows 1-pentanol conversion, selectivity to DNPE and byproducts, and yield of DNPE obtained at 6 h reaction time and 150 °C on the catalysts tested. As can be seen, gel resins are generally more active and selective than macroporous ones. Particularly, gel resins with 4% DVB. As for macroreticular resins, XN1010 is the least active but the most selective to DNPE. Data of CT-165 (gel-type) and those of A-15 and K-2621E (macroporous resins) are very similar. These resins have a very different pore structure, but specific volumes of swollen gel phase are very similar. Thus, we can assume that the reaction occurs mainly within the gel phase, and macro- and mesopores hardly contributes to the reaction. This is a well-established fact for reactions of dehydration of alcohol with generation of water; wherein gel phase swells because of the interaction of the alcohol and water with the resin.

Most S/DVB resins are quite selective to DNPE. The amount of alkenes, especially linear pentenes, and branched ethers, are generally quite similar, whereas that of pentanols are far smaller. This suggests that

branched ethers could be formed primarily by the reaction between pentanols and the appropriate alkene. As can be seen in Fig. 4, S_{DNPE} increases with V_{sp} reaching an almost constant value of about 95% with gel-type resins containing ≤4% DVB. Resins with low V_{sp} (A-35, A-15 and CT-165) are not much selective to DNPE. Fig. 1 shows that micropores in these resins lie in the densest polymer region. On the other hand, in resins with high V_{sp} (A-1200, Dx8, CT-224, Dx4 and Dx2) a part of pores lie in less dense polymer regions, and in the case of Dx2 all the pores lie in a region of low density. Therefore, S_{DNPE} increases as regions

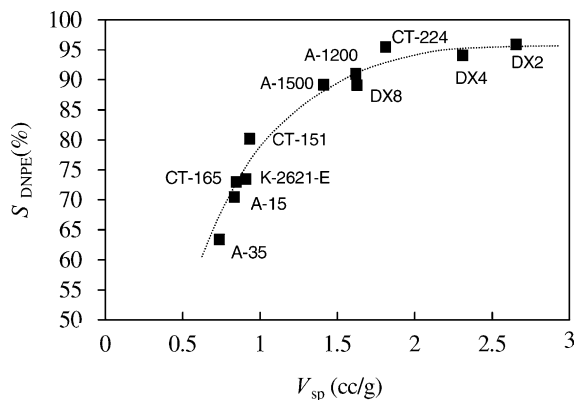


Fig. 4. Selectivity to DNPE at 150 °C as a function of the volume of the swollen polymer phase in water.

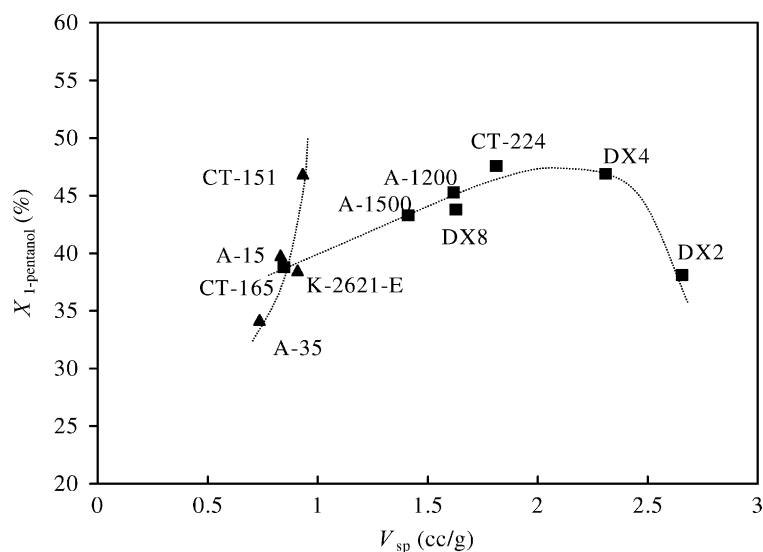


Fig. 5. Conversion of 1-pentanol at 150 °C as a function of the volume of the swollen polymer phase in water: (▲) macroreticular resins; (■) gel-type resins.

of low polymer density within gel phase are accessible. Resins with flexible swollen polymer phase and great V_{sp} values can accommodate better the reaction intermediate. In polymeric catalysts reaction mechanism involves the in situ formation of an oxonium ion, where the catalyst converts the hydroxyl group of the alcohol in a better leaving group by protonation. The ether is then formed by the nucleophilic attack of alcohol on the oxonium ion in a bimolecular reaction (S_N2 type) [9]. The dehydration to pentenes occurs through a monomolecular reaction of elimination (E_1 type). On little swollen polymer the S_N2 reaction is limited to a great extent by steric hindrance and the occurrence of the E_1 increases.

Fig. 5 shows the variation of 1-pentanol conversion with V_{sp} . As can be seen, conversions found on gel-type resins show a smooth maximum, indicating that gel resins able to swell moderately ($1.6 \leq V_{sp} \leq 2.3$) are suitable catalysts for obtaining DNPE. In these resins the fraction of swollen polymer is a sizeable part of the whole bead. Polymer chains are close enough so that the precise concentration (and orientation) of active sites to form the reaction intermediate is available. In the resin with the highest V_{sp} (Dx2), the polymer concentration of $0.4 \text{ nm}^3/\text{nm}^3$ of swollen gel phase corresponds to a greatly expanded polymer. In this

case, the probability of disposing the precise orientation of sulfonic groups to form the reaction intermediate lessens, and 1-pentanol conversion decreases. On the other hand, CT-165 is the gel resin with the lowest V_{sp} . In this case, polymer density of the swollen gel phase is very high, and the formation of reaction intermediate is hindered. Moreover, bead fraction swollen in the reaction medium is small. As a consequence, conversion of 1-pentanol is rather low.

Table 4 shows that the behavior of CT-224 and Dx4, both with 4% DVB is very similar despite CT-224 is an oversulfonated resin and Dx4 is sulfonated conventionally. This fact can be explained because a fraction of additional $-\text{SO}_3\text{H}$ groups gives place to a supplementary cross-linking by sulfone bridges tailoring a better environment for the reaction [11]. As a result, 1-pentene conversion on CT-224 is a bit higher than that of Dx4.

By comparing the conversions found with the macroreticular resins CT-151, A-15, K-2621E, and A-35 it is observed that X increases as V_{sp} increases. When these resins swell, spaces between polymer chains appear only in the densest fraction of gel phase (Fig. 1). It is likely that the increase in X would be due to the increase in volume of swollen polymer available for reaction. However, conversion on A-15

(sulfonated conventionally) is between those of A-35, K-2621E and CT-151 (oversulfonated resins). Therefore, oversulfonation do not give any advantage in the case of A-35, since it is less active and selective than A-15. In the case of CT-151, the same as CT-224, oversulfonation provides a better environment for the reaction. As a result, CT-151 is as active as CT-224, but less selective, since CT-224 is a more expanded polymer in swollen state.

As for XN1010, it is more selective but fewer active than the other macroreticular resins. ISEC shows that gel phase no swells in aqueous media. Gel phase is so stiff that catalysis takes place in the polymer surface (macro- and mesopores). Local concentration of sulfonic groups is there small, and to get the cluster of acid groups to form the reaction intermediate is difficult. Reaction rate is therefore low. Selectivity to DNPE is rather high because there is little steric hindrance to the formation of the ether on polymer surface.

NR50 is the most selective but the least active among catalyst tested. Nafion is a perfluorosulfonate resin whose morphology, in general terms, consists of 30–50 Å clusters of $-\text{SO}_3\text{H}$ -ended perfluoroalkylether side chains, the clusters being dispersed throughout a hydrophobic semicrystalline tetrafluoro-

roalkylether matrix [26]. It is a working hypothesis that polar molecules preferentially migrate to the nanometers-in-size clusters, where the reaction takes place. The perfluoroalkylether chains are flexible enough to accommodate the reaction intermediate so that selectivity to DNPE is very high. Conversion of 1-pentanol is rather low probably because the little concentration of sulfonic groups into the polymer matrix.

Finally, as can be seen in Table 4, Y_{DNPE} and X follow a similar trend.

3.3. Initial reaction rates for DNPE synthesis at 150 °C

Table 4 shows that S/DVB resins whose working phase is gel phase are more active than XN1010 and NR50. In Fig. 6, r_{DNPE}^0 is plotted against V_{sp} . As can be seen, resins able to swell moderately in the reaction medium with V_{sp} ranging from 0.93 to 2.3 cm^3/g are more active. However, a distinct behavior is observed between oversulfonated and conventionally sulfonated resins. Initial reaction rates on conventionally sulfonated resins increase gradually with V_{sp} reaching a maximum with Dx4. Oversulfonated resins show an unexpected increase in r_{DNPE}^0 on catalysts with low

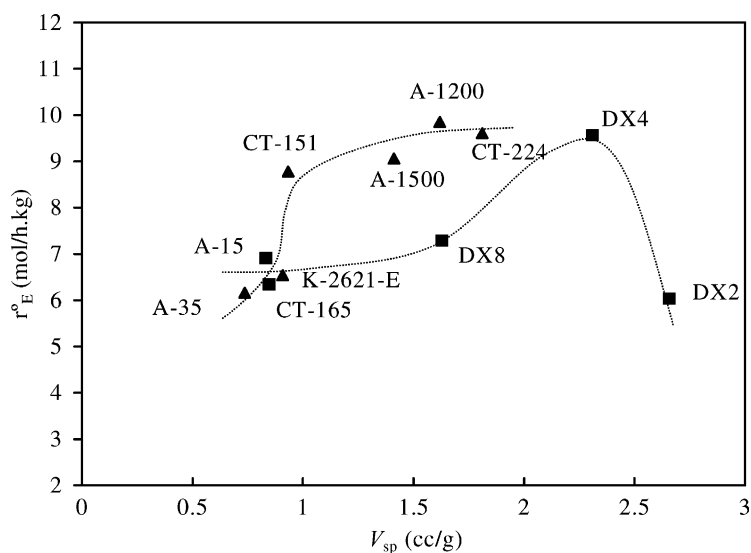


Fig. 6. Initial reaction rates of DNPE synthesis at 150 °C on a dry weight basis as a function of the volume of the swollen polymer phase in water: (▲) oversulfonated resins; (■) resins sulfonated conventionally.

V_{sp} (A-35, K-2621E) and a plateau on catalysts with V_{sp} ranging from 0.93 to 1.8 cm³/g (CT-151, A-1500, A-1200, and CT-224). It is to be noted that initial reaction rates of the last group are very similar to that of Dx4. Low r_{DNPE}^0 values were found on excessively stiff catalysts (narrow pores and low V_{sp}) and on Dx2 whose gel phase is greatly expanded in the reaction medium. In swollen state CT-151, A-1500 and A-1200, show pores mainly in the densest fraction of gel phase, whereas Dx8, CT-224, and Dx4 have pores in less dense fractions of gel phase as well. By comparing initial reaction rates on K-2621E, Dx8, CT-151, A-1200 and DT-224, we can assume that higher rates shown by CT-151, A-1200 and CT-224 are because they provide a better environment to accommodate the reaction intermediate. However, it is possible that little differences in acid site strength between oversulfonated and conventionally sulfonated resins could be also responsible for the differences in r_{DNPE}^0 (and X) measured [28].

As for XN1010, in this resin, whose working phase for catalysis is the macropores surface, the concentration of sulfonic acid groups is very low. As a result, initial reaction rate is clearly lower than those of the rest of S/DVB resins.

Initial reaction rate on NR50 is also very low. However, it is higher than expected by considering its

Table 5

Values of Hammett acidity function (H_0) of some catalysts [27]

Catalyst	$-H_0$
Sulfuric acid (100%)	12.3
Nafion	11–13
A-15	2.2

acid capacity; i.e. acid capacity of Dx4 and NR50 are 5.16 and 0.81 mequiv./g, respectively, but r_{DNPE}^0 on Dx4 is higher than that of NR50 by only 2.5 times. This fact could be explained by the especial morphology of Nafion resins. Concentration of $-SO_3H$ groups in polymer clusters is high enough to fit the reaction requirements, but initial reaction rate is low because the small number of clusters of sulfonic groups. In addition, the unexpected activity of NR50 could be due to the high acid strength of $-SOH$ groups in Nafion resins, which is considerably higher than that of S/DVB resins.

To stress the influence of acid side strength of catalyst on DNPE synthesis, initial reaction rates per equivalent of $-HSO_3$ group, r_{DNPE}^0 , were computed. As can be seen in Table 4, r_{DNPE}^0 of NR50 is far higher than those of S/DVB resins. The values of Hammett acidity function ($-H_0$) of Nafion and a conventional resin are shown in Table 5. It can be seen that although

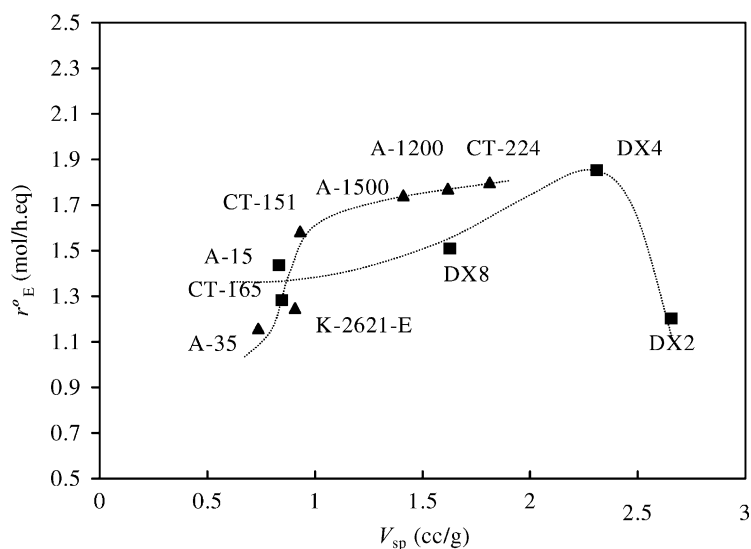


Fig. 7. Initial reaction rates of DNPE synthesis at 150°C/equiv. of sulfonic group, as a function of the volume of the swollen polymer phase in water: (▲) oversulfonated resins; (■) resins sulfonated conventionally.

Table 6

Conversion of 1-pentanol, selectivity to DNPE and initial reaction rates on NR50, CT-224, A-35, CT-165, XN1010, in the range of temperature explored

T (°C)		NR50	CT-224	A-35	CT-165	XN1010
110	X (%)		3.73	6.19	3.11	4.55
	S_{DNPE} (%)		100	93.9	91.7	95.4
	r_{DNPE}^0 (mol/h kg)		0.49	0.61	0.39	0.26
120	X (%)		9.21	12.2	7.82	8.04
	S_{DNPE} (%)		100	79.9	80.4	90.0
	r_{DNPE}^0 (mol/h kg)		1.52	1.34	0.90	0.46
130	X (%)	6.81	18.7	15.9	11.3	11.9
	S_{DNPE} (%)	99.0	99.2	76.8	88.6	84.8
	r_{DNPE}^0 (mol/h kg)	0.94	3.30	1.90	1.50	0.8
140	X (%)		25.7	27.1	19.3	
	S_{DNPE} (%)		98.6	77.8	80.2	
	r_{DNPE}^0 (mol/h kg)		5.81	4.58	2.51	
150	X (%)	22.6	47.6	34.0	38.8	29.2
	S_{DNPE} (%)	98.8	95.5	63.4	73.0	86.4
	r_{DNPE}^0 (mol/h kg)	3.8	9.61	6.16	6.34	4.38
160	X (%)	39.0				
	S_{DNPE} (%)	98.4				
	r_{DNPE}^0 (mol/h kg)	9.18				
170	X (%)	54.6				
	S_{DNPE} (%)	96.9				
	r_{DNPE}^0 (mol/h kg)	14.4				
180	X (%)	83.5				
	S_{DNPE} (%)	95.0				
	r_{DNPE}^0 (mol/h kg)	25.3				

Nafion is not a super-acid, its acid strength is greatly higher than that of A-15. This fact suggests that acid site strength is indeed an important factor for this reaction so that in the case of NR50 acid strength balances and, partially, overcome the effect of the very low acid capacity. Its higher acid strength, in relation to S/DVB resins, is due to the electronegativity of F atoms in the fluoroalkane polymeric chains.

As for S/DVB resins, r_{DNPE}^0 on XN1010, A-35 and K-2621E are similar (Table 4). This fact suggests that all the sulfonic groups of these resins are accessible and take part in the reaction. Since the other S/DVB resins swells in liquid phase more than A-35, XN1010 and K-2621E, we can assume that all sites are equally accessible. As a result, the differences in r_{DNPE}^0 observed in Fig. 7, particularly between over-sulfonated and conventionally sulfonated resins, could be due to the different acid site strength of S/DVB resins.

3.4. The effect of temperature

XN1010, A-15, A-35, K-2621E, CT-165, CT-224 and NR50 were tested at different temperatures. As can be seen in Table 6, 1-pentanol conversion increases with temperature as expected, whereas S_{DNPE} decreases. This fact suggests that dehydration to alkenes is more sensitive to temperature than DNPE synthesis. It is to be noted the very high S_{DNPE} found on CT-224 and especially on NR50 in the whole range of temperatures. Apparent activation energies for DNPE synthesis, E_{app} , computed from the variation of r_{DNPE}^0 with temperature are witnessed in Table 7. As can be seen, all the catalysts have E_{app} values of the same order of magnitude backing up the assumption that the reaction mechanism is essentially the same on all the catalysts. However, E_{app} for A-35 and A-15 (the most rigid polymers among the group of seven catalysts) are a bit lower, within the limits of the ex-

Table 7
Apparent activation energies for DNPE synthesis

Catalysts	E_{app} (kJ/mol)
XN1010	97 ± 8
A-35	81 ± 7
A-15	86 ± 11
CT-165	97 ± 6
K-2621E	98 ± 4
CT-224	99 ± 8
NR50	101 ± 4

perimental error. Table 7 also shows that within the limits of the experimental error, E_{app} increases with V_{sp} , what suggests that in stiffer resins reaction rates could be slightly influenced by internal mass transfer. However, this point needs further experimental work.

4. Conclusions

Sulfonic S/DVB resins are suitable catalysts for de-hydration reaction of 1-pentanol to DNPE. Gel-type resins able to swell moderately in the reaction medium, such as CT-224, are more active and selective even at temperatures as high as 150 °C. This is currently the maximum operating temperature according to manufacturers. Therefore, to improve thermal stability of these resins is a very important matter in order that industrial use of S/DVB resins to produce DNPE is economically attractive in the future. NR50 has a very high thermal stability so that operations up to 200 °C are allowed without stability problems. At 180 °C, it shows a very high selectivity to DNPE (about 95%) and a very interesting activity. However, it is too much expensive for industrial use, especially if we take into account that DNPE would become a commodity rather than a fine chemical.

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