Etherification of glycerol with ethanol over solid acid catalysts

Stephane Pariente, Nathalie Tanchoux and François Fajula*

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Different types of acidic heterogeneous catalysts, including sulfonic resins, zeolites and grafted silicas are used for the synthesis of mono-ethers of glycerol using ethanol as the alcohol. The study shows that the performances of the catalysts are governed by both the acidity and the polarity of their surface. Materials with strong hydrophobic character are not active as they do not allow the adsorption of the glycerol. On the other hand a strong adsorption of glycerol on the polar surfaces leads to low activity as well. The best compromise has been found by using sulfonic-acid polystyrene resins of the Amberlyst family and zeolites with intermediate aluminium contents.

Introduction

Current development of the production of biodiesel from vegetable oil leads to a dramatic increase of the availability of its co-product, glycerol.[1,2,3] In order to ensure the viability of the biodiesel activity there is the necessity not only to upgrade but also to find new large-scale uses of glycerol. Several recent reviews.[1],[4–7] describe upgrading strategies towards fine speciality and bulk chemicals for different industry segments. With regard to the chemistry of glycerol upgrading, these reviews point to several difficulties in developing selective conversion processes associated with the presence of 3 OH groups with identical pK_a, a high viscosity and a high hydrophilicity. Recently, it was shown that glycerol could be selectively transformed into monoalkyl glyceryl ethers (MAGEs) by using acid heterogeneous catalysts[6] MAGEs are interesting intermediates for the production of a variety of chemicals, among which dioxolanes.[8] With the objective of introducing new large-scale processes based on glycerol transformation, dioxanes and dioxolanes can be interesting targets as they constitute excellent candidates to be used as co-fuels for the diesel fraction. Several studies have demonstrated that oxygenates blended with diesel fuel decrease the level of emission of particles and contribute to the reduction of the NO_x produced.[8–12] Among the oxygenates investigated, dioxolanes containing 6–8 carbon atoms in their skeleton revealed to be excellent blends.[13], being compatible with the diesel fuel and featuring a high oxygen molar content with no pending OH group (the latter should be avoided to prevent storage problems). Dioxolanes can readily be obtained from MAGEs by reaction with a carbonyl-group containing substrate, under mild conditions[14]

On the basis of these considerations we have undertaken a study aiming at the exploration of catalytic routes able to produce dioxolanes from glycerol, using a sustainable technology, *i.e.* relying on green processes and compatible with a fuel production (Scheme 1). Owing to its advantages in terms of product recovery, catalyst recycle, waste production and more generally speaking, process operation, a heterogeneous catalytic system has been selected. As the alcohol for the etherification step, keeping in mind a route as green as possible, we have selected ethanol because of its safety and its possible production from biomass fermentation.[15] Selective mono-etherification of glycerol with aliphatic ethers has not been reported yet and seems a demanding process.[6] The reaction is nevertheless of great interest as it could provide the possibility to incorporate bio (agro) ethanol to diesel fuels (the most used fuel in Europe). Moreover, ethanol can be easily dehydrogenated into acetaldehyde (Scheme 1, path 2) and thus provide the carbonyl component for the dioxolane production in the final step (Scheme 1, path 4).

This paper presents the results obtained in our investigations of the first step of the foreseen process (Scheme 1, path 1), namely the preparation of monoethyl glyceryl ethers by reaction of glycerol with ethanol over a series of solid acid catalysts. More precisely our efforts have been dedicated to the selection of a suitable catalyst and to the analysis of the influences of the physico-chemical properties of such catalyst and of the experimental conditions on the reaction.

Experimental section

Catalysts

Resins and zeolites. All the catalysts used in this study, except the grafted silicas (see below) are commercial materials.

Two macroreticular sulfonic resins Amberlyst A15 (4.7 meq $H^+ g^{-1}$, $H_0 = -2.2^{16}$) and A35 (5.2 meq $H^+ g^{-1}$, $H_0 = -2.2^{16}$) were provided by Rohm and Haas. A15 was received in dry form and used as received. A35 was washed with methanol then stored in an oven at 383 K overnight. Nafion NR50 (a hydrophobic strongly acidic macroporous perfluorinated resin-sulfonic acid, 0.81 meq $H^+ g^{-1}$, $H_0 = -11^{16}$) was purchased from Aldrich. NR50 was used as received.

The zeolite samples have been obtained from Zeolyst International. Their main characteristics are listed in Table 1.

Institut Charles Gerhardt, UMR 5253 CNRS/ENSCM/Ufile://ream/WamDocuments/Journals/GC/B905405GM2/UM1, Matériaux Avancés pour la Catalyse et la Santé (MACS), Ecole Nationale Supérieure de Chimie, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France. E-mail: francois.fajula@enscm.fr; Fax: +33 467 163 470; Tel: +33 467 163 478

Table 1 Properties of the different commercial zeolites

Commercial name	Structure type	Catalyst sample	Si/Al	Main pore openings/Å
CP 814 E	BEA	BEA 12.5	12.5	6.6 × 6.7
CP 814 C		BEA 19	19	
CP 814 Q		BEA 25	25	
CP 811		BEA 75	75	
CBV 3024 E	MFI	MFI 25	25	5.1 × 5.5
CBV 5524 G		MFI 15	15	
CBV 10 A	MOR	MOR 6.5	6.5	6.5 × 7
CBV 21 A		MOR 10	10	
CBV 90 A		MOR 45	45	
CBV 600	FAU	FAU 2.6	2.6	7.4 × 7.4
CBV 780		FAU 40	40	

Grafted silica. The grafted silica catalyst was prepared according to the procedure described by Melero *et al.*[17] using a Grace Davison silica (G5H) support. The G5H material is a mesoporous silica with a very narrow pore size distribution centred around 16 nm and a surface area of 513 m^2 g^{-1}. Two grams of silica are outgassed at 423 K for 12 h under vacuum in a 250 mL glass flask. After cooling, 30 mL of anhydrous toluene are added to the silica as well as 2.77 g (8.5 meq, corresponding to 5 mol mm^{-2}) of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) as grafting species. After 30 min of slow magnetic stirring, 153 µL of water are introduced in the reaction medium in order to hydrolyse the $–SO_2Cl$ groups and the $(CH_3O)_3Si–$ moieties of the CSPTMS, in the presence of 15.5 mg of NH_4F acting as the catalyst for the condensation. Magnetic stirring is maintained for 1 h at room temperature, then at 333 K for 6 h and finally for 1 h at 393 K in order to complete the condensation (thermal condensation). The resulting product is washed with toluene, with a mixture of water and methanol (50/50), with pure methanol twice, with diethyl ether and then washed in a soxhlet reactor (solvent: dichloromethane/diethylether 1/1) for 8 h.

The catalyst is then characterized by adsorption/desorption of N_2 at 77 K and by TGA to access the numbers of grafted species.

The grafted material exhibits a surface area of 280 m^2 g^{-1}, with a pore size distribution centered at 14 nm. The amount of organic matter grafted (A_M) has been determined by TGA analysis:

$$A_M = \frac{(\%G/M_G)N_A}{100 - [M_{Gr}(\%G/M_G)] - [\%H_2O/18]}$$

where:

•%H_2O and %G are respectively the mass losses in H_2O and organic grafted species given by the TGA analysis.

•M_G is the molar mass of the grafted species eliminated during the TGA analysis (except for the silica atom from the CSPTMS at the surface of the material).

•N_A is the Avogadro number.

•M_{Gr} is the molar mass of the grafted chain which is equivalent to the molar mass of the silica alone and of the grafted one.

This treatment led to an amount of grafted sulfonic groups corresponding to 0.15 meq H^+ g^{-1}.

Part of the functionalized silica was then passivated. This reaction consists of the exchange of the silanol surface groups with $SiMe_3$ groups which will lead to a hydrophobisation of the surface. One gram of functionalized silica is outgassed in a glass reactor at 393 K under vacuum and magnetic stirring for 12 h. 20 mL of toluene which will act as the solvent and an excess of N,O-bis(trimethylsilyl)trifluoroacetamide (2 mL) is introduced. The reaction medium is then stirred at 333 K for 12 h in order to achieve the largest replacement of silanol groups by $SiMe_3$. The solution is then filtered and the silica is washed with toluene, methanol, dichloromethane and diethyl ether before being oven dried in air at 323 K. Finally, the material is washed in a soxhlet reactor with a mixture of diethyl ether/dichloromethane for 8 h.

Catalyst characterisation

The textural properties of the zeolite samples and of the sulfonic acid-modified silicas have been determined from the nitrogen adsorption–desorption isotherms recorded at 77 K using a Micromeritics ASAP 2010 automatic analyzer. Specific surface areas were calculated by the BET method and external surface areas (in fact the external surface of the zeolite grains plus that of the mesopores generated by the dealumination treatment—zeolite dealumination results in the creation of mesopores with a broad distribution of sizes which favors diffusion of reactants and products in the zeolite grains—the generation of this secondary mesoporosity leads to an increase of the mono-multi layer domain in the adsorption isotherm which is equivalent to the creation of an external surface) were calculated using the t-plot method.[18] Prior to nitrogen adsorption, the samples were outgassed for 8 h at 523 K.

The thermal analyses (TG and DTG) were carried out using a Netzsch TG 209 device equipped with a programmable temperature furnace. The sample (20 mg) was heated from room temperature to 1173 K under air flow at 10 K min^{-1}.

The acidity of the catalysts was determined by temperature-programmed desorption (TPD) of NH_3. The measurements were carried out using a Micromeritics Autochem model 2910 instrument equipped with a programmable temperature furnace and a TCD detector. Fresh calcined samples (100 mg) were pretreated under air flow at 823 K before adsorption of the probe molecules at 373 K. During desorption, the sample was heated under a helium flow (30 mL min^{-1}) at a ramp of 10 K min^{-1}. The amount of probe molecules desorbed from the samples was calculated from the area under the peak corresponding to the TCD responses.

Reaction procedure

Ethanol (99% purity) was used as a reagent and as the solvent in all experiments. Except otherwise specified (*e.g.* Table 2) the composition of the reaction mixture was 8.5 g of glycerol (0.092 mol–1.65 mol L^{-1}) for 39 g of ethanol (0.848 mol–15.13 mol L^{-1}) that is, a 9 : 1 ethanol : glycerol molar ratio, and a constant loading of 0.3 g of catalyst. Catalytic runs were performed at temperatures ranging from 373 to 473 K under autogenic pressure (6 to 21 bar) in a stainless steel reactor of 100 mL stirred at 600 rpm by a mechanic stirrer. The reaction temperature was controlled using a thermocouple immersed in

Table 2 Conversion and selectivity obtained with the acidic resin catalysts[a]

	Co-feed/mol L^{-1}				Selectivity (%)		
Catalyst	DEE	$H_2$0	Temperature/K	Conversion of glycerol (%)	ME	DE	DEE production/mol L^{-1}
A-15	—	—	393	0	0	0	0.5
A-15	—		413	0	0	0	0.7
A-15	—	—	433	32	100	—	1.5
A-15	1.2	—	433	32	100	—	—
A-15	2.4	—	433	32	100	—	—
A-15	—	1.87	433	32	100	—	1.5
A-15	—	2.82	433	32	100	—	1.5
A-15	—	3.75	433	21	100	—	1.5
A-35	—	—	433	52	90	10	2
NR-50	—	—	373	0	—	—	0.5
NR-50	—	—	433	0	—	—	2.4

[a] $m_{\text{cata}} = 0.3$ g, EtOH = 0.848 mol (15.13 mol L^{-1}), glycerol = 0.092 mol (1.65 mol L^{-1}), reaction time = 6 h.

the reaction mixture. The evolution of the composition of the reaction medium as a function of time was monitored between 30 min and 10 h using A-15 and BEA-12.5 as catalysts. For these two series of experiments a fresh sample of catalyst was used for each reaction time.

Reaction media were analyzed by gas chromatography (GC; Varian 3900 chromatograph) using a BP20 (SGE) capillary column [30 m × 0.32 mm, film thickness = 0.25 μm] and a flame ionization detector. Decane was used as an external standard.

Results and discussion

Acidic resins

Fig. 1 reports the evolution of the composition of the reaction medium as a function of time for an experiment performed at 433 K using A-15 as catalyst. Two parallel etherification reactions are observed leading, on the one hand, to the production of the glycerol monoethoxy ethers (ME, 3 : 1 mixture of 3-ethoxy-1,2-propanediol and 2-ethoxy-1,3-propanediol) and, at higher conversion (*ca.* ≥ 40% glycerol transformation) of the glycerol diethoxy ethers (DE, 3 : 1 mixture of 1,3-diethoxy-2-propanol and 1,2-diethoxy-3-propanol) (Scheme 1, paths 1 and 3) and, on the other hand to the formation of diethylether (DEE) *via* ethanol dehydration (Scheme 2). The ratio between the two isomers of the monoethoxy- and of the diethoxy-glycerol ethers was barely modified in the various runs. Therefore in the following each mixture will be considered as a single component.

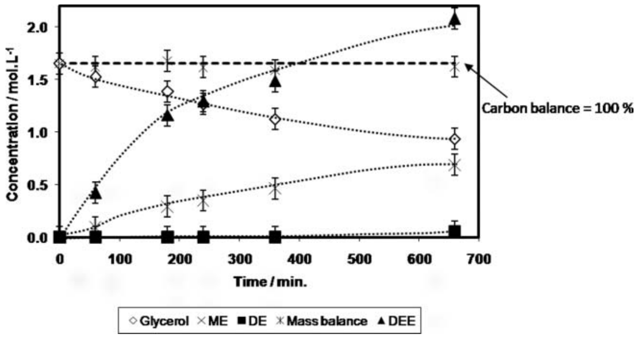
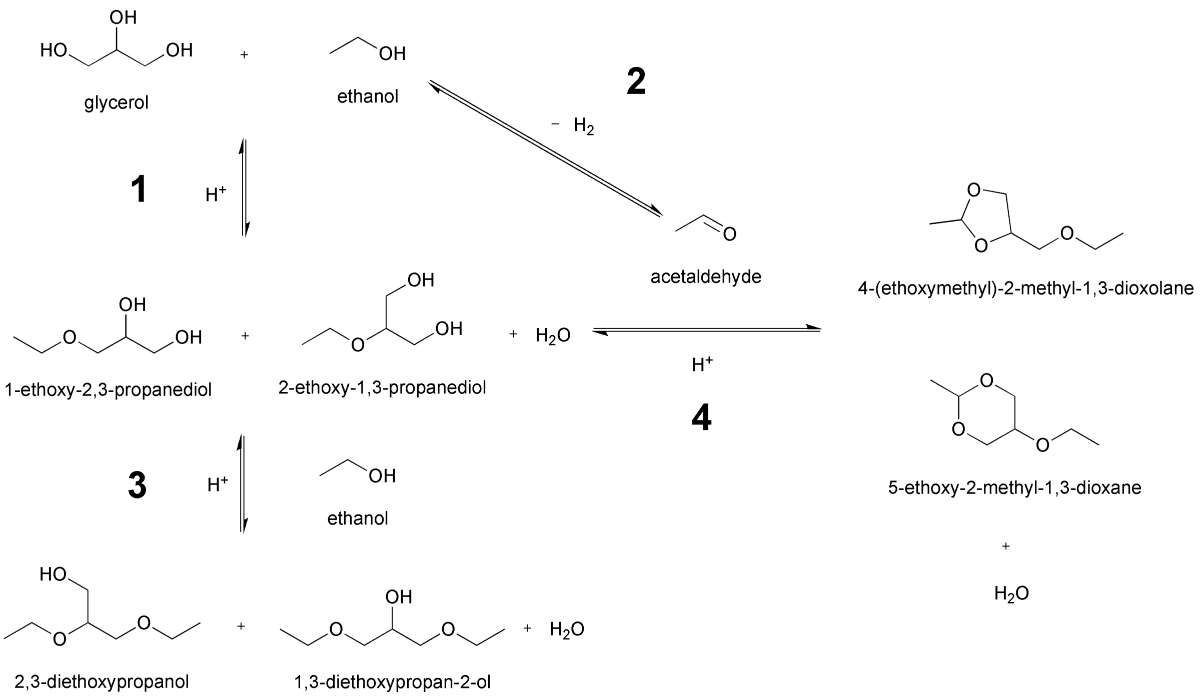


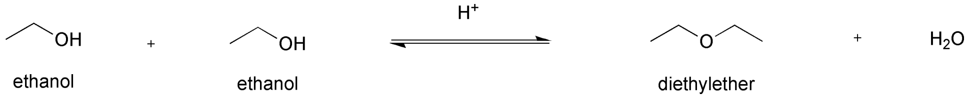
Fig. 1 Evolution of the concentration of the different products during the reaction ($T = 433$ K, $p = 12$ bar, catalyst = A15).

Under the conditions of the test, due to the large excess of ethanol in the medium, the formation of DEE was the main process (Scheme 2). The formation of DEE did not affect however the reaction of etherification of glycerol as it will be shown below. Triethoxy propane and oligomerization products were not detected in the reaction products. Because such products could have been formed but not desorbed from the catalyst, material balances based on the carbon content in the unconverted glycerol and in the glycerol ethers were systematically calculated. The data in Fig. 1, and the good material balances obtained, definitely show that ME and DE are the only products resulting from the etherification of glycerol, even after 10 h of reaction.

The results obtained after 6 hours reaction over the sulfonic-acid resin catalysts are reported in Table 2. With the Amberlyst A-15 resin, no glycerol etherification is observed below a temperature of 433 K while the catalyst is active for DEE formation at a temperature 60 K lower. This indicates that glycerol etherification is a more demanding process, under the reaction conditions, than formation of diethylether. The addition of DEE to the feed had no influence on the glycerol conversion. The same is true when water is introduced in amounts nearly equivalent to those of glycerol. This result is of interest as it shows that the use of rough agro-ethanol and glycerol can be tolerated in such a process. However, in the presence of a larger amount of water (corresponding to 3.75 mol L^{-1}), the conversion of glycerol decreases while the production of DEE is unaffected, suggesting that water poisons the stronger sites, those responsible for glycerol adsorption and reaction. In line with its higher density of sites, A-35 proves more active than A-15 for the two etherification reactions. However, from the results obtained with the Nafion NR-50 catalyst it is clear that the acidity of the catalysts, both in terms of number and strength, is not the only parameter determining the activity of the catalysts for the etherification of glycerol. Actually, NR-50 does not show any activity for the glycerol conversion, even at a temperature of 473 K. By contrast, the activity of NR-50 for the formation of DEE is significantly higher than that of the other resin catalysts. This suggests that the two etherification processes are governed by different parameters. Ethanol (dielectric constant $€_0 = 25$) can be readily etherified on any type of acidic surface while the hydrophobic character



Scheme 1 Overall reaction network for the production of dioxolanes from glycerol and ethanol.



Scheme 2 Diethylether formation by ethanol dehydration.

of the Nafion resin prevents the adsorption of the highly polar (dielectric constant €$_0$ = 42.5) and hydrophilic glycerol molecule, and does not allow its activation by the acid sites.

Sulfonic-acid grafted silicas

Sulfonic-acid grafted silicas have demonstrated high activity and selectivity at temperatures below 373 K for the etherification of glycerol with a series of alkylaromatic and allylic alcohols but proved inactive with aliphatic alcohols at these temperatures[6]. As shown in Table 3, the only reaction observed at 433 K was the etherification of ethanol into DEE while at 473K a high conversion of glycerol was obtained, confirming that glycerol etherification is a more difficult reaction than ethanol etherification. The passivation of the surface of the grafted silica by SiMe$_3$ groups, which confers a hydrophobic character to the surface[19,20], led to a significant decrease of the catalyst activity, more pronounced for the glycerol etherification than for the formation of DEE. This finding is in line with the conclusion reached above in the case of the acidic resins.

Zeolites

The acidity and textural characteristics of the zeolite catalysts and their activity in the target reaction are summarized in Table 4. The catalysts demonstrated marginal or no activity at temperatures below 473 K. Under the conditions applied ME was obtained selectively for glycerol conversions lower than 20%. The results confirm that formation of DEE and glycerol etherification result from two parallel processes since large differences in the glycerol conversion are observed while the production of DEE was nearly constant in all runs, amounting to 2.6 ± 1.5 mol L^{-1} and corresponding to 15–20% conversion of ethanol into DEE. As in the case of the A15 catalysts, the only

Table 3 Conversion and selectivity observed with the sulfonic-grafted silica catalysts[a]

			Selectivity (%)		
Catalyst	Temperature/K	Conversion of glycerol (%)	ME	DE	DEE production/mol L^{-1}
Grafted silica	433	—	—	—	1.5
Grafted silica	473	68	75	25	2.5
Passivated grafted	473	20	100	—	1.8

[a] m_{cata} = 0,3 g, EtOH = 0.848 mol (15.13 mol L^{-1}), glycerol = 0.092 mol (1.65 mol L^{-1}), reaction time = 6 h.

Table 4 Acidity, textural properties and activity of the zeolite catalysts[a]

Exp.	Catalyst	Acidity/ mmol.g^{-1}	Surface area/m^2 g^{-1}	External surface/m^2 g^{-1}	Conversion of glycerol (%)	Selectivity (%)		DEE production/ mol L^{-1}
						ME	DE	
1	MOR 6.5	1.25	425	27	< 2	100	—	2.8
2	MOR 10	0.95	500	44	< 2	100	—	3.0
3	MOR 45	0.47	500	56	25	85	15	2.45
4	FAU 2.6	1.9	730	66	< 5	100	—	3.1
5	FAU 40	0.53	780	113	< 5	100	—	2.4
6	MFI 25	0.9	400	131	41	80	20	3.8
7	MFI 15	1.4	425	105	44	80	20	4.1
8	BEA 12.5	1.4	680	221	54	75	25	2.9
9	BEA 19	0.88	710	207	47	75	25	3.05
10	BEA 25	0.84	730	211	57	75	25	3.1
11	BEA 75	0.47	720	217	17	90	10	1.3

[a] Temperature = 473 K, m_{cata} = 0.3 g, EtOH = 0.848 mol (15.13 mol L^{-1}), glycerol = 0.092 mol (1.65 mol L^{-1}), reaction time = 6 h.

products detected were DEE, ME and DE and 100% carbon balance were achieved even after 10 h of reaction.

From the data of Table 4, no unique relationship between the catalytic activity and the structure type, the textural or the acidity characteristics of the zeolite catalyst can be drawn. The most direct parameter to be considered, namely the structural type, which determines the size of the micropores[21], cannot be considered as relevant since MFI-type catalysts (exp. 6 and 7) with the smallest pore sizes of the series feature a higher activity than the MOR (exp. 1, 2 and 3) and FAU-type (exp. 4 and 5) catalysts.

The same is true for the textural characteristics. The presence of mesopores or large external surface areas—which should favor the access to the active sites——does not seem to constitute neither a key parameter (compare exp. 5, 7 and 11). It seems therefore clear that only a fraction of acid sites are actually involved in the catalytic process, probably on account of diffusion limitations in the microporous networks due to the high viscosity of glycerol. The absence of any structure effect on activity is reinforced by the unique correlations found between selectivity and conversion (Fig. 2) at the two temperatures of 433 and 473 K. Regardless of the nature of the catalysts surfaces and of their textural characteristics, all the materials studied behave similarly and the selectivity is only determined by the conversion, at a given temperature.

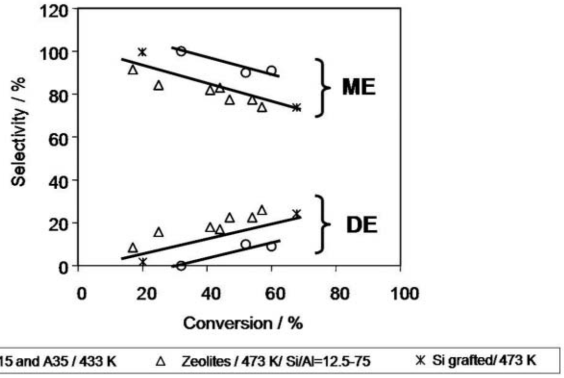


Fig. 2 Selectivity *versus* conversion for all the catalysts at different temperatures.

The influence of the zeolite composition on the activity of the catalysts proves more complex. Materials with the highest contents of acidic sites prove either inactive or highly active (compare for instance exp. 1, 4, 7 and 8). With regards to the strength of the zeolite acid sites, which is expected to increase when the aluminium content decreases in the case of the FAU catalysts (exp. 4 and 5)[22], no positive influence is noticed as well, as it was the case when comparing the performance of Amberlyst and Nafion. However, it is well known that the composition of a zeolite, namely its aluminium content, determines both the acidity and the polarity of the surface. High aluminium contents generate a high density of acid sites and a high polarity of the surface.[22,23] Although not all acid sites of the catalysts are involved in the reaction, as we have seen above, a specific activity of the different zeolite catalysts (expressed as a turn over number, TON, or number of glycerol molecules converted per acid site in 6 hours) has been calculated. The only assumption made for such a calculation is that the number of sites actually involved in the reaction is proportional to the total number of acid sites of the zeolite. The result of the calculation is shown in Fig. 3 where the TON of the 10 zeolite catalysts is plotted as a function of their aluminium content.

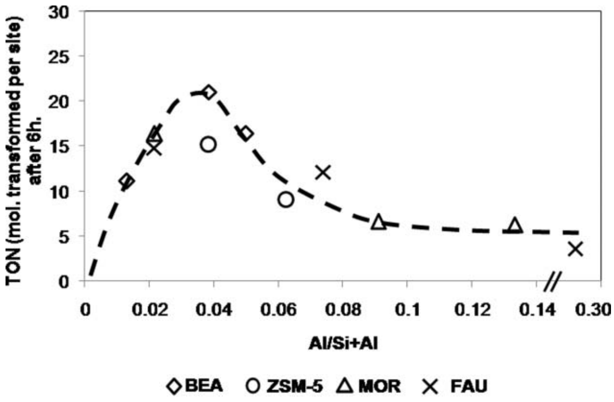


Fig. 3 Turn Over Numbers (TON, moles of glycerol converted site) after 6 h of reaction over zeolite catalysts as a function of their aluminium content (T = 473 K, p = 21 bar).

The bell shape of the curve is typical for the occurrence of a compensation effect resulting from the influences of the acidity and of the hydrophobicity of the catalyst surface on activity. At low aluminium contents, the reaction is limited by both the weak acidity (low density of sites) and the high hydrophobicity. When the Al fraction increases the surface becomes less hydrophobic, allowing glycerol adsorption, and the acid sites promote its activation up to a point, at ca Al/Al + Si = 0.04 (or Si/Al = 25) where the increase of the number of acid sites is balanced by the strong adsorption of glycerol due to a higher polarity of the surface. A further increase of the aluminium content, and of the density of acid sites, results in a continuous decrease of the activity, the process being limited by the hydrophilic character of the zeolites.

Catalyst reuse

Fig. 4 depicts the results of consecutive catalytic runs performed by reusing the A-15 and BEA 12.5 catalysts under the optimal reaction conditions defined in this study. After each catalytic run, the catalyst was recovered by filtration, washed with ethanol at room temperature and then dried in an oven at 383 K overnight before being used again in a new reaction. From the results shown, with the A-15 catalyst, no loss of catalytic performance is observed after three catalytic cycles. For the BEA 12.5 catalyst, a loss of activity, corresponding to a decrease of about 25% of the glycerol conversion, is observed, along with an increase of the selectivity in ME, in line with the change in conversion (see Fig. 2). In order to achieve full regeneration of the zeolite, we performed a calcination at 823 K for 8 h. After this treatment, the activity of the fresh zeolite was fully recovered. It can be thus concluded that the reaction medium and the experimental conditions applied do not damage the catalyst during the reaction, making possible their use in continuous processes.

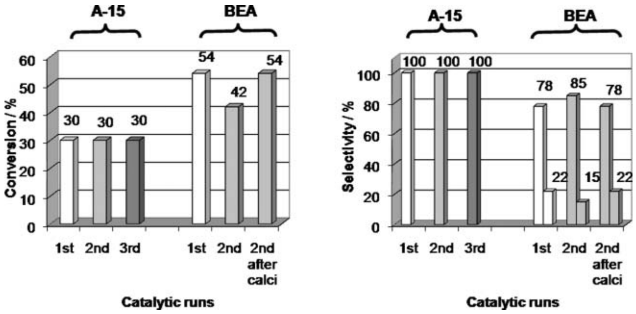


Fig. 4 Catalyst reuse: glycerol conversion and selectivity to ME and DE after 6 h of reaction in successive runs.

Conclusions

The etherification of glycerol with ethanol has been investigated over a series of solid acid catalysts with the aim of producing selectively mono ethers. Depending on the nature of the catalyst, the reaction temperature stands in the range 433–473 K. Under these conditions etherification of ethanol into diethyl ether proceeds to a large extent but the presence of DEE in the medium does not affect the transformation of glycerol. The activity of the catalysts for the etherification of glycerol is governed by both the acidity and the polarity of their surface. Regardless of the density and strength of the acid sites, materials featuring hydrophobic character are not active as they do not allow the adsorption of the glycerol. On the other hand a too strong adsorption of glycerol on the polar surface of zeolites with high aluminium contents leads to low activity as well. The best compromise has been found by using sulfonic acid polystyrene resins of the Amberlyst family and zeolites with intermediate aluminium contents, corresponding to Si/Al ratios around 25. With the Amberlyst resin, monoethoxy glyceryl ethers are selectively produced up to a glycerol conversion of *ca.* 40% at a temperature of 433 K. Zeolites are active at higher temperature, at 473 K, and prove less selective. Though significant, this difference of activity and productivity between the two families of catalysts could be well counterbalanced by the benefits gained by the use of a catalyst with improved thermal and mechanical stability. On-going studies on process development should decide which type of material is the most adapted. Finally, the reaction tolerates the presence of significant amounts of water. This result is of paramount importance for considering the future use of rough ethanol and glycerol as fuel components.

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