

Effect of the solvent in the liquid phase rearrangement of 1,2-epoxyoctane over Al-MCM-41 and Al-TS-1 catalysts

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Abstract

The role of solvent nature in the liquid phase rearrangement of 1,2-epoxyoctane over Al-TS-1 and Al-MCM-41 catalysts is reported. The main reaction product is the aldehyde, while other rearrangement products, mainly allylic alcohols and diol are obtained. The solvent polarity influences strongly on the activity and product selectivity. The catalytic activity decreases with the increasing of solvent polarity especially for Al-MCM-41 materials. The use of acetonitrile as solvent yields a low conversion of epoxide as a consequence of its basic character. Formation of bulky by-products was detected when dimethylcarbonate was used as solvent over Al-MCM-41. Toluene displays the best catalytic performance in regards to activity and selectivity towards valuable products, with both Al-TS-1 and Al-MCM-41 catalysts, in comparison to those obtained with more polar solvents.

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1. Introduction

Products formed by rearrangement of epoxides provide useful intermediates in organic synthesis. Pioneering works on epoxide rearrangement in liquid phase date from the 50 and most of them were carried out using homogeneous Lewis acid catalysts. Likewise, most of the substrates tested were highly reactive epoxides, such as cyclic alkane, alkyl aromatic and tertiary epoxides [1]. Catalytic rearrangement of epoxy compounds is catalyzed homogeneously by Lewis (e.g. ZnCl_2 , SnCl_2 or AlCl_3) or Brønsted (e.g. HF, HCl or HI) acid catalysts [2,3] and by strong bases (e.g. LiBr, LiI, LiClO_4 or lithium dialkylamides) [4]. Homogeneous acid-catalyzed epoxide rearrangements leads, usually to, ketones and aldehydes, but the use of strong non-nucleophilic bases as homogeneous catalysts yields allylic alcohols as main products [5].

Substitution of homogenous systems by alternative heterogeneous catalysts is of high interest because they can be separated from the product reused and they do not cause environmental and corrosion problems. The activity of metal oxides, mainly silica and alumina, metal sulfates, supported metals and a variety of precipitated phosphates has been tested in the catalytic rearrangement of aliphatic, cyclic or terpenic oxides [6]. Because of these conventional catalysts often result in low aldehyde selectivity, in the last years zeolitic materials have gained importance to catalyze this kind of processes. Their well-defined pore systems may suppress side reactions, as well as, prevent coking and thereby increasing catalyst lifetime. A number of zeolites, including HZSM-5, H-Beta, Mordenite, Y and X, have been tested in the rearrangement of aromatic or cyclic alkane epoxides as well as epoxides with tertiary carbons linked to the oxirane ring [7–10]. Some reports have been published on the use of zeolites as catalysts in the isomerization of small size aliphatic epoxides, such as ethylene and propylene oxides [11,12]. However, there is a clear lack of studies focused

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on the rearrangement of long straight-chain 1,2-alkane epoxides. It must be pointed out that this kind of epoxides are low reactive substrates, hence the isomerization to the corresponding aldehyde requires strong reaction conditions (high temperature, catalysts loading and reaction time), and therefore highly active catalysts [13,14].

These previous works prompted us to study the selective rearrangement of long straight-chain epoxides in liquid phase towards aldehydes over heterogeneous catalysts. Linear aldehydes can be oxidised towards the corresponding carboxylic acid or reduced to primary alcohols. Additionally, monounsaturated terminal alcohols can be also formed from the epoxide as interesting valuable by-products, which may be selectively hydrogenated to the corresponding linear alcohols. The commercial value of linear carboxylic acids, and particularly of their salts and esters, is mainly based on their synthetic utility. Much of them are used as intermediates for textile chemicals, dyes, drugs, plastics and agricultural chemicals. Industrially, the higher alcohols can be separated into plasticizers (C₆–C₁₁) and fatty alcohols (C₁₂–C₁₈) used for detergents. Likewise, aliphatic alcohols are applied as solvents and diluents for paints, intermediates in the manufacture of esters and in the preparation of a wide range of organic compounds.

Recently, we have investigated the catalytic rearrangement of 1,2-epoxyoctane in liquid phase over different acid solid catalysts [15], having a variety of acid properties and structural features, including different zeolites, amorphous and mesostructured materials. It was found that mesoporous materials present much higher activities per active site in comparison to those obtained with zeolitic materials, probably arising from its larger pore sizes, whereas acid sites in the amorphous materials show a poor catalytic activity. The main rearrangement products obtained with most of the catalysts tested were the aldehyde, allylic alcohols and diol. Zeolites enhance the formation of the aldehyde and/or octen-1-ols in comparison to the results obtained over amorphous materials. Thus, Al-TS-1 zeolite yielded high selectivity towards these valuable products reaching a value of 75%. Nevertheless, Al-containing mesostructured materials synthesized by a sol–gel method provided the highest selectivities to valuable products. In particular, Al-MCM-41 catalyzed the isomerization of 1,2-epoxyoctane with selectivities to octaldehyde and octen-1-ols of 40.6 and 44.7%, respectively.

The crucial role of solvent nature (polar–apolar, protic–aprotic, hydrophilic–hydrophobic, etc.) in liquid phase reactions is well known [16]. Therefore, the present work has been addressed to elucidate the influence of the solvent nature in the catalytic activity and product distribution for the liquid-phase rearrangement of long straight-chain epoxides over Al-containing zeolitic and mesostructured materials. In particular, the results obtained in the rearrangement of 1,2-epoxyoctane, chosen as a model molecule, over Al-TS-1 zeolite and Al-MCM-41 mesoporous material are discussed in regards to the role of different solvents conventionally used in these isomerization processes.

2. Experimental

2.1. Synthesis and characterization of catalysts

The catalysts used in this work were synthesized in our laboratory according to procedures published in literature.

Al-TS-1 zeolite was synthesized by hydrothermal crystallization of wetness impregnated SiO₂–TiO₂–Al₂O₃ xerogels. The amorphous Al₂O₃–TiO₂–SiO₂ mixed oxide used as raw materials for the Al-TS-1 synthesis was prepared following a two step sol–gel process described elsewhere [17]: (1) acid-catalyzed hydrolysis of the respective precursors (2) basic condensation with tetrapropylammonium hydroxide (TPAOH; Alfa). The resulting solid was wetness impregnated with aqueous 20 wt.% TPAOH solutions (1.6 g of TPAOH solution per 1 g of dried cogel). The crystallization of the incipient wet Al₂O₃–TiO₂–SiO₂ cogel was carried out in teflon-lined autoclaves under autogenous pressure and static conditions at 170 °C for 24 h. After this treatment, the solid product of the synthesis was separated by centrifugation, washed several times with distilled water and dried overnight at 110 °C. The calcination of the sample was carried out in air at 550 °C for 7 h.

Mesostructured Al-MCM-41 sample was prepared following a sol–gel approach at room temperature [18]. Two solutions were prepared under gentle stirring: solution A, formed by 20 g of tetraethylorthosilicate (TEOS; Alfa) and 0.7 g of aluminium isopropoxide (IPA; Aldrich); and solution B, formed by 36.5 g of hexadecyltrimethylammonium chloride (CTACl; Aldrich) and 6.6 g of hydrogen chloride. Once these solutions were perfectly homogenised, solution A was added to solution B and the mixture was stirred for 75 min. Thereafter, 54 g of a 2 wt.% aqueous ammonia solution were added dropwise and stirred for 1 h. The obtained sample was filtered, washed with deionized water and dried at 110 °C for 12 h. The final product was obtained by calcination in static air at 550 °C for 12 h.

The samples were characterized by different techniques. Crystallinity and purity of the zeolitic material as well as mesoscopic ordering were checked through X-Ray diffraction (XRD) patterns acquired with a Philips X'PERT MPD diffractometer using Cu K α radiation. The Si/Al atomic ratio of the samples was determined by induced coupled plasma-atomic emission spectroscopy (ICP-AES) with a Varian VISTA-AX apparatus. Nitrogen adsorption–desorption isotherms at 77 K of the calcined catalysts were obtained using a Micromeritics ASAP 2010 porosimeter. Previously, the samples were outgassed under vacuum at 200 °C for 5 h. The surface areas were determined according to the BET equation whereas the pore size distribution in the mesopore region was obtained applying the BJH method to the adsorption branch of the isotherm. The total pore volume was determined from the nitrogen adsorption at $p/p_0 = 0.99$.

The coordination of aluminum atoms within the catalysts was checked by ²⁷Al-MAS-NMR spectra of the cal-

Table 1
Physicochemical properties of the catalysts

Catalyst	Molar chemical composition	Pore diameter (Å)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^a	Acidity (mmol g ⁻¹) ^b	T _{max} (°C) ^b
Al-TS-1	Si/Al: 122, Si/Ti: 83	5.5	490	0.19	0.17	331
Al-MCM-41	Si/Al: 39	21	1087	0.68	0.28	275

^a Total pore volume measured at $p/p_0 = 0.99$.

^b Calculated from ammonia TPD measurements.

cined samples. The spectra were recorded at 104.26 MHz in a VARIAN Infinity 400 spectrometer at spinning frequency of 4 KHz. Intervals ranging from 5 to 30 s between successive accumulations were selected according to the structural nature of the sample. The external standard reference was [Al(H₂O)₆]⁺³ and all measurements were carried out at room temperature. The coordination of the titanium atoms in Al-TS-1 zeolite, as well as the possible presence of extraframework TiO₂ phases, was determined by means of DR UV–vis spectroscopy using a Varian Cary 500 spectrophotometer equipped with a diffuse reflectance accessory under ambient conditions.

The acid properties of the catalysts were determined by ammonia temperature programmed desorption (TPD) in a Micromeritics 2910 (TPD/TPR) equipment. Previously, the samples were outgassed under an helium flow (50 Nml min⁻¹) with a heating rate of 15 °C min⁻¹ up to 560 °C and kept at this temperature for 30 min. After cooling to 180 °C, an ammonia flow of 35 Nml min⁻¹ was passed through the sample for 30 min. The physisorbed ammonia was removed by flowing helium at 180 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550 °C with a heating rate of 15 °C min⁻¹, this temperature being kept for 30 min. The ammonia concentration in the effluent stream was measured through a thermal conductivity detector (TCD).

2.2. Catalytic experiments

The catalytic experiments were carried out at 120 °C in a 0.1 L stirred batch autoclave, equipped with a temperature controller and a pressure gauge, for different reaction times under stirring (550 rpm) and autogenous pressure. The reactor is also provided with a device to feed the epoxide once the reaction temperature is reached. The solvent and the catalyst are initially placed in the teflon-lined reactor. The zero time of the reaction is considered when the temperature reaches the set-point value and the epoxide is loaded into the reactor. The composition of the reaction mixture was as follows: 1 g of 1,2-epoxyoctane, 20 g of solvent and 40 mg or 400 mg of catalyst depending on its activity. The catalyst, prior to reaction, was dried overnight at 140 °C to remove adsorbed water.

The reaction products were analyzed with a VARIAN 3800 chromatograph equipped with a capillary column (HP-FFAP) with dimensions 60 mm × 0.32 mm, using a flame ionization detector (FID). Identification of the different reac-

tion products was performed by mass spectrometry (VARIAN SATURN 2000).

3. Results and discussion

The main physicochemical properties of the catalysts used in this work are summarized in Table 1. Al-TS-1 is a zeolitic material with both Lewis and Brønsted acid sites due to the simultaneous presence of titanium and aluminium atoms into the framework. It presents a well-defined three-dimensional pore system with a mean pore diameter around 5.5 Å. Characterization results of this sample depicted in Fig. 1 show a XRD pattern corresponding to a pure MFI zeolitic structure (Fig. 1a) and the type I isotherm typical of microporous materials (Fig. 1b). The XRD spectra of calcined Al-MCM-41 sample show only one reflection at low angles typical of 2D hexagonal symmetry (Fig. 1a). Nitrogen adsorption isotherm at 77 K of this sample shows a type IV isotherm in the IUPAC classification with a H1 hysteresis loop (Fig. 1b). Both characterization results confirm the mesoscopic ordering of the Al-MCM-41 material used as catalyst in this research.

The results obtained by ²⁷Al-MAS-NMR analysis indicate that calcined Al-MCM-41 shows two clear peaks centred at ~4 and ~50 ppm originated from octahedrally and tetrahedrally coordinated aluminium species (29 and 71%, respectively; Fig. 1c). The spectra of calcined Al-TS-1 sample displays a unique peak centred at ~50 ppm confirming the absence of extraframework aluminium species for this material (Fig. 1c). DR UV–vis spectra of Al-TS-1 sample exhibits a strong absorption band at 210–220 nm, confirming the incorporation of the Ti atoms in framework positions of the zeolite lattice. No absorption around 330 nm is detected, indicating the absence of extraframework TiO₂ phases. From the ammonia TPD measurements it can be concluded that Al-MCM-41 possesses acid sites with medium acid strength

Table 2
Properties of solvents

Solvent	Boiling point (°C)	Dipole moment	Distance (Å)	
			(1–2)	(3–4)
Toluene	111	0.38	5.84	4.96
Dimethyl carbonate	90	0.00	4.17	2.26
Acetonitrile	82	3.92	2.62	1.81
Tetrahydrofuran	66	1.63	3.97	3.25
Dichloromethane	40	1.60	2.33	2.76
Diethyl ether	35	1.15	4.16	3.11

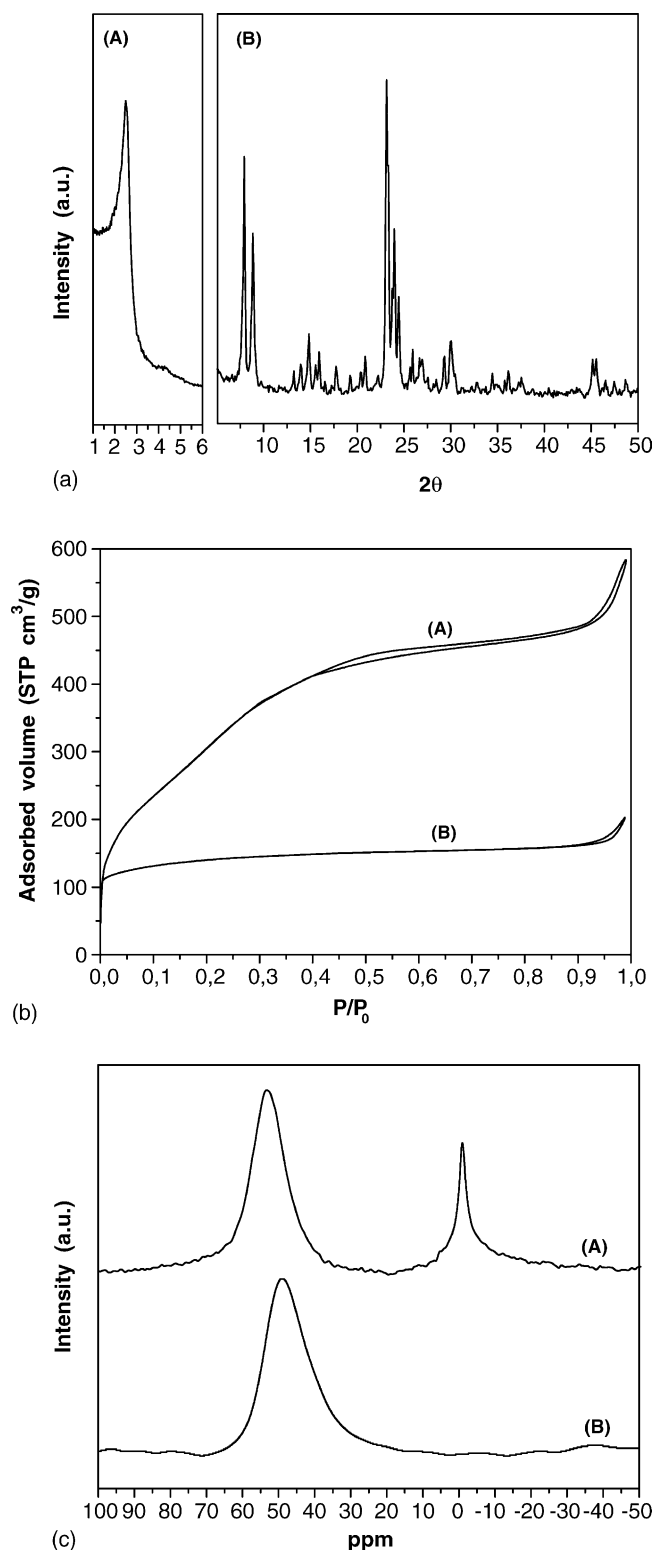


Fig. 1. Characterization results of Al-MCM-41 (A) and Al-TS-1 (B). (a) XRD (b) N₂ adsorption isotherms (c) ²⁷Al-MAS-NMR.

since the peak maximum for ammonia desorption is placed around 275 °C. In contrast, Al-TS-1 exhibits a peak maximum at 331 °C confirming the presence of stronger acid sites typical of Al-containing zeolitic materials.

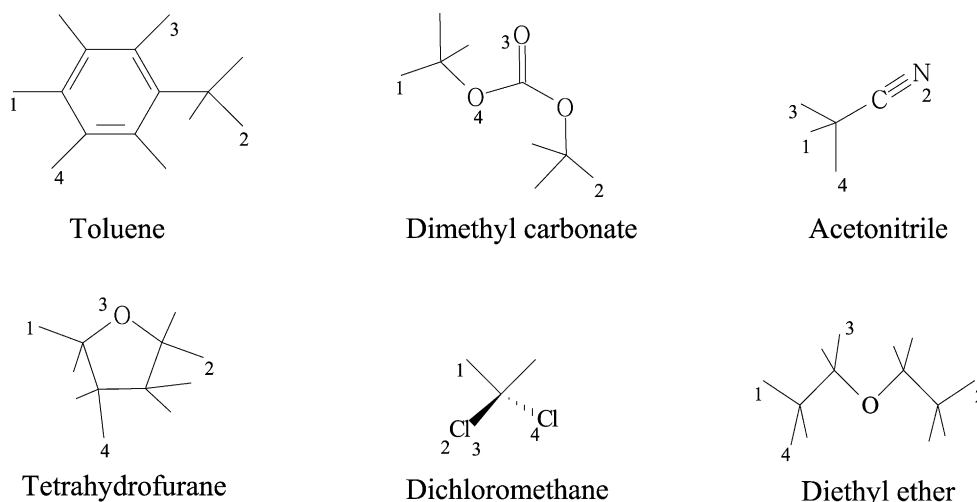
A variety of organic compounds with different physico-chemical properties have been selected in this work as solvents for the liquid-phase rearrangement of 1,2-epoxyoctane. Table 2 lists the polarity and boiling point of the solvents. Although, methanol and other alcohols are common solvents used in organic synthesis, they have been discarded in this work since the presence of these nucleophilic polar agents would lead preferentially to the formation of glycol ethers from the epoxide. Table 2 also includes the molecular dimensions of the different solvent molecules at the reaction temperature calculated by Cerius² Dynamic Simulation with Universal Force Field parameters (UFF) [19] (Scheme 1).

The effect of the solvent nature on the catalytic activity and selectivity towards the different products of the reaction is depicted in Figs. 2 and 3 for Al-MCM-41 and Al-TS-1 catalysts, respectively. Preliminary experiments with these materials (not shown) yielded a sharp enhancement of the catalytic activity when Al-MCM-41 was used as catalyst compared with that obtained over Al-TS-1. Therefore, the Al-MCM-41 catalyst loading was reduced by a factor of 10 times (ca. 40 mg) in order to obtain comparative epoxide conversions.

It is well established that the acid-catalyzed reactions of the oxirane ring involves two different pathways (Scheme 2):

- (i) *Electrophilic oxirane ring opening.* Acids catalyze the ring opening of epoxides in absence of a nucleophile. The common pathway observed in most of the systems involves the initial attack of the electrophilic reagent to the oxirane ring followed by ring opening giving two intermediate carbocations (I and II) that subsequently may progress to aldehyde (1) and ketone (2), respectively. The formation of different octenols (3 and 4) and 1,4-epoxyoctane (5) is explained in terms of the different transpositions of the positive charge of the carbocation (I). For all the solvents tested, the main product coming from these transposition reactions was 2-octen-1-ol (3) since the formation of the allylic alcohols is always favoured.
- (ii) *Nucleophilic attack of the oxirane ring.* In the presence of water this reaction leads to the formation of the diol, whereas in the presence of alcohols yields glycolethers. It must be pointed out that, when nucleophilic agents are present in the reaction system, this kind of attack is favoured in regards to the electrophilic ring opening. The formation of relatively large amounts of diol indicates the presence of water probably coming from the solvents and/or originated from the dehydroxylation of silanol groups located on the surface of the catalysts [15].

Another type of product obtained in the rearrangement reaction of 1,2-epoxyoctane over heterogeneous catalysts is 2-oct-2-enyloxy-octan-1-ol (7), whose presence has been confirmed by mass spectrometry. In a previous work [15], we have disclosed that this compound is formed by the nucleophilic attack of octenols to the epoxide (Scheme 3). Moreover, products coming from aldolic condensation of aldehydes are not detected under the reaction conditions studied.



Scheme 1. Structural formulas and numbering of atoms for solvent molecules.

The comparison among the different solvents has been carried out on the basis of the epoxide conversion and selectivity towards valuable products. Linear aldehydes are conveniently transformed into linear carboxylic acids or terminal alcohols, important precursors in industrial organic chemistry. Moreover, octenols can be also selectively hydrogenated to linear alcohols [20]. In this sense, both compounds will be considered as valuable reaction products.

The results obtained in the 1,2-epoxyoctane rearrangement over Al-MCM-41 with different solvents (Fig. 2), denote that the nature of the solvent influences significantly on the catalyst performance. Dimethylcarbonate promotes the 1,2-epoxyoctane rearrangement over Al-MCM-41 with an epoxide conversion close to 100%, whereas toluene yields a significant epoxide conversion (30%) in comparison to those obtained with the rest of solvents tested. Fig. 4 depicts the epoxide conversion as a function of the polarity for the differ-

ent solvents using Al-MCM-41 as catalyst. It can be observed a clear lowering of the epoxide conversion as the solvent polarity increases. This fact might be attributed to a decrease in the substrate concentration within the pores of the catalyst as the polar nature of the solvent increases.

Acetonitrile as solvent leads to a significant low epoxide conversion. In addition to its high dipole moment, this result can be also attributed to the basic character of the solvent, which neutralizes Brønsted acid centers of the catalyst hindering the participation of the proton in the solvolysis of the oxirane ring (Scheme 4). Nevertheless, it is noteworthy that the significant selectivity towards octenols obtained (close to ca. 90%) which might be related with the basic character of the acetonitrile.

The selectivity towards the different reaction products is also governed by the solvent properties. The use of diethyl ether and tetrahydrofuran over the Al-MCM-41 catalyst

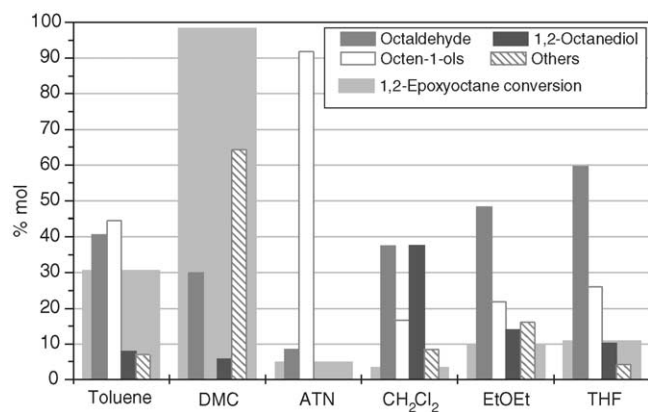


Fig. 2. 1,2-Epoxyoctane rearrangement over Al-MCM-41. Reaction conditions: catalyst loading, 40 mg; temperature, 120 °C and time, 2 h. DMC: dimethylcarbonate; ATN: acetonitrile; CH₂Cl₂: dichloromethane; EtOEt: diethylether; THF: tetrahydrofuran; Others including: 2-Octanone; 1,4-epoxyoctane; 2-oct-2-enyloxy-octan-1-ol; glycoethers and 2-methoxyoctyl 1-(methoxymethyl)heptyl carbonate.

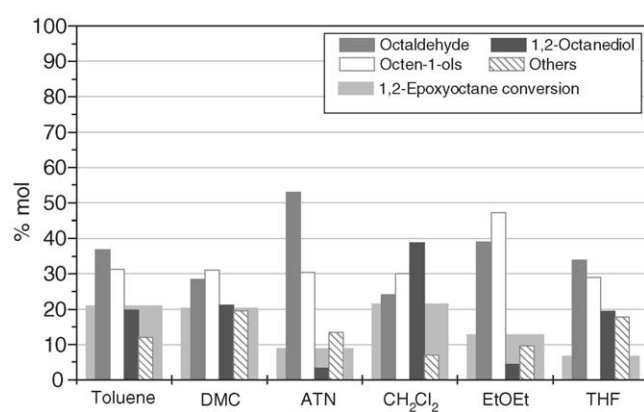
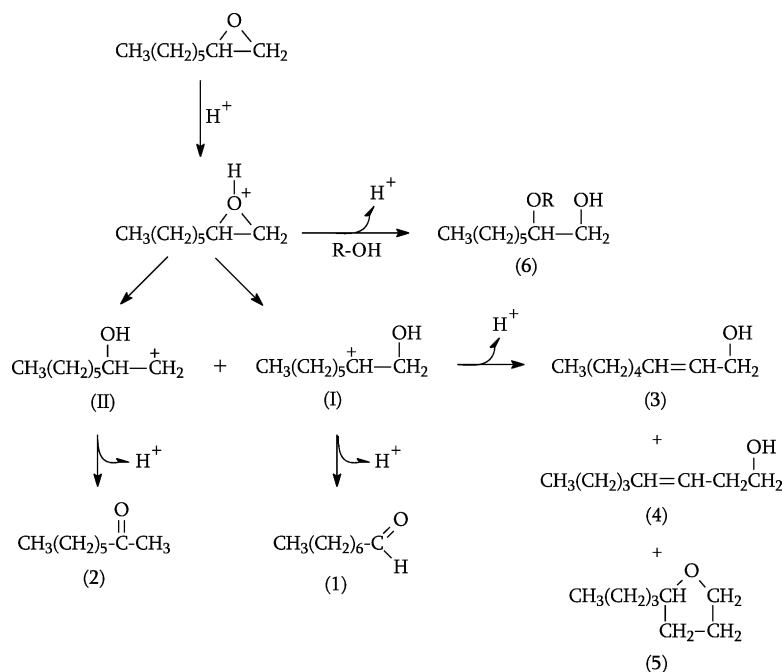


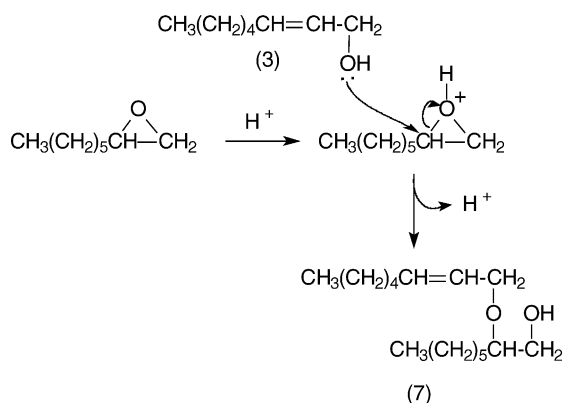
Fig. 3. 1,2-Epoxyoctane rearrangement over Al-TS-1. Reaction conditions: catalyst loading, 400 mg; temperature, 120 °C; time, 3 h. DMC: dimethylcarbonate; ATN: acetonitrile; CH₂Cl₂: dichloromethane; EtOEt: diethylether; THF: tetrahydrofuran; Others including: 2-Octanone; 1,4-epoxyoctane; 2-oct-2-enyloxy-octan-1-ol; glycoethers and 2-methoxyoctyl 1-(methoxymethyl)heptyl carbonate.



Scheme 2. Acid catalyzed mechanism of the isomerization of 1,2-epoxyoctane: (1) Octaldehyde; (2) 2-Octanone; (3) 2-octen-1-ol; (4) 3-octen-1-ol; (5) 1,4-epoxyoctane and (6) 1,2-glycolethers.

yields the formation of octaldehyde as main product, with selectivities in the range 50–60%, accompanied with lower amounts of octen-1-ols.

Formation of bulky by-products was detected when dimethyl carbonate was used as solvent over Al-MCM-41 (denoted as others in Fig. 2). These compounds have been identified as glycol ethers (18.2% of selectivity) and 2-methoxyoctyl 1-(methoxymethyl)heptyl carbonate (40.2%) by mass spectrometry. We propose that the formation of these by-products arise directly from the use of dimethyl carbonate and the presence of methanol impurities in the solvent as briefly outlined in Scheme 5. The latter would allow the formation of both methoxy alcohols (8 and 9) by nucleophilic attack of methanol molecules to the oxirane ring. Additionally, it is known that dimethyl carbonate can react with



Scheme 3. Nucleophilic attack of octenols to the epoxide: (7) 2-oct-2-enyloxy-octan-1-ol.

methoxy alcohols to yield methanol and the corresponding product of condensation [21]. In this way, the reaction between two molecules of glycol ethers and dimethyl carbonate might explain the presence of 2-methoxyoctyl 1-(methoxymethyl)heptyl carbonate (10). Moreover, the methanol so originated would promote again the formation of a higher amount of methoxy alcohols. This important secondary reaction justifies the almost complete conversion of epoxide obtained in the experiments with dimethyl carbonate as solvent.

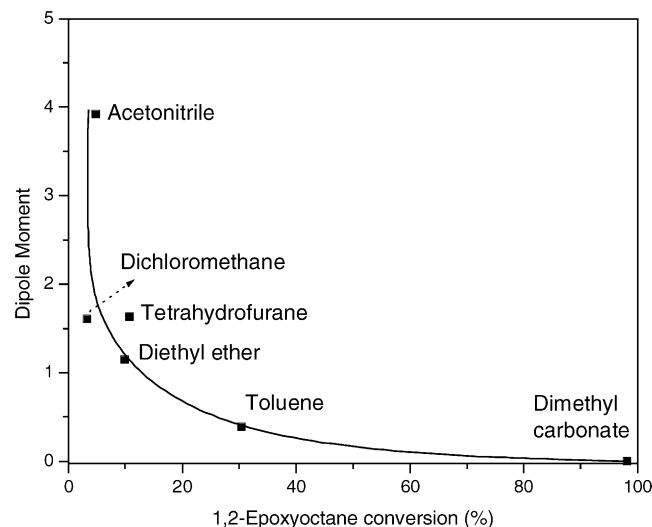
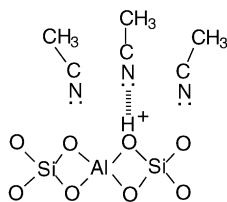


Fig. 4. 1,2-Epoxyoctane conversion over Al-MCM-41 as a function of the polarity of solvents.



Scheme 4. Neutralization of acid sites by acetonitrile.

Finally, isomerization of 1,2-epoxyoctane over Al-MCM-41 with toluene as solvent yielded as main reaction products octaldehyde and octenols with selectivities around 40 and 45%, respectively, and a low formation of 1,2-octanediol (7.9%). From these results, it can be concluded that the best catalytic performance, regarding both activity and valuable product distribution, in the isomerization of 1,2-epoxyoctane over Al-MCM-41 is obtained when toluene is used as solvent.

On the other hand, for Al-TS-1 most of the solvents evidence a different catalytic performance in comparison with that observed in Al-MCM-41 materials (Fig. 3). The use of dichloromethane leads to an epoxide conversion higher than those obtained with diethylether and tetrahydrofurane, in spite of having similar dipole moments. In contrast, a low polar solvent such as toluene shows the same epoxide conversion as dichloromethane. This catalytic performance over Al-TS-1 could be more related with intraparticle diffusion problems, arising from the limited pore size of the zeolitic material, than with the polarity effects.

It is worthy to note a significant lowering of epoxide conversion over Al-TS-1 as compared to that obtained over Al-MCM-41 using dimethylcarbonate as solvent. This fact probably arises from the Al-TS-1 small pore size which hinders the formation of the bulky compounds (8), (9) and (10). Likewise, the basic character of acetonitrile seems to limit the extent of the isomerization reaction as occurred over the Al-MCM-41 catalyst.

Fig. 5 compares activity of both catalysts for the different solvents in terms of moles of epoxide converted per mol of active site and hour (Turnover frequency, TOF). It is remarkable that the Al-MCM-41 material presents much higher activi-

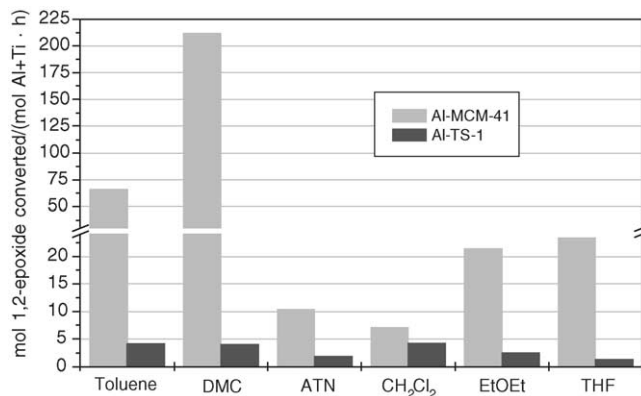
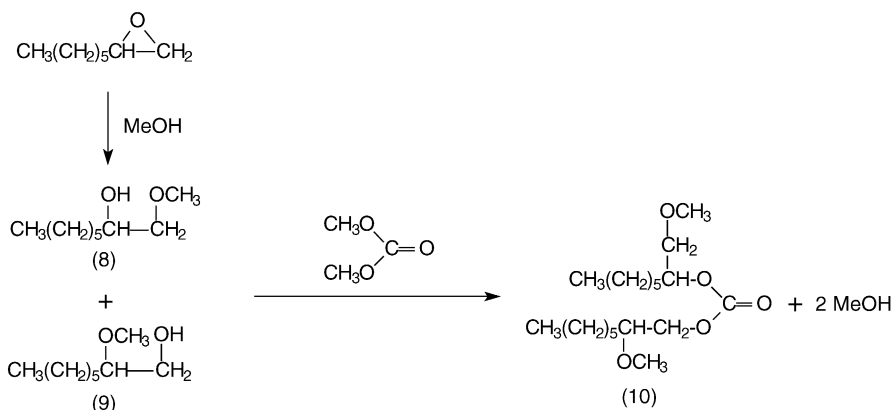


Fig. 5. Turnover frequency in 1,2-epoxyoctane isomerization over Al-MCM-41 and Al-TS-1 catalysts.

ties per active site than those obtained with Al-TS-1 zeolite in spite of its lower acid strength and independent of the type of solvent. The presence of larger pores in the mesostructured materials avoids the diffusional problems present in zeolitic catalysts, being responsible for the enhancement of the catalytic activity. Note that, TOF values for the mesostructured material are about one order of magnitude higher than in Al-TS-1 for most of the solvents. These catalytic results show that both medium acid strength and high accessibility of the acid sites are essential factors to obtain a high activity in the rearrangement of linear epoxides.

The difference between Al-TS-1 and Al-MCM-41 activities is more accentuated when toluene and dimethylcarbonate are used as solvents, which confirms the great influence of the catalyst pore size on the extent of the reaction, since the small pore size of Al-TS-1 zeolite hinders the access of both solvent and substrate molecules to the catalyst pores. In line with this issue, it is noteworthy that the polar/apolar nature of the solvent influences in less extension on the activity when Al-TS-1 is used as catalyst.

Regarding to the molar product distribution, most of the solvents promote over Al-TS-1 a higher formation of 1,2-octanediol accompanied, in general, with lower values towards valuable products in comparison with the results



Scheme 5. Formation mechanism of glycolethers (8) and (9) and 2-methoxyoctyl-(methoxymethyl)heptyl carbonate (10) using dimethyl carbonate as solvent.

obtained over Al-MCM-41. The small pore size of the Al-TS-1 material avoids the formation of bulky compound 2-methoxyoctyl 1-(methoxymethyl)heptyl carbonate (10) when dimethylcarbonate is used as solvent. However, the external sites of Al-TS-1 seem to be acidic enough to catalyse the formation of 2-oct-2-enyloxy-octan-1-ol (7), since this material shows selectivities around 3% with all the solvents tested. The octaldehyde selectivity with acetonitrile over Al-TS-1 is higher than that obtained over Al-MCM-41 and accompanied with a much lower selectivity towards octen-1-ols. Considering activity and selectivity towards valuable products (octaldehyde and octen-1-ols), the best catalytic performance is again obtained when toluene is used as solvent.

4. Conclusions

The influence of the solvent nature on the catalytic performance of Al-TS-1 and Al-MCM-41 materials has been investigated in the liquid phase rearrangement of 1,2-epoxyoctane. Most of the solvents tested promote the isomerization of the epoxide to the corresponding aldehyde, but, other products, mainly octen-1-ols, are obtained. The latter must be considered as interesting products as they can be hydrogenated to terminal alcohols with a high added-value. The complete absence of water and alcohols is a necessary requirement in order to avoid the nucleophilic attack of the oxirane ring with the consequent formation of diol and glycolethers.

The solvent polarity has a significant effect on the reaction activity and selectivity. Indeed, highly polar solvents probably compete with the reactant molecules for diffusion into the catalyst pores and for adsorption on the acid sites, which significantly reduces the conversion. This effect is more accentuated when strongly hydrophilic Al-MCM-41 is used as catalyst. Toluene displays the best catalytic performance regarding both the activity and selectivity towards valuable products (octaldehyde and octenols) with both Al-MCM-41 and Al-TS-1 catalysts. For most of the solvents tested, TOF values obtained with Al-MCM-41 mesostructured material are about one or two orders of magnitude higher than with Al-TS-1 zeolite, as a consequence of the better accessibility of the acid sites.

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References

- [1] K. Arata, K. Tanabe, *Catal. Rev. Sci. Eng.* 25 (3) (1983) 365.
- [2] J.M. Coxon, E. Dansted, M.P. Harsthor, K.E. Ritchards, *Tetrahedron* 25 (1969) 3307.
- [3] S.M. Naqvi, J.P. Horwitz, R. Filler, *J. Am. Chem. Soc.* 79 (1957) 6283.
- [4] S. Murata, M. Suzuki, R. Noyori, *J. Am. Chem. Soc.* 101 (1979) 2738.
- [5] J. Marc, *Advanced Organic Chemistry*, John Wiley, New York, 1985.
- [6] K. Arata, K. Tanabe, *Bull. Chem. Soc. Jpn.* 53 (3) (1980) 299.
- [7] W.F. Hölderich, J. Röseler, G. Heitmann, A.T. Liebens, *Catal. Today* 37 (1997) 353.
- [8] R.A. Sheldon, J.A. Elings, S.K. Lee, H.E.B. Lempers, R.S. Downing, *J. Mol. Catal.* 134 (1998) 129.
- [9] J.A. Elings, H.E.B. Lempers, R.A. Sheldon, *Stud. Surf. Sci. Catal.* 105 (1997) 1165.
- [10] R. Dimitrova, V. Minkov, N. Micheva, *Appl. Catal.* 145 (1996) 49.
- [11] C. Neri, F. Buonomo, US Patent 4,495,371 (1985) to ANIC S.p.A.
- [12] M.J. Faraj, US Patent 4,312,995 (1993) to Arco Chemical Technology.
- [13] D. Brunel, M. Chamoumi, P. Geneste, P. Moreau, *J. Mol. Catal.* 79 (1993) 297.
- [14] G.D. Yadav, D.V. Satoskar, *J. Chem. Tech. Biotechnol.* 69 (1997) 438.
- [15] D.P. Serrano, R. van Grieken, J.A. Melero, A. García, *Appl. Catal. A: General* 269 (2004) 137–146.
- [16] L. Gilbert, C. Mercier, *Stud. Surf. Sci. Catal.* 78 (1993) 51.
- [17] G. Ovejero, R. van Grieken, M.A. Uguina, D.P. Serrano, J.A. Melero, *Catal. Lett.* 41 (1996) 69.
- [18] J. Aguado, D.P. Serrano, J.M. Escola, *Microporous Mesoporous Mater.* 34 (2000) 43.
- [19] Cerius² is a modelling and simulation software package, created by Accelrys. See <http://www.accelrys.com/cerius2/>.
- [20] G. Szöllösi, I. Kun, B. Török, M. Bartók, *Stud. Surf. Sci. Catal.* 125 (1999) 539.
- [21] T. Tatsumi, Y. Watanabe, K.A. Koyano, *J. Chem. Soc. Chem. Commun.* (1996) 2281.