

Preparation of non-fused heterocycles in zeolites and mesoporous materials

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Abstract

The use of zeolites and mesoporous materials in synthesis and industrial applications are extremely important due to their acidity properties and their reuse facility. In this review, is presented the use of zeolites and mesoporous materials in the preparation of non-fused heterocycles compounds, with particular emphasis in epoxidations, aziridinations and the Beckmann's rearrangement.

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1. Introduction

Recently, several immobilization methods have been developed in organic synthesis with the main goal of creating cleaner and cheaper processes than the traditional ones. The importance of catalysis as one of the fundamental pillars in green chemistry and as a source of low-cost methodologies, has driven considerable attention to the immobilization processes, because of their advantage in product isolation and catalyst reuse. Due to the relevance of heterocyclic compounds, such as biological properties, considerable efforts have been done by the synthetic community in order to achieve practical and low-cost methodologies for their preparation, so is not surprising that the synthesis of these important molecules has become the subject of study of many researchers involved in heterogeneous chemistry.

Several reviews were published emphasising the many aspects of the heterocycles synthesis on solid support [1–3] and fluorous solid phase separation [4]. Taking in consideration the importance of this growing area of interest, this review aims to underline the significance of zeolites and mesoporous materials as catalysts and as catalysts immo-

bilization supports in the heterogeneous synthesis of heterocyclic compounds, fulfilling a gap in the zeolites existent literature [5–8].

This review is organized according to the methodologies implemented, and subdivided by ring's size and compound's families, with the sense to focus various synthesis methods of small molecules.

2. Three-membered rings

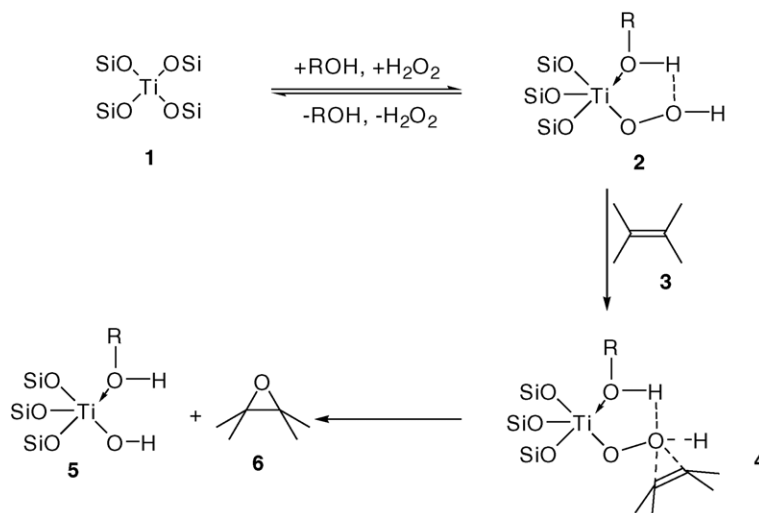
2.1. Epoxides

It is well known that, catalytic oxidation processes play an important role in the industrial production of fine chemicals and several other commodities [9]. Therefore, it is not surprising that several methods to perform olefins epoxidation have been developed.

2.1.1. Titanium-contained zeolites

Over the last few years, zeolite-based metal oxide systems, particularly titanium containing zeolites, proved their effectiveness as catalyst in several selective oxidations. For instance, the titanium substituted silicate (TS-1) catalyst, introduced by *Enichem*, represents one of the most efficient

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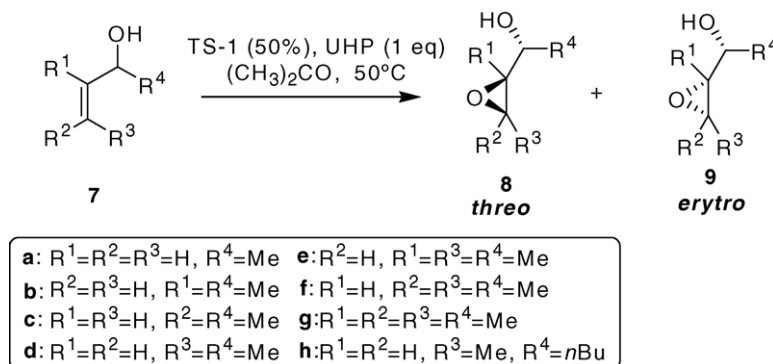
Scheme 1.

zeolite-based methods for the epoxidation of allyl alcohols, with up to 86% yield, using hydrogen peroxide as the oxidant [10].

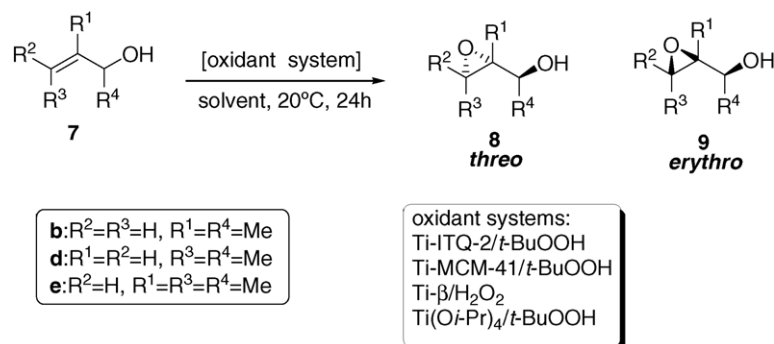
In the oxidation of smaller olefins by TS-1, under mild conditions with hydrogen peroxide, was observed that, the yields and the reaction rates were decreased by increasing the chain length or the olefin cross-section, by electron-withdrawing substituents and by solvents in the following order methanol > ethanol > *t*-butanol [11]. Considering the epoxidation rate, the initial independence from the TS-1 crystallites size was observed, becoming slower with larger crystals, after 30% H₂O₂ conversion, meanwhile it was detected the formation of solvolysis products. A mechanistic rationalisation was proposed based on specie **4** as an intermediary (Scheme 1). The solvent efficiency series shown above can be justified by the result of decreasing electrophilicity and increasing steric constraint of specie **4**. The increasing of R group size in the alcohol facilitates the formation of **2** and favours the approach of the olefin **3** in the more hindered oxygen-transfer step (**4**). In respect to the catalyst, the catalytic activity is decreased by higher concentration of basic substrates and is improved by the presence of acids.

The selectivity in allylic alcohols oxidation is greatly dependent on the structure of the unsaturated alcohol. For instance, the oxidation of the alcohol functional group to aldehyde or ketone of unsaturated alcohols with an internal double bond becomes, competitive with the epoxidation reaction, while the epoxidation of terminal double bond is very slow when compared to internal ones. According to the authors, these selectivity differences can be explained in terms of the double bond ability to coordinate to the Ti active site as well as by sterically demands [12].

The first diastereoselective epoxidation of acyclic systems reported, makes use of Titanium silicate 1 (TS-1)-urea hydrogen peroxide adduct (UHP), in a sense to minimize the risks inherent to the use of hydrogen peroxide (Scheme 2) [13]. With this work, the authors demonstrated that substrate-specific selectivities were obtained when 1,3-allylic strain (caused by R³ and R⁴) was present in the substrate (**7**), and that R¹ substituent exerted no significant influence on this diastereoselectivity. In other words, despite that R¹=R³=CH₃, the *threo* isomer is still obtained in high diastereomer ratio (81:19).



Scheme 2.



Scheme 3.

In an attempt to determine, which one of the Ti-based catalytic systems was the most suitable system to perform the olefin epoxidation, Adam et al. [14,15] studied the following systems: Ti-β/H₂O₂, Ti-MCM-41/*t*-BuOOH and Ti-ITQ-2/*t*-BuOOH. In this study were tested several allylic alcohols and it was observed that when substrates containing the *cis*-methyl group were used, the *threo* epoxide was preferentially formed with all the oxidant systems. In contrast, in substrate **7b** (Scheme 3) (without a *cis* methyl group) the epoxide preferentially formed was the *erythro* (**9b**) diastereoisomer for Ti-ITQ-2, Ti-MCM-41, as so for the homogeneous version Ti(O*i*-Pr)₄, while Ti-β yielded a mixture of 1:1 *threo/erythro*. Indeed, for the majority of the substrates tested, the heterogeneous oxidant systems Ti-MCM-41/*t*-BuOOH and Ti-ITQ-2/*t*-BuOOH proved to influence the diastereoselectivity in the same way as the homogeneous system Ti(O*i*-Pr)₄/*t*-BuOOH.

In the epoxidation of 3-alkyl-substituted cyclohexene derivatives, no significant difference in the diastereoselectivity was observed for Ti-MCM-41 and Ti-ITQ-2, nevertheless when large-pore zeolite Ti-β was used, the *trans* epoxide was formed in large excess. According to the authors, a transition structure, analogous to the one proposed for Ti(O*i*-Pr)₄/*t*-BuOOH, can be applied to Ti-ITQ-2/*t*-BuOOH and Ti-MCM-41/*t*-BuOOH oxidant systems, in which the substrate is fixed by metal–alcoholate bonding and with a dihedral angle of 70° < α < 90° for the oxygen transfer (Fig. 1). In a way to confirm the reaction occurrence within the zeolite, *tert*-butyl substituted allylic alcohols were used as substrates. These alcohols were not epoxidized by TS-1 due to the zeolite cavity small size while Ti-β functioned as an epoxidation catalyst confirming the occurrence of the reaction inside the zeolite.

A curious study about the influence of the aluminium content on a Ti-β zeolite in the epoxidation selectivity was taken by Cambor et al. [16]. The authors synthesised an Al-free Ti-β oxidation catalyst for the first time, and confronted

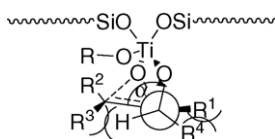


Fig. 1.

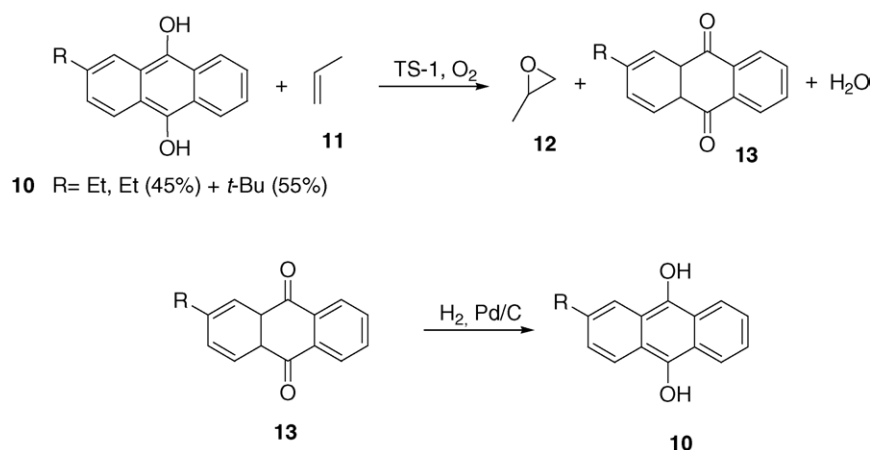
these catalysts with the ones previously tested in the oxidation of hex-1-ene. They observed that the catalyst Al content decreased the epoxide selectivity, notwithstanding the reaction increased conversion. This aspect was explained by the presence of strong acid centres that can catalyse the ring opening to yield the methyl glyco ether. An alternative route to obtain optical active epoxides in the presence of Ti-β zeolite, was to use the oxidant agent as a chiral inducer, i.e., using chiral hydroperoxides with a minimum optical purity of 10% [17].

Bekkum and co-workers [18] performed a study in which aluminium-free zeolite Ti-β catalyst was compared with TS-1, Ti,Al-β and Ti-MCM-41 in the epoxidation of oct-1-ene and norbornene with hydrogen peroxide. Taking in consideration the substrates used, the conclusions were:

1. for linear alkenes TS-1 is the preferred catalyst (furthermore it is restricted to linear alkenes), with Ti,Al-β and Ti-MCM-41 showing poor activity, according to the authors because of their interior hydrophilic;
2. Ti-β is highly active and selective for several non-branched alkenes with lower alkenes being epoxidized faster than bigger ones as so the reaction being faster for internal double bonds;
3. in the epoxidation of bulky alkenes, Ti-β proved to have a higher catalytic activity and showed that the lower activity per titanium site for the Ti,Al-β catalyst was probably caused by the protic aluminium sites. It was either proved that when two double bonds are present, Ti-β does not have any preference between them, catalysing the reaction in both;
4. the epoxidation reaction inside Ti-β not only depends on electronic effects, but also of substrate's steric effects.

Considering the epoxidation of propene, great advances have been done as consequence of the enormous interest demonstrated by the fine chemicals industry [19]. Probably, in industry one of the most solicited zeolites is TS-1, not only for the *Enichem* process [10], but also because it has very interesting catalytic properties, with high utility in alkenes epoxidation using hydrogen peroxide as oxidant.

After the first studies conducted by Clerici et al. about the epoxidation of propylene with TS-1 as catalyst [20], Roland



Scheme 4.

and Thile [21] observed that the catalytic activity and propylene oxide selectivity were related with the acidity of water coordinated to the active titanium sites, and its reversible deprotonation inhibits the formation of the active species for epoxidation. They also observed that the catalyst deactivation causes a blockage of the zeolite micropores with propylene oxide oligomers, nevertheless refluxing the catalyst in dilute aqueous hydrogen peroxide regenerates the catalyst activity by the oxidative breakdown of these oligomers.

One year later, on basis of the anthraquinone process developed for the hydrogen peroxide production, Clerici and Ingallina [22] combined this process with the titanium silicate mediated epoxidation. The process consisted in an attempt to avoid the use of large amounts of hydrogen peroxide, by production in one pot reaction of the epoxide **12** and water derived from the reaction between an alkylated anthrahydroquinone **10** with molecular oxygen and a small olefin (only the propylene (**11**) oxidation is reported), in the presence of titanosilicate TS-1. The process gave yields up to 78% with selectivity being controlled by the TS-1, and the cycle was closed by subsequently catalytic hydrogenation of corresponding anthraquinone **13** (Scheme 4).

Continuing on propylene epoxidation, a method was described in which platinum impregnated in Pd/TS-1 catalyst was used in the epoxidation with oxygen and hydrogen [23]. The authors observed that changing the catalyst to (Pd-Pt/TS-1), calcination and the reduction methods, a significant change occurred in the selectivity and propylene oxide yield, concluding that without any calcination step prior to reduction, temperatures below 200 °C and a very low hydrogen concentration in the catalyst bed favours the epoxide formation. The platinum loading, should not exceed 0.02 wt% in order to obtain the highest propylene oxide yield (11.7%) although with low selectivity (46%).

2.1.2. *Y*- and *X*-framework zeolites

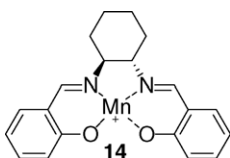
Corma et al. [24] synthesised chiral complexes $\text{MoO}_2(\text{acac})\text{L}$, where L are bidentate O,O-ligands derived from (L)-*trans*-4-hydroxyproline, with compounds bearing

an $\text{Si}(\text{OEt})_3$ group being heterogenized by anchoring into modified USY-zeolites. The heterogeneous system was used in the epoxidation of geraniol and nerol allylic alcohols, and yielded good conversions and selectivities but only modest ee (respectively 47 and 64%). Surprisingly the observed enantioselectivity is considerable higher for heterogeneous catalyst than for the homogeneous ones. The major advantages of this heterogeneous system, when compared to homogeneous system, are the possibility to recycle the catalyst up to five consecutive cycles, and the simplicity of work-up procedure (simple filtration).

A zeolite-promoted oxidation of 1,1-diarylethylenes initiated by irradiation was reported, however, due to the non-selectivity of radicals species, the reaction is not very clean, giving products resulting from over oxidation and rearrangement [25]. This reaction was achieved in presence of a Y zeolite characterized by four 7.4 Å windows tetrahedrally arranged around a 13 Å diameter supercage, and molecular oxygen. Adam et al. [26] described another reaction performed on this type of zeolite, in the presence of methyltrioxorhenium (Herrmann catalyst), and using hydrogen peroxide as the oxidant system, this proved to be highly selective and to yield good conversions. The disadvantages of this process rely on the use of an 85% hydrogen peroxide aqueous solution, making the process hazardous and environmental unfriendly due to the use of MTO. In order to circumvent this last limitation, Schuchardt and co-workers [27] used inorganic rhenium compounds, such as Re_2O_7 and ReO_4^- , as catalysts. To perform the epoxidation reaction, the catalyst was supported on Y zeolite, mixed with silica-alumina and pure alumina and the oxidation agent, anhydrous H_2O_2 . However, was noted that, in some cases, the acidic Re centres in the catalyst could promote the ring opening originating the diol product.

By making use of immobilization into the supercages of large pore Y zeolite, the heterogenization of an analogous Jacobsen catalyst was tried, after molecular modelling predicted that, either the salen ligand or the corresponding (salen) Mn(III) complex **14** could be easily accommodated

inside those supercages [28]. The use of this analogous was justified by the prediction that the actual Jacobsen's catalyst would not fit inside the Y zeolite supercages because of the four bulky *tert*-butyl groups. The preparation of this (salen) Mn(III) complex in the intracrystalline cages of zeolite, consisted in the condensation of *trans*-(*R,R*)-1,2-diaminocyclohexane and salicylaldehyde in the presence of Mn(II) metal ions resident in the supercages, and a final oxidation step. Concerning the reaction enantioselectivity catalysed by this complex immobilized in Y zeolite, the results obtained in the epoxidation of 1-methyl-cyclohexene and styrene, were as good as the ones reported for the Jacobsen's catalyst with the same substrates. Performing this reaction with two other substrates (*trans*-methyl-styrene and indene) the epoxidation occurred in moderate to good enantioselectivity.

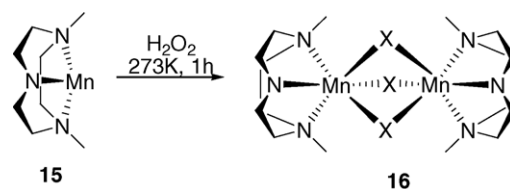


After encapsulation of the *cis*-[Mn(bpy)₂]²⁺ complexes in the supercages of zeolites X and Y, these were tested as catalysts in the selective epoxidation of several alkenes. Higher selectivities were observed when MnX was used. This fact was attributed to the weaker acidity of MnX zeolite, making possible to select the intermediate product (epoxide, diol or diacid) with the adjustment of the reaction conditions. Using a peroxide/substrate ratio of 5:1 in the cyclohexene oxidation, the catalyst remained effective for up to 1000 cycles [29].

DeVos et al. [30] reported the preparation of a manganese faujasite containing the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn). This zeolite was prepared by reacting a Mn(II)NaY zeolite (0.8 wt% Mn, or nearly one metal ion per four supercages) dehydrated at 250 °C, in the presence of the polyamine ligand for 10 h at 150 °C under inert atmosphere and occasional shaking. The homogeneous catalysts were prepared in situ by adding a solution of ligand in organic reaction solvent and MnSO₄·H₂O dissolved in water, to the reaction mixture. The manganese faujasite containing 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) was tested in the epoxidation of styrene and cyclohexene. With [Mn(tmtacn)]²⁺-NaY as a catalyst, good selectivities were achieved (97.7% for 19.3% styrene conversion and 95.4% for 25.3% cyclohexene conversion) by cooling the reaction mixture to 0 °C, with gradual hydrogen peroxide addition and using acetone as solvent. According to the authors, the interaction of [Mn^{II}(tmtacn)]²⁺-NaY with H₂O₂ in a water/acetone medium leads to intrazeolite formation of Mn^{III}-Mn^{IV} dinuclear complexes (Scheme 5) or other dimerization products (X = O²⁻, OH⁻, or other oxygen bridges).

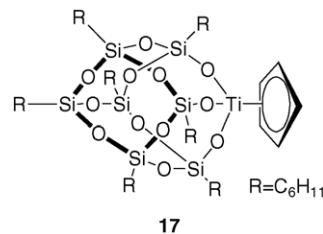
2.1.3. MCM-framework zeolites

Abbenhuis et al., after their first communication on the titanium silasesquioxanes catalysed epoxidation by



Scheme 5.

tert-butyl hydroperoxide (TBHP), in which the titanium is, incorporated via spatially oriented siloxy bonds (Ti–O–Si) [31], reported the heterogenization version of the catalyst. The immobilization of titanium(IV) silsesquioxane [$\{(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\}\text{Ti}(\eta^5\text{-C}_5\text{H}_5)$] (17) was achieved by its strong adsorption to MCM-41 channel molecular sieve [32,33]. This methodology was applied to the epoxidation of cyclooctene at 50 °C, as so extended to epoxidation of norbornene and oct-1-ene (80% conversion and selectivity after 24 h).

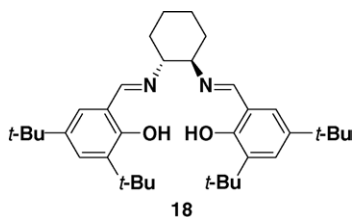


Making use of *tert*-butylhydroperoxide (TBHP), at least two other references can be found, Kulkarni's group reported the use of transition metal-MCM-41 as catalysts in the oxidation of *trans*-stilbene and anthracene with TBHP. In this case the *trans*-stilbene's oxidation, using benzene as solvent, Cr-MCM-41 (5 wt% Cr) gave the best conversion results (60%) when compared with the analogous modified MCM-41 catalysts [34]. In a more specific approach, Farzaneh et al. [35] synthesised a vanadium containing MCM-41 by one pot synthesis and tested it as a catalyst in the oxidation of several olefins as well as in the oxidation of *trans*-2-hexen-1-ol, with TBHP as the oxidizing agent. Despite the modest conversion obtained (56%), the oxidation of the allyl alcohol in refluxing chloroform generated the correspondent epoxide with maximum selectivity, with the proposed mechanism being similar to the one presented by Sharpless for the Vanadium catalysed epoxidation of allylic alcohol. Previously, the same authors published a similar study of olefin oxidation, with NaY transition metal exchanged zeolite, in which were obtained poor conversions and epoxide selectivities [36].

Several modified mesoporous MCM-41 (Ti-, V-, Cr-, Mn-, Fe- and Co-) were synthesised and their activity as catalysts in the liquid phase oxidation of cyclohexane in the presence of aqueous H₂O₂ or TBHP was determined [37]. It was observed that for Ti-, Mn-, Fe- and Co-MCM-41 the oxidation activity was lower than the one observed for TS-1 catalyst with hydrogen peroxide as the oxidant. Surprisingly when TBHP was used as the oxidant, instead of H₂O₂ and with cyclohexane

as the solvent, the Mn- and Co-MCM-41 activity increased almost by four-fold. Making use of TBHP as the oxidant, V- and Cr-MCM-41 showed better activities in cyclohexane than in acetone.

Hutchings and co-workers [38–40], attempted the immobilization of a Mn(III)–salen complex in a Y zeolite, in order to achieve the epoxidation of styrene and *cis*-stilbene. After realized that using PhIO, NaBO₃, LiClO₄ and NaOCl as oxygen donors the catalyst was inactive in the absence of a modifier, the authors tried the immobilization of the same Mn(III)–salen complex in a mesoporous MCM-41. It was observed that the immobilization of Mn²⁺ within the Al-MCM-41 mesopores enhanced the activity for epoxidation and that the best modifier was the chiral salen ligand **18**. This Mn–salen Al-MCM-41 externally surface immobilized is a catalyst which showed to have similar product selectivity and enantioselectivity than the equivalent homogeneous Mn–salen complex. Furthermore, silanisation of the Al-MCM-41 external sites catalyst showed that the initial sites had a crucial influence on the selectivity towards the *cis*-epoxide formation.



Studying the effects of the manganese concentration in Mn-exchanged Al-MCM-41, the effect of temperature on the *cis:trans* epoxide product ratio, the effect of reaction time on the enantioselectivity, and the effect of iodostilbene on the heterogeneous catalyst, the authors concluded that:

1. the level of Mn exchange does not affect the reaction's enantioselectivity, so as well the total yield. The *cis*-epoxide is the major product formed at lower Mn concentrations;
2. at higher temperatures the *cis:trans* ratio decreases, with the *cis*-epoxide always being the major product;
3. the enantioselectivity of the homogeneous reaction is non-dependent of reaction time, but the heterogeneous reaction has better enantioselectivity at shorter reaction times;
4. after iodobenzene addition to the homogeneous reaction system (no significant changes in results were noticed), the addition of iodobenzene to the Mn-exchanged Al-MCM-41 epoxidation system in the absence of stilbene (to decompose to O₂ and Iodobenzene), decreases the rate of iodostilbene decomposition, showing that PhI can act as a poison agent of the Mn active centres.

In the second experiment, PhI was added to the reaction system before the addition of PhIO, decreasing the rate of reaction, as well as the total yield of epoxide and the enantiomeric excess of *trans*-epoxide. With these facts, the authors asserted that PhI acts as a catalyst poison for

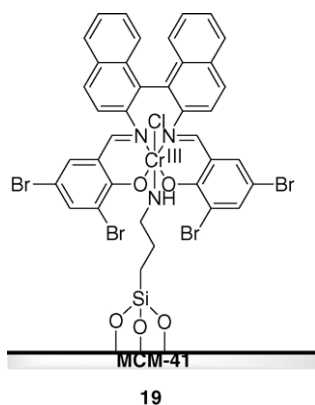
the Mn-Al-MCM-41 heterogeneous system, leading to a loss of enantioselectivity induced by the catalyst.

Previously, Iwamoto and co-workers developed a template ion-exchange (TIE) method for the preparation of Mn-MCM-41. Appealing to the use of TBHP, iodostilbene or gaseous oxygen, the catalyst was tested on the oxidation of *trans*-stilbene in acetonitrile, resulting in poor to moderate conversions. These results were greatly improved when DMF was employed as a co-solvent, in a 9:1 ratio. When stilbene derivatives were used in the referred system, was observed that the reaction proceeds with almost total *trans* selectivity and could be reused at least for five times without catalytic activity loss [41]. Another reference to aromatic olefin oxidation in mesoporous Al-MCM-41, was presented by Kim et al. [42], in which manganese 2,2'-bipyridine complex cations were immobilized in the previous zeolite (Al-MCM-41-[Mn(bpy)₂]²⁺) and three different styrene oxidation agents were evaluated, iodostilbene, hydrogen peroxide and TBHP. Notwithstanding the fact that the immobilized catalyst proved to be very active for styrene oxidation by bulky TBHP (up to 94% conversion), the reaction is highly non-selective, with ten oxidation products been formed. For the other two oxidants, despite the lower conversions, the selectivity for the epoxide formation increased (94% conversion to the PhIO Al-MCM-41-[MnL₂]²⁺ (5 or 7%) system and 50% epoxide selectivity).

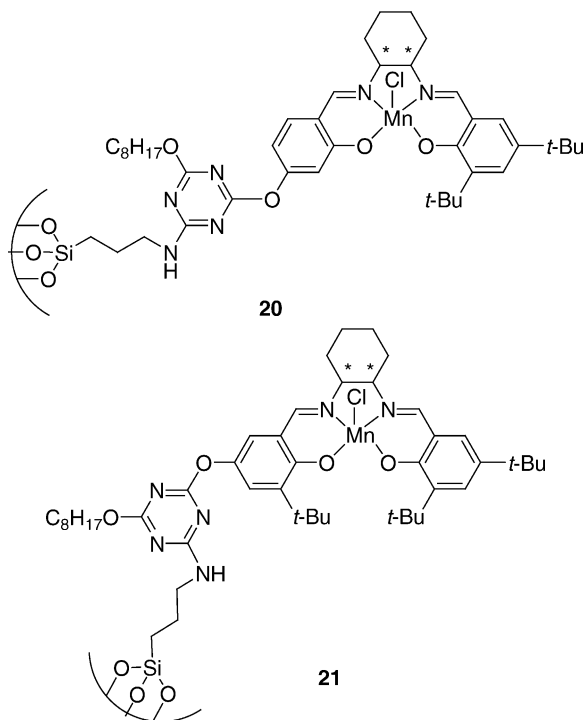
The [Mn(bpy)₂]²⁺ was encapsulated in cubic Al-MCM-48 and the complex was tested as catalyst for the styrene oxidation yielding styrene oxide as the main product but only in 40% conversion. Nevertheless, this result showed that this system possesses a higher turnover number (TON = 82) than [Mn(bpy)₂]²⁺ complex alone (TON = 7), or even the previous Al-MCM-41-[Mn(bpy)₂]²⁺ (TON = 58) [43].

Latter, and with the objective of immobilize salen Mn(II) complexes on MCM-41, Kim and Shin [44] heterogenized these complexes by a grafting method using (3-aminopropyl)trimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. Chiral epoxidation reactions were carried out with styrene and α -methylstyrene in a *m*-CPBA/NMO system at 0 and –78 °C in the presence of several Mn–salen complexes catalysts, resulting in a significant improvement on the reaction enantioselectivity at low temperature. Selectivity up to 86% ee were obtained in the epoxidation of styrene at –78 °C in a 4h reaction time for a 77% conversion, and a heterogenized Mn–salen/MCM-41 catalyst.

In another approach, the asymmetric epoxidation was achieved through the immobilization of a chromium binaphthyl Schiff base complex on a modified MCM-41 with 36 Å pore size [45]. In this process the catalyst was immobilized by a simple procedure, generating complex **19** with which several aromatic olefins were tested in the oxidation with iodostilbene. Despite the moderate yields observed (up to 61%), relative good ee's were obtained, with 73% for *cis*- β -methylstyrene.



Recently, Bigi et al. designed an unsymmetrical (salen)-manganese(III) complex in which the ligand was covalently bounded to an amorphous KG60 silica or mesoporous MCM-41, through a single linker, allowing the maximum conformational mobility of the complex (**20** and **21**). It was notice that, in both cases, the heterogenization of the catalyst did not cause any significant drop in the enantioselectivity of the reaction, and ee's up to 84% were obtained. Four distinct olefins were submitted to the reaction conditions (1-phenylcyclohexene, styrene, 1,2-dinitronaphtalene and indene) with *m*-CPBA/NMO as the oxidant system in dichloromethane, and the differences in reactivity were assumed to be caused by olefin's steric effects [46].



Jacobs and co-workers [47] presented the first example of a catalytically active, non-aromatic Mn complex, immobilized on a glycidylated surface. The investigators anchored triazacyclononane (tacn) in the modified MCM-41 surface (reacted with 3-(glycidyloxypropyl)trimethylsilane

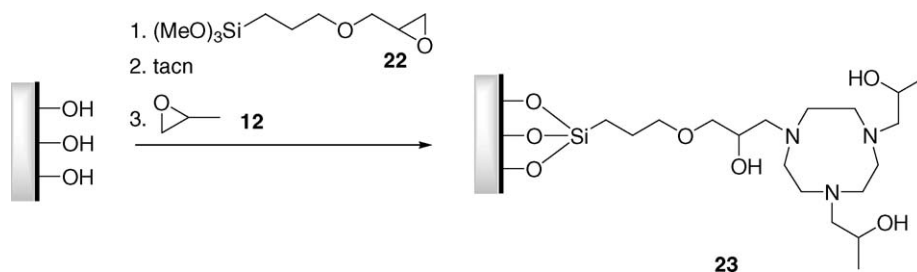
(**22**)) and with propylene oxide (**12**) (Scheme 6). The modified complex Mn-MCM-GP-tacn was tested in the styrene and cyclohexene oxidation with aqueous H₂O₂ in acetone, yielding very good epoxide selectivities (up to 90%). Taking in consideration the reaction turnover numbers, results that when methanol was used a more efficient catalytic system (TON = 50) was obtained, nevertheless higher epoxide selectivity were detected when acetonitrile and acetone were used.

Thomas, Ingold and co-workers [48] studied two kinds of modified Ti-MCM-41 epoxidation catalysts. These catalyst can be represented as Ti → MCM-41, in which the titanium ions are accommodated inside the walls of the mesoporous silica (framework-embedded), and as Ti ↑ MCM-41, with the tetracoordinated Ti ions grafted in the inner surfaces of the mesoporous host (surface grafted). Some important facts must be enunciated, the first is that the oxidation of cyclohexene and *cis*-stilbene proved to be more efficient when 2-methyl-1-phenyl-2 propyl hydroperoxide (MPPH) was used as the oxidant (up to 36%), when compared with TBHP. The second fact concerns with the reaction diastereoselectivity, for example the reaction of *cis*-stilbene in presence of both catalysts generated only *cis*-stilbene oxide (up to 18% yield). Comparing both catalysts is possible to conclude that Ti ↑ MCM-41 allows higher activity than Ti → MCM-41 in the alkenes epoxidation. Organic-inorganic self-assembled Ti-MCM-41 materials have been prepared by one step synthesis, yielding Ti-MCM-41 very active and selective materials with methylated silicons. It was observed that increasing the level of silylation (more than 40% silylation coverage was required), the catalyst activity and selectivity increases [49,50].

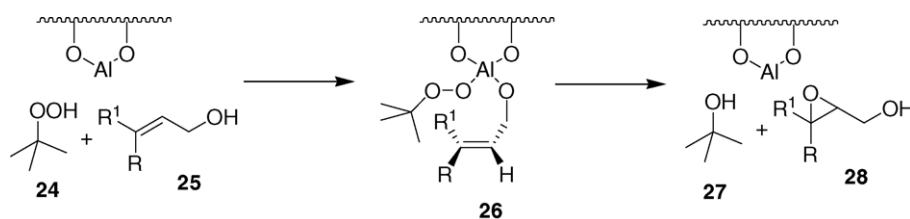
2.1.4. Others framework zeolites

Palombi et al. reported a method for the epoxidation of primary and secondary allylic alcohols with an excess of *tert*-butyl hydroperoxide **24** (TBHP) in the presence of thermally activated 4 and 3 Å molecular sieves [51]. Low to satisfactory yields were obtained, up to 67% using 4 Å molecular sieves, and up to 89% using 3 Å molecular sieves. The regioselectivity of this reaction, which occurs when using primary alcohols as substrates, was justified through a sharpless-type reaction, and based on an analogous path proposed by Oshima and co-workers [52] (Scheme 7). The use of this oxidant system zeolite/TBHP in the epoxidation of homoallylic alcohols proved to be effective (up to 53% yield) notwithstanding the very long reaction times (up to 2 h).

Another epoxidation was achieved in the cages of the zeolite EMT, using different chiral salen catalyst [53]. For this study three distinct EMT zeolites were synthesised: 1-EMT—chloro[*N,N'*-bis(3-*tert*-butyl-5-methylsalicylidene)cyclohexanediamine]manganese(III); 2-EMT—chloro[*N,N'*-bis(salicylidene)-cyclohexanediamine]manganese(III) and 3-EMT—chloro[*N,N'*-bis(3-*tert*-butyl-5-methylsalicylidene)cyclohexanediamine]manganese(II). In this work, the authors observed that 1-EMT was more active than 2-EMT in



Scheme 6.



Scheme 7.

the epoxidation of *cis*- β -methylstyrene, and that the catalytic activity increases with the addition of pyridine *N*-oxide as an axial ligand. However, using PhIO as the oxidant, instead of NaOCl, the catalytic activity was inverted, turning less active the bulkier complex. Taking in consideration the zeolite selectivity, was reported by the authors that smaller alkenes such as 2,3-dimethylbut-2-ene results in higher conversions comparatively with aromatic alkenes epoxidation, and so, a strong influence of the zeolite pore structure on diffusional access to the active salen complex, trapped in the zeolite host was suggested.

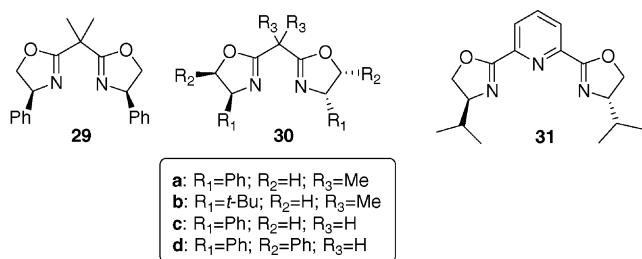
2.1.5. Aziridines

In 1992, the Hutchings group was the pioneer, so as notable, in the heterogenization of an aziridination catalyst, by immobilization in a zeolite, starting with a CuHY zeolite as the catalyst and [*N*-(*tolyl-p*-sulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrogen source [54,55]. After zeolite Y was exchanged with several cations, they observed that Cu^{2+} was the only that showed to be efficient, this group designed a catalyst for the enantioselective aziridination of alkenes based on copper-exchanged zeolite HY. One additional and interesting fact in this work, was the absence of aziridination reaction of *trans*-stilbene, after Evans et al. [56] observed the aziridination of *trans*-stilbene when homogeneous copper catalysts were used. This could be explain by appealing to the impossibility of the aziridine product to diffuse from the pores of CuHY because was too bulky, although it could be constructed within the zeolite supercages (confirmed by molecular modelling studies). The non-activity of the others exchanged-metal zeolites can be due to the ability of those metals to catalyse the breakdown of the PhI=NTs yielding iodobenzene and sulfonamide. With this work, the authors also studied the water effect as a reaction inhibitor, concluding that the reaction rate drastically decreases even with low water quantity and demonstrated the need to use dry solvents

to perform the reaction in these conditions. Considering the catalyst recycle, it was possible to recover and reuse over 13 consecutive assays, and only small traces of copper(II) were lost from the reaction medium. As previously said, the study was extended to the use of modified CuHY catalyst, with a chiral bis(oxazoline). The use of 2,2-bis-[2-((4*R*)-(1-phenyl)-1,3-oxazoliny)]propane (**29**) in the reaction mixture, induced the formation of *N*-tosylaziridine with up to 42% ee, when styrene was used. As expected, lowering the temperature, the reaction became more enantioselective than when it was performed at room temperature (25 °C, ee 18% versus -20 °C, ee 34%).

Later, a study about the influence of the copper exchange level in the zeolite was made by the Hutchings group, they observed that the same yield and rate of aziridine formation were obtained, although the ratio of external to internal sites were significantly different [57,58]. With these results, the authors concluded that the sites on the external crystallite surface were not playing a crucial role in the reaction, or perhaps the reaction was occurring in the intracrystalline space of the zeolite. According to the authors, when chiral bis(oxazoline) ligands **30–31** were used, the yield of the aziridine was determined by the competing processes for the tosylnitrenoid active species within the zeolite, whereas the ee were determined by competing processes via the diastereoisomeric transition states. Moreover, when an excess of bis(oxazoline) was used, the yield of aziridine was reduced indicating that it blocked the zeolite active pores, with yield (78%) and enantioselectivity (ee 85%) being maximized when a molar ratio of PhI=NNs:bis(oxazoline) = 1:0.05 was employed. Interestingly, for some ligands the enantioselectivities were considerable higher in the heterogeneous system than for the homogeneous catalyst (e.g., ee 82% versus 54% for **30c**). These results are in line with prior observations, which confirm that the design of chiral ligands for heterogeneous systems should not be necessarily

be based on the best chiral ligand obtained for homogeneous systems.



In order to demonstrate that other types of silicate framework could be used, the same type of experiment was carried out using copper(II)-exchanged MCM-41, in which yields of the aziridine up to 87% were obtained although with moderate ee (37%). The best advantage of this zeolite relies on the possibility of using it with larger alkenes, as so the possibility to use larger chiral ligands as part of the system's heterogeneity.

In an attempt to determine the reaction mechanism, an EPR study was made by the same group. They concluded that a diamagnetic intermediate is formed, involving $\text{PhI}=\text{NTs}$ and the Cu(II) -bis(oxazoline) complex inside the Y zeolite, which after reaction with styrene regenerates a paramagnetic Cu(II) complex. The impossibility to obtain more information was due the fact that Cu(III) and Cu(I) species are EPR silent [59].

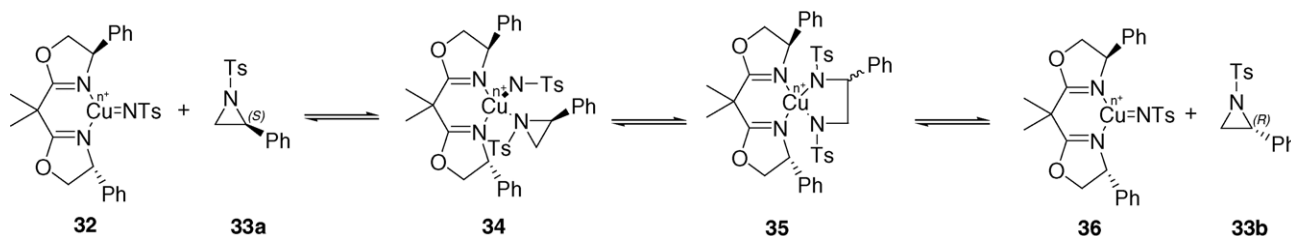
To study the effect of nitrene donor on enantioselectivity, the same research group compared both catalytic systems (homogeneous and heterogeneous) with two possible nitrene donors ($[\text{N}-(p\text{-tolylsulfonyl})\text{-imino}]$ phenyliodinane ($\text{PhI}=\text{NTs}$) and $[\text{N}-(p\text{-nitrophenylsulfonyl})\text{-imino}]$ phenyliodinane ($\text{PhI}=\text{NNTs}$)) with several chiral modifiers (**30–31**), as so with several metal-exchanged zeolite Y (Zn^{2+} , Ni^{2+} , Fe^{3+} , Mn^{2+} , Co^{2+} , Cu^{2+}), appealing to styrene as the main substrate [60]. In relation to the use of these other metals it was observed that, using $\text{PhI}=\text{NNTs}$ as the nitrene donor, not only CuHY catalysed the reaction but also ZnHY and FeHY , contrarily with what happened when $\text{PhI}=\text{NTs}$ was employed where only CuHY gave significant aziridine yields. However, in both cases, CuHY showed to be the most efficient catalyst, minimizing the formation of side products such as benzaldehyde. Optimizing the reaction conditions, the best enantioselectivity was obtained when a slight nitrene donor excess (nitrene donor:styrene = 1.5:1) was used, and when

the nitrene donor concentration was increased there was a drop on the aziridine yield, probably because of the formation of benzaldehyde by-product. Despite not all the chiral modifiers returned the same results, relatively to the ee in the homogeneous system, the same did not happened in the heterogeneous phase, with which all of them originated the products with similar enantioselectivity. Moreover, controlling the substrate:nitrene donor molar ratio and using the bis(oxazoline) (**30a**) enantiomeric excesses up to 90% were obtained. With this study, was observed that the staged addition of the nitrene donor (up to four equal portions) increase the yield of aziridine but lower the ee, as so the use of this heterogeneous catalyst gave much higher enantioselection than the correspondent homogeneous catalyst, when some chiral ligands were used [61]. Later, and still studying the effect of the nitrene donor, chloramine-T and bromamine-T were tested. The main conclusion rising from this study was that they could not be used because they destroy the integrity of the heterogeneous catalyst [62].

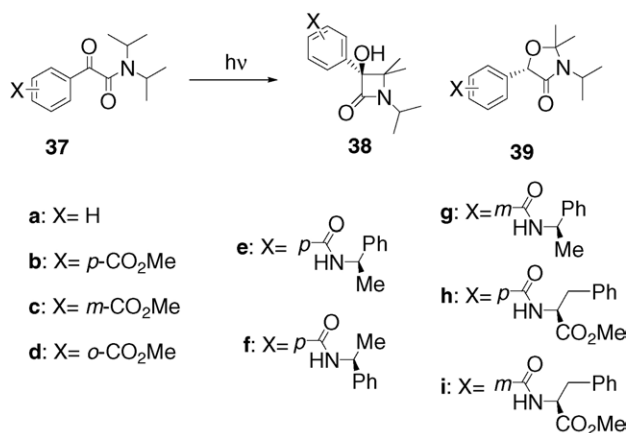
Studying the relationship between ee and conversion during the aziridination reaction in a heterogeneous catalytic system, an enhancement in ee with simultaneous increased yield of aziridine and styrene conversion was observed. This enhancement was consider to be due to the preferential reaction of (*S*)-aziridine with the reaction components leading to an enhancement in the (*R*)-aziridine in the product ratio, once that when the aziridine interacts with the copper/bis(oxazoline)/nitrene donor complex, the system's steric bulk can be so high that it may favour this enantiomer conversion. This interconversion can occur via the aziridine ring opening, once that the free copper catalysed rotation of the C–C bond can invert the asymmetric centre (Scheme 8) [63,64].

As previously mentioned other metals-exchanged Y zeolite were tested, such as Cr-, Mn-, Fe- and Co-exchanged zeolites. Although low yields were obtained, they were all higher than the ones obtained for the blank reactions, with the main disadvantage that significant levels of benzaldehyde was obtained as a side-product [65].

To complete all the studies made on this methodology, one final issue should be mentioned, the catalyst stability. It was observed, again by the Hutchings group, that there was always a leached portion of the catalyst in the reaction mixture in the free Cu^{2+} form, which increased with the reaction time, nitrene donor concentration and by the presence of the chiral



Scheme 8.



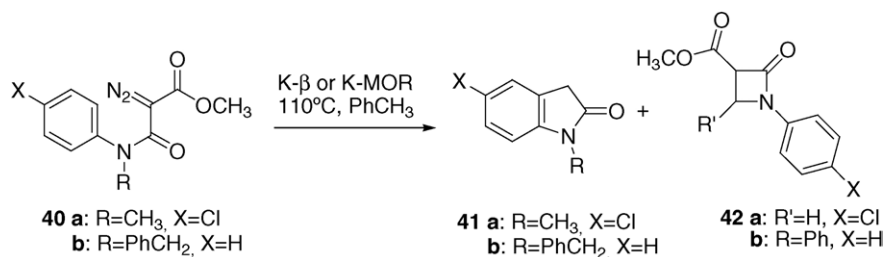
Scheme 9.

modifier. Lastly, comparing both nitrene donors referenced above as leaching causers, PhI=NNS exhibited worst results than PhI=NTS for the same aziridine yield [66].

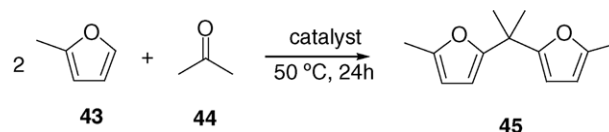
3. Four-membered rings

Considering the β -lactams preparation, Natarajan et al. [67] developed a method to achieve stereocontrol in the photochemical conversion of several α -oxoamides (**37**) into the respective lactams (Scheme 9), irradiating ionic and covalent chiral auxiliary in the interior supercages of zeolites. Despite the modest ee's obtained (up to 44%) when several achiral substrates were tested (**37a–d**) with MY zeolite loaded with distinct chiral inductors, the de's were quite good (up to 88%) when covalent chiral auxiliary-containing α -oxoamides were photolized in the interior cavities of the same MY zeolites, emphasizing the NaY zeolite results. Because of the vast results obtained, varying between each substrate, the authors explained that the results differ between each substrate because of the fit of the α -oxoamide (**37**) guest in the zeolite host. In the same base, the overall difference in de/ee can be attributed to the fact that when the reactant and the chiral inductor are separated identities it will be very unlikely that both unities get together in zeolite supercage.

Previously, Smith and Bahzad [68] studied the decomposition at 110 °C of 2-diazo-2-methoxycarbonyl-*N*-aryl-*N*-alkylethanamides (**40**) over different materials, among them β , Y, X, MOR, ZSM-5 and A zeolites. The authors tried



Scheme 10.



Scheme 11.

to circumvent the observed limitation of the decomposition of α -diazocarbonyl compounds with dirhodium(II) catalysts, achieving better results although only better than in the absence of catalyst. It was observed the preferential formation of bi-fused indolin-2-one derivatives (**41**) (up to 81%) but also a considerable amount (up to 43%) of the respective β -lactam **42** (Scheme 10), particularly when potassium zeolites were used.

4. Five-membered rings

After the Rhijn communication about a new sulfonic acid functionalised MCM or HMS as catalysts tested in the synthesis of 2,2-bis-(5-methylfuryl)propane (**45**) (BMP) [69], Li et al. reported the same molecule synthesis, based upon a supported-Mo/Zr mesoporous MCM-41 material [70]. Both synthesis are based on the condensation of 2-methylfuran (**43**) with acetone (**44**) (Scheme 11).

In both works, was observed that the major problem was to oppose the strong adsorption of BMP or other reaction intermediates in the zeolite pores that usually led to extensive polymerization, with the zeolite pores being consequently block and the catalyst deactivated. This aspect derives from the high reactivity of these substrates towards electrophilic aromatic substitution, as was observed with zeolite catalysts such as H- β and H-US-Y. Something interesting about this later work is the fact that, when 10% MoO₃/7% ZrO₂/MCM-41 calcinated at various temperatures was used as a catalyst, the conversion was increased with the temperature from 560 to 750 °C but slightly decreased when 800 °C were reached, and most important was the independency of BMP selectivity in respect with the calcination temperature. Demonstrating the great utility of this catalyst, the authors performed the 2% MoO₃/14% ZrO₂/MCM-41 system reutilization after 24 h reaction and showed that, despite the catalyst presented a slight decrease in the activity, the selectivity for BMP remains unchanged as 95–96% after the catalytic system reutiliza-

tion [70]. Similarly, dimethylfuran can be obtained in good yield (97%) by intramolecular cyclization of acetylacetone at 350 °C over a H-ZSM-5 zeolite with a Si/Al = 300 [71].

Furan derivatives (**50**) can be achieved by olefinic alcohols (**48**) cyclization over TS-1 in an aqueous hydrogen peroxide mild medium (Scheme 12) [72]. According to the authors, in the presence of aqueous hydrogen peroxide TS-1 formed the titanium hydroperoxo species (**47**) which can epoxidize the double bond of the olefinic alcohols (**48**) and catalyse the intramolecular attack of hydroxy nucleophile to open the epoxide (**49**), resulting on the oxacyclic ring (**50**) formation.

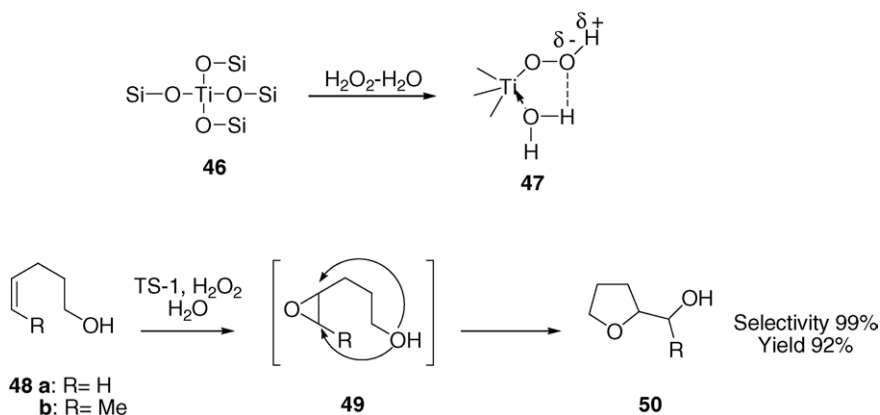
Appealing to the use of zeolite-encapsulated rhodium(I) dicarbonyl species, Currie and Andersen compared three different heterogeneous catalytic systems in hydroformylation reactions of prop-2-en-1-ol (**51**), among other substrates [73]. With this substrate, the homogeneous system originated predominantly butane-1,4-diol (68%) and 2-methylpropan-1-ol (32%) as products, but surprisingly when [(CO)₂Rh-zeolite]PEt₃ was used (zeolite = X, Y or ZSM-5) the main products were 2-ethoxytetrahydrofuran (**52**) (up to 62%), 4,4-diethoxybutan-1-ol (**53**) (up to 10%), diethoxy-2-methylpropan-3-ol (**54**) (up to 28%) and 1,1-diethoxypropane (**55**) (up to 15%) (Scheme 13). Zeolites Y and ZSM-5 proved to achieve better selectivities than zeolite X, according to the authors due to the higher concentration of sodium ions in this last zeolite. With this work was proved one more time that, the zeolite participation in the catalytic reaction alters not only the reaction selectivities but also the products distribution.

By hydroxylation of cyclic ethers with *tert*-butyl hydroperoxide and hydrogen peroxide catalysed by manganese and iron bipyridine complexes included in zeolite Y and bentonite, tetrahydrofuran-2-ol was obtained in good yields from THF and dihydropyran in any of the catalytic systems tested (Fe³⁺-Y, [Fe(bpy)₂]³⁺-Y, Fe³⁺-bentonite, [Fe(bpy)₂]³⁺-bentonite), using H₂O₂ as the oxidant specie. Using TBHP as the oxidant and manganese(II) zeolite encapsulated as catalysts, the conversion slightly decreased but the selectivities remained unchanged [74]. A process for the

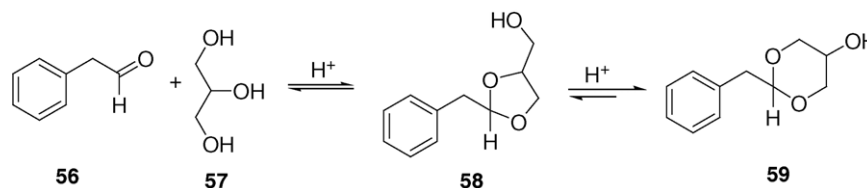
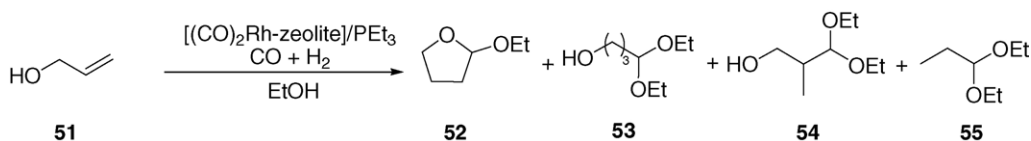
oxidation of *n*-heptane over molecular sieves was described with SAPO originating reasonable conversions of 2-methyl-5-ethyl-furan and 2,6-dimethyl-pyran among other products (up to 18% yield), in a bed flow reactor in an oxygen atmosphere [75].

A simple process for the preparation of 5-hydroxy-2(5*H*)-furanones from furan was achieved with excellent yields. Furan was treated with aqueous hydrogen peroxide in acetonitrile in the presence of TS-1, the corresponding lactone was obtained in yields that depended on the H₂O₂:furan molar ratio. The authors observed the formation of the derived furanone in high yields (98.3%) in 8 h using 2.4 hydrogen peroxide equivalent and only 7.5 wt% of TS-1 catalyst [76]. Previously, a similar approach was taken for saturated ethers, particularly in the case of the cyclic ones such as tetrahydrofuran and tetrahydropyran that were oxidized with the TS-1/H₂O₂ system in reasonable yields (55 and 42%, respectively) at 70 °C over 12 h. These authors tested the use of other metal-based silicates, such as chromium-based (CrS-1 and CrS-2) and vanadium-based (VS-1 and VS-2), nevertheless only poor yields were observed when chromium-based silicates were used (11%) and no activity was detected in the case of vanadium-based [77].

After the work developed by Corma and Climent on the formation of cyclic ethylene acetals catalysed by faujasites in form of HY zeolite [78], the formation of the same family compounds was studied in the presence of HZS-360 [79]. This last procedure, consisting in refluxing the mixture of the carbonyl compound, the selected diol in toluene over the zeolite and removal of water, yielded moderate to high yields for a considerable range of substrates tested. 1,4- and 1,3-Diketones were tested and the products obtained depended on the capacity of the substrate to enolize. Highly enolizable compounds (e.g., 1,3-cyclohexadione) yielded the double 1,3-dioxolanes or in cases where one carbonyl group is less reactive (e.g., 1-phenyl-1,3-butanedione) originated the mono 1,3-dioxolane. The catalyst was recycled for five cycles with no conversion decrease as so the reaction of chiral substrates occurred with total retention of optical activity.



Scheme 12.



About 1,3-dioxolanes, several applications were made in the synthesis of fragrances. Corma and co-workers recently applied the zeolite technology in the synthesis of hyacinth, vanilla and blossom orange fragrances [80]. The acetalization of phenylacetaldehyde (**56**) with glycerol (**57**) to originate hyacinth fragrance was performed in the presence of USY zeolite (Si/Al = 35) at 146 °C in toluene. After 2 h, the conversion obtained was 95% with 64% of the 1,2-addition product **58** and 31% of the 1,3-addition product **59**. The compound **58** isomerizes to the thermodynamically more stable **59** (Scheme 14).

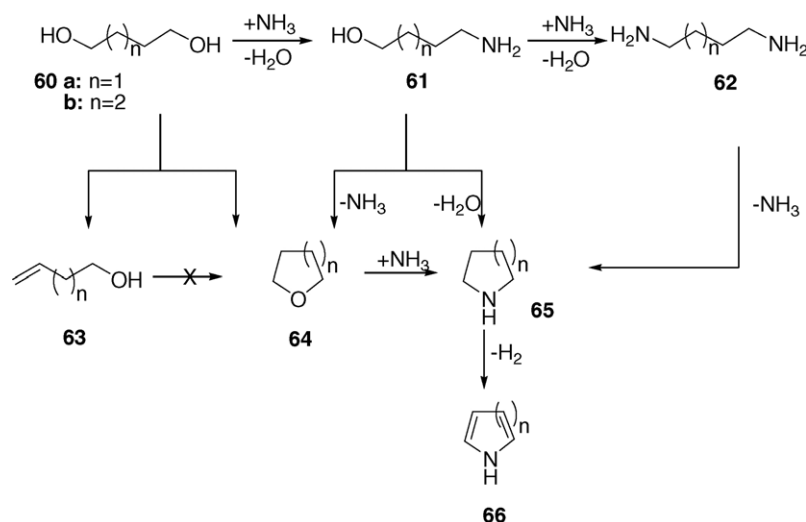
In an attempt to verify the influence of the catalysts pore size, other catalysts were tested: USY, β , mordenite (MOR), MCM-41 and ZSM-5. Considering the results obtained, for hyacinth and vanilla synthesis, the authors concluded that the reaction is diffusion controlled in ZSM-5 and MOR (ratio **58/59** = 7.7 and 5.6, for hyacinth synthesis, respectively) and that these zeolites present a transition state shape selectivity effect, with the isomerization of **58–59** being strongly disfavoured within their pores. Through the study of catalyst Si/Al ratios influence on the reaction extent, an effect of the zeolites polarity was observed, i.e., more hydrophobic catalysts due to higher Si/Al ratios results on a decreasing of activity. The most active catalysts experimented in the acetalization of phenylacetaldehyde with glycerol were β -zeolite (Si/Al \approx 100) and USY (Si/Al = 35–50), regardless the isomerization of **58–59**. Considering the preparation of vanillin propylene glycol acetal, ITQ-2 catalyses the reaction in a good extent in solvent-free conditions with the reaction being performed in direct distillation. Previously, the same research group studied the possibility of using zeolites as catalysts in the synthesis of the fructone fragrance from ethyl acetoacetate and ethylene glycol. Several zeolites were tested with β and USY, giving the best results and an optimum in activity when a compromise between the number of acid sites and hydrophobicity was achieved, like a Si/Al ratio between 25 and 50 for β and approximately 20 for USY. Like before, the conversion could be increased with simultaneous water removal by azeotropic distillation with toluene or, by work-

ing in an 8 Torr vacuum. After optimized conditions, excellent conversions with 99% selectivity were achieved, but unfortunately, the catalyst had to be fully regenerated after each cycle [81].

Martin and Lucke applied ZSM-5, mordenite (MOR) and a highly dealuminated faujasite (DAY), in the H form, as catalysts in O/N transformation of 2-methylfuran and ammonia or *n*-alkylamines. When they focused on the reaction with ammonia, the best conversions and selectivities were achieved in the presence of H-ZSM-5 and in a temperature range of 210–360 °C, e.g., at 360 °C the 2-methylpyrrole was obtained with 85% furan conversion and 99.6% selectivity. When *n*-alkylamines were used as co-feed in the presence of HZSM-5, maximum conversions were reached at the low-temperature range, by increasing the amine chain length. According to the authors, 1-H substituted pyrroles block the acid sites stronger than 1-alkyl substituted ones and a fast deactivation occurs due to the increasing size of transition complexes by blockage of the zeolite active surface [82,83].

Taking in consideration the terminal diols cyclization, Rani et al. [84] studied this reaction over modified ZSM-5 zeolites with 30 Si/Al ratio as catalysts (H-, Cr-, Fe-, Mn-, Cu- and LaZSM-5) based on the presence of strong acidic sites on zeolite channels. Starting from butane-1,4-diol (**60a**), at least four possible products could be obtained (Scheme 15, $n = 1$), and it was seen that depending on the metal modified ZSM-5 catalyst the selectivity was different. The best selectivity for THF (**64a**) was obtained when 5 wt% CrZSM-5 was used as the catalyst (53% selectivity and 86% conversion) over 3 h in presence of water and ammonia at 250 °C with 0.5 h⁻¹ WHSV.

As shown in Scheme 15, pyrrolidine (**65a**) and pyrrole (**66a**) can be obtained by the same process. Considering the first of them, Fe-ZSM-5 modified zeolite proves to be the best catalyst yielding 96% of pyrrolidine in the same reaction conditions described above, concerning the pyrrole (**66a**) formation, it was obtained in 94% yield when LaZSM-5 was used. For the preparation of pyrroles there is a BASF reference (patent) based on the conversion of



Scheme 15.

1,4-dimethoxytetrahydrofuran over a borosilicate zeolite catalyst [85]. 2-Methyl-1,2-dehydropiperidine can be obtained by cyclization of 6-aminohex-1-yne over Zn-BEA (1.4 wt% Zn^{2+}). It was observed that the material activity increases with zinc loading up to 0.21 mmol Zn^{2+} per zeolite gram, evidencing not only a correlation between zinc loading and catalytic activity but also the capability of protons to act as co-catalysts. In respect to this, was observed that the activity of Zn-BEA increases with Zn^{2+} loading until a Zn^{2+}/H ratio of 1 is reached [86].

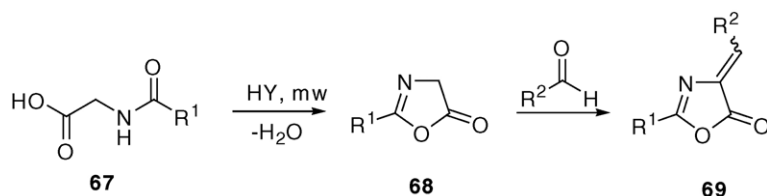
HZSM-5 was used as catalyst, after proper activation, in the preparation of 1,3-dioxolan-4-one through carbonylation of formaldehyde with carbon monoxide. The optimization of the process revealed that the yield of the desired product decreases with the increase of Si/Al ratio and that despite the yield increased with the increasing of reaction temperature starting from 80°C , it begins to fall off at 160°C . About the CO pressure, the maximum yield was obtained at 55 MPa of initial pressure [87].

In an attempt to solve the problems inherent to cyclodehydration of *N*-acylamino acids, specially the formation of undesirable side products. Boruah et al. [88] developed a simple method based in the cyclization of *N*-acylamino acid (**67**) in presence of HY zeolite and microwave energy. The residue obtained was reacted with aromatic aldehydes in order to originate 4-arylidine-2-oxazolin-5-one (**69**) (Scheme 16).

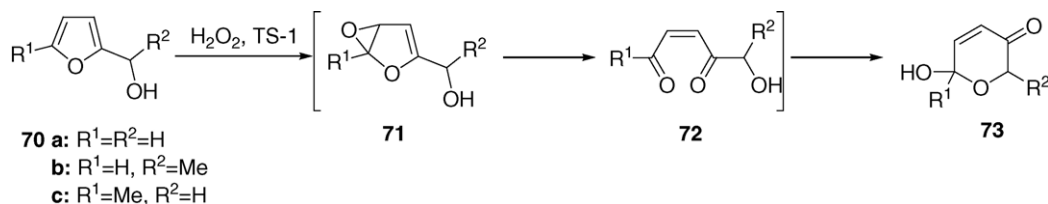
5. Six-membered rings

In the same study performed by Rani et al. [84] here presented, pyran (**64b**) and piperidine (**65b**) were obtained simply by altering the substrate, using pentane-1,5-diol (**60b**) instead of butane-1,4-diol (**60a**) (Scheme 15, $n=2$) and slight modification of the reaction conditions. These modifications consisted on 280°C instead of 250°C and the utilization of HZSM-5 with different Si/Al ratios (30, 41, 129, 280). The best piperidine selectivity was achieved when HZSM-5 (41 Si/Al ratio) was used, yielding 81% of the desired product, and HZSM-5 (129 Si/Al ratio) to yield 39% pyran.

In an attempt to simplify the general alcohol protection by 3,4-dihydro-2*H*-pyran (DHP), Kumar et al. tried the protection of several alcohols in the presence of HY zeolite. Good to excellent results were achieved (60–95% efficiency) with mild conditions (*n*-hexane and reflux during up to 10 h depending on substrate) and a simple workup procedure (filtration). The catalyst was reused by heating it at 500°C in air presence [89]. Later, Sartori and co-workers [90] studied the DHP protection and deprotection of some substituted phenols and aliphatic alcohols over HSZ-330 and HSZ-360 zeolites in a solvent free medium and catalyst reuse. The results were better than the previously related, moreover with good yield protection for menthol, 79% instead the 70% reported by Kumar et al. [89].



Scheme 16.



Scheme 17.

Likewise, the approach developed for epoxidation with TS-1 with hydrogen peroxide, Jacobs and co-workers recently developed a method for the preparation of 6-hydroxy-2*H*-pyran-3(6*H*)-ones (**73**) through alkyl-substituted furfuryl alcohols (**70**) oxidation [91]. This oxidation occurred at room temperature in 24 h reaction time, with acetonitrile as solvent. In the oxidation of furfuryl alcohol (**70**), 6-hydroxy-2*H*-pyran-3(6*H*)-one (**73**) was obtained at 90% yield. The substrate was epoxidized and the unstable epoxide (**71**) (not observed) rearranges to an enedione alcohol (**72**), which undergoes cyclization by intramolecular attack of the hydroxy group on the carbonyl group (Scheme 17).

In relation to the effects that can control the reaction, we have to focus on the steric effects caused by R₁ group, e.g., substrate **70c** was converted in a 79% extent while furfuryl alcohol (**70a**) was converted in 99%. Other aspect to be considered is the lower conversion rate for alkyl-substituted furfuryl alcohols (**70**) compared to the oxidation of alkyl-substituted furans, due to the electron-withdrawing effect of the hydroxy moiety. The catalyst activity had drastically decreased over three cycles due to the drying treatment of TS-1 at 60 °C between each run, nevertheless calcination of the used TS-1 fully restores the catalyst activity.

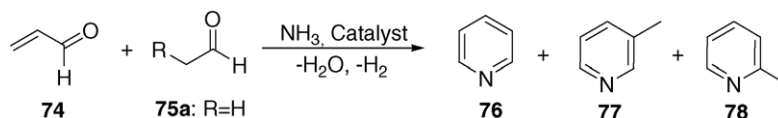
Considering the pyridines formation, some methods have been developed and most of them patented. The most recent one makes use of the known process of condensation of aldehyde or ketone with allylic alcohol or aldehyde in the presence of ammonia in gas phase and one of several zeolite catalysts. With this process, aryl pyridines can be synthesised with good overall yields consisting on making react both components at high temperatures in presence of one of the next catalysts: ZSM-5, ZSM-11, HY-a crystal structure of faujasite, HBEA Al-MCM-41, MCM-41 or HX. Among these catalysts, LaY (5 wt% and 5 Si/Al atomic ratio) proved to be the best catalyst, at least for the condensation of acetophenone and prop-2-en-1-ol yielding 2-phenyl pyridine in 92% selectivity [92].

Proceeding with the same approach, acetaldehyde (**75a**) and acrolein (**74**) were condensed with ammonia in the pres-

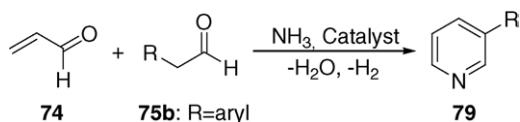
ence of modified ZSM-5 zeolite with indium, silver, germanium and gallium ion as so with mixtures of tungsten and indium or indium and molybdenum (Scheme 18). All the reaction generated a mixture of three products, pyridine (**76**), β-picoline (**77**) and α-picoline (**78**). Taking in consideration the pyridine synthesis, the best catalyst tested was the Ag-ZSM-5 loaded with 4.0 wt% in indium and 1.0 wt% in tungsten, yielding 53% of pyridine (**76**), 28% of β-picoline (**77**) and only 1% of α-picoline (**78**). The best selectivity towards β-picoline (**77**) was achieved (30% yield) using an USY type zeolite (Si/Al = 160). Together with β-picoline (**77**), 25% of pyridine (**78**) and 1% of α-picoline (**78**) were obtained. With this process, [93] the inventors tried to suppress the use of toxic metals such as thallium and lead as developed previously.

Shimizu et al. [94] developed a procedure for the synthesis of pyridine and pyridine derivatives in which the best results were obtained with the modified ZSM-5 pentasil zeolite. The results obtained when Pb-, Tl- and Co-ZSM-5 were used increased about 20% when compared with non-modified ZSM-5 (42% pyridine yield). The authors had also developed a catalyst regeneration technique, in which, besides the aeration with addition of a noble metal, a second aeration in the presence of a small amount of alcohol was carried out, with the catalyst life being expanded by more than 10 times. According to the authors, the alcohol effect settles on decreasing the acidity strength of catalyst and accelerating desorption of adsorbed coke or coke activation by alcohol in the catalyst by cooperation with oxygen. Part of this process was patented latter by Koei Chemical Co. [95]. Meanwhile, through substitution of Tl-ZSM-5 by CoO and PbO, new metal oxide modified zeolites were introduced in condensation of aldehydes and/or ketone in ammonia presence introducing no better results than the ones described for the non-oxide zeolites [96].

Previously, a method employing other metals modified ZSM-5 zeolites had been developed for these syntheses. Platinum, rhodium and palladium modified zeolites were experimented and originated good pyridine yields (85, 84 and 86%,



Scheme 18.



Scheme 19.

respectively) and selectivities at 430 °C in a fluid bed reactor for 2 h with the main innovation being the addition of hydrogen to the reaction process [97].

BASF developed a series of modified borosilicate and aluminosilicate zeolites of the pentasil type with several metals, for the condensation of acrolein (**74**) and aryl aldehydes (**75b**) in the presence of ammonia at 400 °C (Scheme 19). Depending on the substrates, excellent yields were achieved, with particular success for borosilicates-based zeolites (up to 90% pyridine derivatives (**79**)) [98].

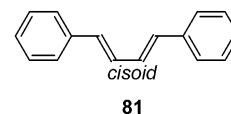
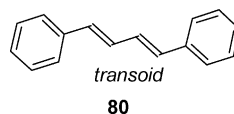
The first pyridine synthesis method employing zeolites as catalysts was described by *Mobil*. HZSM-5 catalyses the acetaldehyde condensation in the presence of ammonia (Chichibabin reaction) at 427 °C yielding reasonable yields of a products mixture. The modified Cd-, Cu- and Ni-HZSM-5 were tested yielding an increased products mixture and worsening the selectivity [99]. Based on this *Mobil* pioneer process, MCM-22 was experimented as a catalyst in the condensation of acetaldehyde and formaldehyde in presence of ammonia, yielding 9.3 wt% of pyridine [100]. In a way to adjust the total yield of pyridine and/or alkyl-substituted pyridines Feitler and Wetstein inserted a third aldehyde or ketone in the reaction mixture, that when adjusted, altered the reaction selectivity. This reaction was performed in presence of a pentasil-type zeolite catalyst, containing also kaolin and amorphous silica-alumina [101,102].

After the work developed by *Mobil* in conversion of aniline to α -picoline (**78**) in H-ZSM-5 zeolite in which pyridine (**76**) was made to react with 2.9 MPa NH₃ at 510 °C with 52% selectivity and very low conversions (13%) [103], Stamm et al. studied different zeolites catalysts in the same transformation not only to ascertain which of them were most effective for this reaction but also to determine the exact transformation mechanism. The main conclusion about the best zeolite was the use of three-dimensional pore structures such as Y, β and ZSM-5, due to higher selectivities achieved, particularly with ZSM-5, which despite the narrowest pores of the three-dimensional ones resulted in highest selectivity. About H-ZSM-5, the authors observed that the increasing of Si/Al ratio causes a decrease in the conversion due to the reduction of acidic sites [104].

When we focus on six-membered rings with two oxygen atoms, we cannot do it without mention the cyclodehydration of diethylene glycol catalysed by HZSM-5 [105]. To verify if ZSM-5 was the best zeolite to perform the transformation to 1,4-dioxane, other catalysts were tested (Cu-NaY and HY among them) with all low yields and low selectivities obtained. At 225 °C HZSM-5 (Si/Al = 40) yielded 64% of the desired product, and appealing to a study of

the effect of temperature it was observed that in the range of 175–225 °C for higher temperatures the diethylene glycol conversion decreases despite the selectivity remained unchanged, notwithstanding with increasing time on stream, the zeolite activity decreases. With the use of higher homologues, was observed a decrease in 1,4-dioxane yield, increasing molecular weight. By NH₃ absorption, it was proved that despite the weakly acidic sites have no activity, the strongly acidic sites are crucial in the cyclodehydration of diethylene glycol, moreover the increasing in density of acidic sites increases the activity of zeolite for 1,4-dioxane formation.

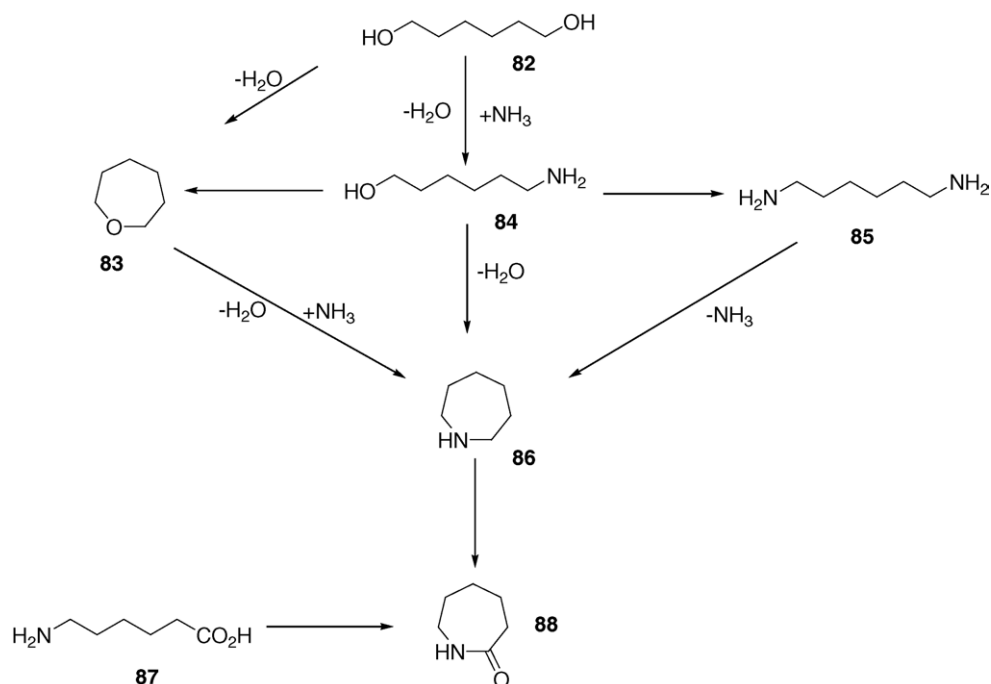
Tung et al. developed a curious method for the preparation of endoperoxides. It consists in the 9,10-dicyanoanthracene and hypocrellin A-sensitized photooxidation of *trans,trans*-diphenyl-1,3-butadiene (DPB) absorbed on the internal surface of ZSM-5, with the reaction taking place by a 1,4-cycloaddition with singlet oxygen. In contrast, with the general idea of Si/Al zeolite having a crucial role acting as catalyst, this reaction does not depend on the zeolite Al content (Si/Al = 55 or 25 showed no effect on the oxidation product distribution). However, when the effects of coadsorbed water on product distribution were studied, a direct influence of water in selectivity for high Al content in ZSM-5 was observed. Since that two conformational isomers exists in solution: *transoid* **80** and *cisoid* **81**, being main conformer the *transoid* (**80**) (ca. 99%), the bulkiness of the *transoid* conformer (5.5 Å for *transoid* (**80**) and 5.1 Å for *cisoid* (**81**)) does not allow it to fit into the channels of ZSM-5 and so, the *transoid* (**80**) first isomerizes to the *cisoid* (**81**) form and then it can be accommodated inside the zeolite channels. With this methodology, excellent yields were achieved for production of the correspondent DPB endoperoxide, in contrast with the same reaction performed in absence of zeolites in which six different products were obtained [106].



5.1. Seven-membered rings

5.1.1. ϵ -Caprolactam and Beckmann's rearrangement

In the preparation of hexamethyleneimine (**86**) few reports have been published, Rani et al. appealing to the amino cyclization of terminal (α,ω)-diols over modified ZSM-5 catalysts [84] had successfully developed a method for its preparation as so an alternative method for the preparation of ϵ -caprolactams (**88**), instead the usual Beckmann rearrangement of cyclohexanone oxime (Scheme 20). CeZSM-5 showed to be very promissory, a total conversion was obtained with 88% selectivity for hexamethyleneimine (**86**) and complete suppression of oxepane formation. The direct synthesis of ϵ -caprolactams (**88**) through 6-amino caproic acid (**87**) cyclization in water at 350 °C over ZSM-5 cata-



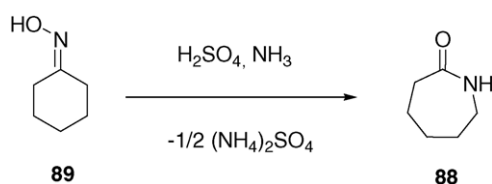
Scheme 20.

lyst was tried. A 77% yield was obtained when HZSM-5 (Si/Al = 129) was used, proving the efficiency and selectivity of the process.

The formation of ϵ -caprolactam (**88**) has been intensively developed due to the high importance of this molecule for Nylon industry, since that it is an important intermediate for Nylon 6 production. The molecule is produced industrially by the Beckmann rearrangement of cyclohexanone oxime (**89**) using sulfuric acid as catalyst. However, this process leads to undesirable high quantities of ammonium sulfate when compared with the desired ϵ -caprolactam (Scheme 21). Moreover, the use of sulfuric acid should be avoided, for environmental and economic reasons, and also because of the corrosiveness of the reaction medium. Hence, several heterogeneous catalysts were developed during the last 20 years. Nevertheless, only last 10 of those will be referred here due to all the attention that this process had been subject in the literature in the last years [107]. Hence, the Beckmann rearrangement had been studied in several zeolites and mesoporous materials such as high silica MFI zeolites, silicalite-1, SAPO-11, H- β , MCM-41, MCM-22, FSM-16, HZSM-5, zirconia-supported boron catalyst, USY, ferrierite

zeolites and others. Despite the controversy around the catalytic activity of high silica MFI type zeolites, there is now some general agreement about the active sites of MFI zeolites. Several groups had disagreed about the adequate Beckmann rearrangement active sites, while Aucejo et al. [108] claimed, in the beginning of decade, that the crystalline silica-alumina strong acid sites were favourable, Curtin et al. [109,110], through alumina-supported boron TPD investigations, demonstrated that acid sites with intermediate strength enhanced the lactam yield. Hence, Holderich and co-workers [111] acidified inactive amorphous silica with HCl, in order to create active silanol groups, observing a 50% yield and an enhancement of the selectivity, considering the vicinal silanols as more favourable sites than their terminal counterparts. In the use of silicalite-1 the author claims the presence of vicinal-hydrogen bonded silanols, as being indispensable in raising the catalyst selectivity and activity, i.e., the generation of well-distributed silanol nests, that can be achieved by a basic treatment with aqueous ammonia as described by Kitamura et al. [112]. Later was observed that ϵ -caprolactam selectivity increased by feeding ammonia into the reactor, not affecting the catalyst activity neither the conversion [113].

Recently, Corma and co-workers [114] demonstrated through a combination of solid state NMR spectroscopy and theoretical calculations, that the silanol groups present in zeolites β -D e H- β -D are not acidic enough to perform the acetophenone oxime protonation, whereas the *N* protonation occurs readily over Brønsted acid sites in Al-H- β -D at room temperature. Once that both sites are catalytic active, it was concluded in this study, that there are two possible reaction pathways for this rearrangement, depending on the acid



Scheme 21.

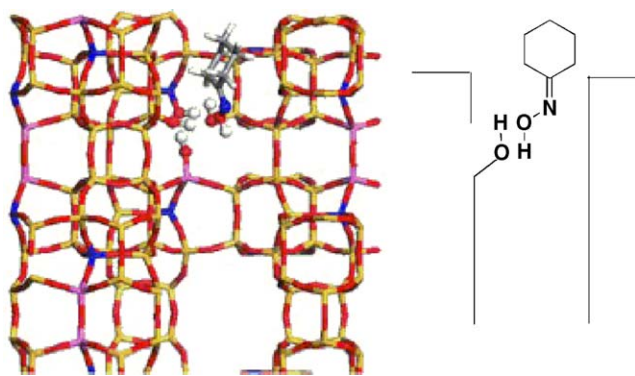


Fig. 2.

strength of the active centre. The reaction conditions and the possibility of different rate-determining steps existence over different active sites were also mentioned.

This theory about the silanol nests importance, was very supported by Ichihashi et al. [107,115], which after methylation of the existent silanol groups (due to the presence of methanol) in the external surface of the MFI zeolite concluded, that terminal silanol were not the active sites toward Beckmann rearrangement, suggesting that, the blocking of terminal silanols was responsible for the high selectivity achieved (up to 95%). Flego and Dalloro [116] elucidated this mechanism recently, pointing the interaction through two neighbour hydroxyls of silanol nests with silicalite-1, facilitating the interaction of the cyclohexanone oxime and cooperating in the rearrangement, one hydroxyl group interacts with the substrate's basic oxygen atom and the other one with both nitrogen and vicinal carbon atom. Other recent mechanistic study, invoking the silanol nests importance, was performed through DFT calculation in which the authors state that the hydrogen bond of silanol nests is the first step for vapour phase Beckmann rearrangement (Fig. 2) [117]. Previously, another study regarding the mechanistic implications was performed grounding in the different reactivity's of H-ZSM-5 (Si/Al = 20), H-ZSM-5 (Si/Al = 54), H-MOR, silicalite and H-ferrierite. The authors proposed the very weak acid sites as the zeolite active sites once that, silicalite-1 with small aluminium content (Si/Al > 1000) does not permit the oxime to penetrate inside the pore, as so, the lactam can only be adsorbed on the ZSM-5 (Si/Al = 20) external surface [118]. Moreover, from all the catalysts tested in vapour phase Beckmann rearrangement, zeolites with weak acid sites like Ca-A, Na, K-clinoptilolite showed the best selectivity towards ϵ -caprolactam (**88**), up to 89%, notwithstanding the low conversions, up to 34%.

Another aspect that influences the Beckmann's rearrangement in silicalite-1, the solvent effect, has been studied. In this study was observed that short hydrocarbon chains like ethanol and methanol are the best solvents for the vapour-phase reaction once that they obstruct the formation of a hydrophobic layer that difficult the oxime's approximation to the active site [119]. In concern to the pore size influence on the zeolite

catalytic activity, Weitkamp and co-workers [120] performed this reaction over α , β and silicalite-1 zeolites. In the case of α zeolite, the substrate adsorption was only observed on the zeolite external surface, due to the small pore size, while in the other two cases, the pores were accessible at temperatures as low as 85 °C. Hence, the authors results are in contrast to the mechanistic considerations previously related that established the lactam-non-capacity of fitting inside the zeolite pore. Moreover, the authors invoked that the proposed mechanism by Sato et al. for smaller zeolites did not explained the selectivity enhancement, justified by the internal zeolite surface contribution to the reaction to a significant degree. Hence, the authors are in agreement with Corma and co-workers [121] relatively to the conversion in liquid phase, with the possibility of the rearrangement taking place completely inside the zeolite or simultaneously in the micropores and at the external surface of the crystallites.

Recently, another study about the silicalite-1 pore size influence was performed [122], with the smaller crystals (2.5 μm) yielding the best conversions after calcination at 450 °C and exchanged in NH_4NO_3 aqueous solution. Considering the ϵ -caprolactam (**88**) selectivity, it was seen that it is directly related with crystal size. The authors pointed out this relation to the different distribution of the silanol groups in internal and external catalyst surfaces, with the H-bonded silanols located in the internal surface being responsible for the Beckmann rearrangement and the terminal silanols distributed on the external surface being responsible for the oxime's non-selective conversion.

About the new developments on the zeolites Beckmann rearrangement field, Holderich and co-workers employed boron-MFI zeolites [123,124], developed by BASF, in the Beckmann's rearrangement vapour-phase reaction by performing a complete study about the influence of temperature, pressure dependence, residence time, solvent effect, water in fixed bed and time on stream, gas flow and water addition in fluidized bed. The conditions investigated to achieve selectivities up to 95% were the best at reduced overall pressure of 0.1 bar and 300 °C. However, the catalyst life was not increased in this conditions, only retarded the deactivation rate by adding water to the reaction mixture with no limitations about the water quantity added, notwithstanding a mass ratio of water and oxime of 1:1 was optimized. When the process was transposed to a fluidized bed of laboratory scale, both selectivity and initial conversions maintained close to the ones obtained in the fixed bed reactor while the catalyst life decreased due to the insufficient mixing of fluidized particles. Later, the same research group determined by a SIMS/XPS study that the catalyst deactivation could be attributed to pore blockage caused by an enrichment of nitrogen-containing species. On the other hand, the formation of this species is caused by oligomerization or polymerization of species like hexene nitriles [125]. Later was observed that the catalyst activity increased by calcination of B-MFI zeolite at 600 °C, mild acidic treatment and mild basic treatment [126]. As well as proposed for silicalite-1, silanol nests and vicinal-bridged

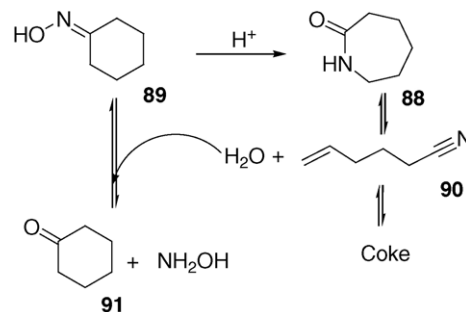
hydroxyl group were proposed to have extremely importance in catalytic performance of B-MFI, moreover a positive influence of boron oxide species on conversion and catalyst time was observed.

Comparing several zeolites, SAPO-11, ALPO_4 -11, silicalite-1 and ZSM-5 with different Si/Al ratio, Singh et al. [127] identified the efficient SAPO-11 with high silica content as the best catalyst tried on the Beckmann's rearrangement (99.88% conversion and 85.72% selectivity), while the use of ZSM-5 with high content in strong acid sites originated the ϵ -caprolactam in low selectivities due to the great amount of fragmentation products. When acidity was decreased and the amount of silanol groups increased, the ϵ -caprolactam selectivity increased like when dealuminated ZSM-5 and silicalite-1 were used. Taking these results in account, the authors point the external surface as the place where the reaction occurs in a higher extent, like was pointed by Sato and Ichihashi [107] for the MFI zeolites catalytic activity and by Holderich and co-workers [125] for B-MFI zeolites. A notorious study about the acid site strength in Beckmann's rearrangement was performed, for zeolites ASA, Y, β , MOR and ZSM-5 changing the Si/Al ratio [128]. When caprolactam yield was plotted against the ratio for Brønsted or Lewis acidity, it can be seen that the best yields were obtained with catalysts that own the smaller strong/weak acid sites ratio. About the catalyst deactivation, Takahashi et al. [129], after testing H-ZSM-5 and boron modified H-ZSM-5 observed that, increasing the amount of strong acid sites increased the catalyst deactivation coefficient. Latter, the same research group studied the pore size as well the acid strength influence on the selectivity towards ϵ -caprolactam formation and the catalyst deactivation rate for MFI type zeolites compared with MOR and Y [130]. When methanol and benzene were used as diluent solvent, it was seen that lowering the acidity (increasing the Si/M ratio, M = Al or Indium) increased the reaction selectivity as so the deactivation factor, on the other hand, increasing pore size caused a decrease on the selectivity as well as a decrease in the catalyst lifetime. According to the authors, the Beckmann's rearrangement mechanism in vapour phase is almost the same as the rearrangement in liquid phase with sulfuric acid catalysis, via the same carbenium ion and the influence of alcohol as the solvent suggests the removal of the lactam produced in the acid sites.

The modified Si-MCM-41 and Al-MCM-41 zeolites with different Si/Al ratios (43.9, 23.3 and 14.3) were tested as catalysts for the Beckmann's rearrangement [131]. The H-Al-MCM-41 acidity was determined by pyridine desorbed beyond 100 °C. The authors observed that increasing the aluminium content, increased the acidity and despite the oxime conversion remained constant, the reaction selectivity improved, hence Al-MCM-41 turns out to be a better catalyst than Si-MCM-41 for this transformation. According to the authors, the Si-MCM-41 silanol groups are not acid enough to catalyse the rearrangement, but they can be responsible for the formation of by-products resulting from

hydrolysis. Comparing the results obtained with the ones observed for the influence of the aluminium content in MFI zeolites, the authors justified the differences on the base of the different strengths of the acid sites of both systems and the relatively small amounts of hydroxyl groups in MFI. With this methodology, using Al-MCM-41 as the catalyst, at 360 °C and a 0.53 h of contact time, was obtained an 87% yield of lactam. Using H-MCM-41 and H-FSM-16 as the catalysts of this reaction, and testing methanol and hexan-1-ol as solvents was seen that the use of hexan-1-ol increased both the selectivity and the conversion (99.8% conversion and 92.0% selectivity for H-MCM-41) [132]. According to Chaudhari et al. [131], this selectivity increased due to the attenuation of the strong acidity by the water formed during the solvent dehydration, while the authors attribute the conversion augment to the use of more polar solvents, like methanol, that can block the contact of the reagent with the zeolite acid sites by competitive adsorption. Maheswari et al. performed the Beckmann's rearrangement for the first time on phosphotungstic acid (PWA)-supported Si-MCM-41 catalyst with an oxime conversion superior to 99% and 75% selectivity towards ϵ -caprolactam using a 30 wt% PWA/Si-MCM-41 at 325 °C, a 10 wt% oxime feed in acetonitrile and $\text{WHSV} = 3.24 \text{ h}^{-1}$ [133].

The first application of MCM-22 as a catalyst in the Beckmann's rearrangement was described emphasizing the great capacity of the zeolite to be recycled [134]. After 40 cycles, the selectivity (ca. 85%) and the conversion (ca. 68%) maintained unchanged, however the results obtained remained below the ones obtained with B-MFI or silicalite-1. Recently, the comparison of (Na,H)-MCM-22 and H-MCM-22, showed that the strength acid sites enriched material originated a better ϵ -caprolactam (**85**) selectivity [135]. With these sites being of major importance in the reaction selectivity, the authors proposed a new mechanism for this transformation over H-MCM-22. The mechanism grounds in three principal reactions, rearrangement reaction of cyclohexanone oxime (**89**), ring opening reaction of ϵ -caprolactam (**88**) and hydrolysis reaction of cyclohexanone oxime (**89**), with the opening of ϵ -caprolactam (**88**) being catalysed by the strong acid sites of MFI zeolites (Scheme 22). Concerning the relation of the catalyst stability and the solvent used, the use of ethanol as the inductor of long life for the catalyst can be due to



Scheme 22.

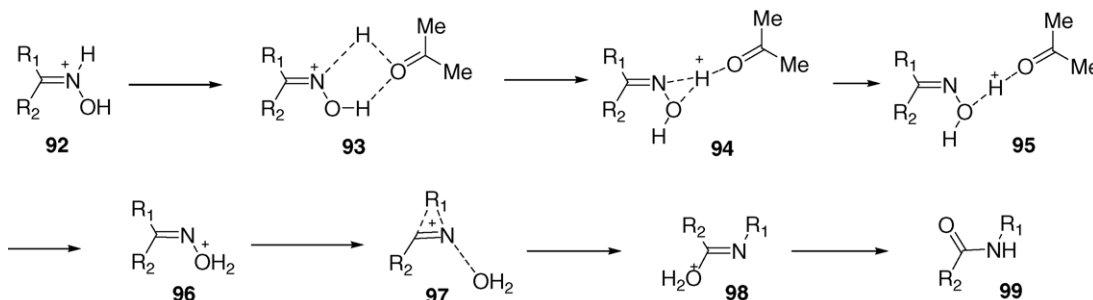
the water formation that inhibit the polymerization of the coke precursors on the catalyst external surface. The temperature influence was determined as being less important in conversion than in selectivity once that, the use of higher temperatures induced the ϵ -caprolactam polymerization and at low temperatures the ϵ -caprolactam desorption on the acid sites occurred, being converted to other products.

There have been several approaches on the use of boron supported as Beckmann's rearrangement catalysts. This structure was already immobilized in Al_2O_3 , TiO_2 , SiO_2 , MgO , H-ZSM-5 and zirconia. This last is until now one of the best supports reported considering both selectivity and conversion in the vapour phase reaction [136]. Comparing all the support types, it was observed that, at 300 °C the B_2O_3 catalysts supported on TiO_2 and H-ZSM-5 deactivate rapidly while the supported on ZrO_2 , SiO_2 and Al_2O_3 are less deactivated. Despite oxime's conversion rapidly decay when the two formers are used, the lactam selectivity remains high (ca. 95%) while the use of SiO_2 and Al_2O_3 supported catalysts a medium lactam selectivity (ca. 70%) is obtained. Recently, as regards to the use of ZSM-5 zeolites, Takahashi and Kai [137] observed that the catalyst life of the modified zeolite with noble metals (like Ru, Rh, Pd, and Pt) is higher than the unmodified zeolite in the Beckmann rearrangement using CO_2 and methanol as the diluent gas and diluent solvent, respectively. Moreover, the use of a small amount of oxygen as the diluent gas improved the catalyst life of the modified zeolite. The deactivation of the unmodified H-ZSM-5 (Si/Al=90) at 400 and 500 °C when catalysing the Beckmann's rearrangement, was described as being caused by the formation of a tetramer at the acid sites in the extra-lattice of the zeolite, with the oligomer formed being a coke precursor that can be removed by polar solvent vapour, such as alcohol or acetonitrile [138]. Previously, when the acid site strength of several zeolites was studied it had already been observed that MCM-41, β and ASA were not extremely affected by the coke formation, whilst Y, ZSM-5 and MOR were highly affected even by small amounts of coke [128].

The use of β zeolite in the Beckmann rearrangement was reported for the first time by Tatsumi and co-workers [139,140] with conversions around 100% and selectivities up to 96% depending on the solvent used. The authors observed that the use of alcohols as diluents improved the selectiv-

ity towards the ϵ -caprolactam formation and that this one linearly increased with the alcohol carbon number yielding the maximum 96% selectivity when hexan-1-ol was used. The use of β zeolite was investigated in its modified form, Holderich and co-workers [141] had synthesised Al- β and B- β and employed them in the Beckmann's rearrangement as so tried to determine the active sites of both catalysts. The authors tried several chemical modifications that return with no better results except when Al- β was treated with an HCl aqueous solution of 0.01 M in which a slightly increase in selectivity was observed. Like previously reported, for the case of H-ZSM-5, the authors attribute the Al- β catalyst activity to the vicinal hydrogen bonded hydroxyls. The boron remove of B- β cause a slightly decrease in both catalyst activity and selectivity.

The solvent effect on the activity of H- β zeolite as a catalyst for the Beckmann's rearrangement in the liquid phase was determined to be dependent of the polarity. Hence, when a polar protic medium is used, the competition between solvent/substrate by the zeolite increases and the selectivity lowers, whereas the use of polar aprotic solvents or even non-polar ones provides some better results [142]. About the reaction mechanism, it was suggested that in the liquid phase the rearrangement's initial step would be the *N*-protonation of the oxime (**92**) and that the 1,2-*H*-shift connecting the two protonated isomers would be more energy-demanding than the consequent rearrangement. An observation of an interaction between *N*-protonated oxime and a polar solvent and the attribution of a catalytic role to the solvent molecules, hypothesise the existence of a quite strong complex formed by the interaction between both elements. The 1,2-*H*-shift is accelerated in this complex by the solvent involvement in the transition state, with this step being the rate determining in solution phase ((**93–95**) Scheme 23) [143,144]. In gas phase reaction on typical oxide catalysts ($\text{SiO}_2\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and ZnO) it was determined by a theoretical study that the transfer of the alkyl group and the elimination of the hydroxyl group of the oxime by interaction with hydrogen of Brønsted site is the rate determining step [145]. In this case, polar and protic solvents originate an increase of activity and selectivity, probably due to absorption of the solvent on the Brønsted acid sites of the zeolite, preventing their contact with the oxime [146].



Scheme 23.

Corma and co-workers [121] performed a study in the liquid phase at 130 °C employing the use of β zeolites with different Si/Al ratios, with and without internal silanol groups, in the Beckmann's rearrangement of three different substrates, cyclohexanone, cyclodecanone and acetophenone oximes. In this study, the authors documented the important observation that demonstrates the non-viability of transpose the results obtained for the vapour phase to the liquid phase, once that in the reaction in liquid phase the Brönsted acid sites are more effective than the silanol groups. With all four catalysts used (β -ND, β -D, H- β -ND and H- β -D) after 24 h reaction time it was only observed the presence of the lactam, starting material, correspondent amide and ketone, and never the presence of side products like aniline or 5-cyanopent-1-ene like which were observed in the most of the reported cases. In an attempt to determine the silanol groups' importance, the results obtained with β -ND (a totally siliceous containing only external silanol groups) and β -D (an all-silica β sample prepared by dealumination of a zeolite with a Si/Al ratio of 800 with internal silanols) were compared. Notwithstanding that in the first case did not return any conversion, when β -D was used 38% conversion and a selectivity superior to 98% towards the ϵ -caprolactam was obtained. Hence, the authors posted the internal silanol groups as being inductors of some selectivity in the liquid phase transformation of oximes towards Beckmann's rearrangement. With the use of introduced Al framework zeolites, H- β -ND, both activity and selectivity were extremely high, demonstrating that the bridging hydroxyl groups are effective and selective in the transformation. Comparing all the results obtained with all the four zeolites, the authors concluded that whilst the internal silanol groups are active and selective in most cases, Brönsted acid sites associated with bridging hydroxyl groups are even more active. Hence, non-acidic silanols preferentially catalyse oxime hydrolysis, whilst weakly acidic and/or internal silanol can either catalyse the Beckmann rearrangement. When H- β , H-LTL, H-OFF-ERI, silicalite-1, H-USY and H-MOR were compared in the vapour phase Beckmann rearrangement, Tatsumi and co-workers [139] observed that zeolites with 12-membered ring structure and weak acidity, increase catalyst life, activity and selectivity towards the ϵ -caprolactam formation with the use of hexan-1-ol as diluent. For instance, the use of H-LTL and H-OFF-ERI as catalysts allowed a ca. 100% conversion and lactam selectivity above 95% for 6 h reaction time, as so in use of H- β .

Also in the use of H-USY zeolites in the vapour phase, the solvent effect was studied as also the Si/Al ratio influence [147]. The use of hexan-1-ol as diluent increases the catalyst activity, and an optimum Si/Al ratio of 27 and 62 was determined for the best activity, selectivity and stability with the by-products formation being retarded. According to the authors, an appropriate amount of relatively weak acid sites is effective to a high selectivity in the Beckmann rearrangement.

The utilization of mesoporous material, FSM-16 and Al_2O_3 /FSM-16, towards the Beckmann's rearrangement was

described with the mesoporous material having four different active sites that catalyse the formation of by-products [148]. According to the authors the four places (A, B, R and α), are divided with the following characteristics; site A is responsible for oximes conversion to yield nitrile, site B catalyses cyclohexanone formation, site R is composed by two components (acidic silanol and basic siloxane) converting the ϵ -caprolactam towards nitrile and site α as being a nitrile adsorption site. If so, the addition of organic acids increases the process' selectivity and the catalyst life. It was seen that selectivity towards ϵ -caprolactam increases when FSM-16 is supporting metal oxides (Al_2O_3 , ZnO and CdO), notwithstanding the presence of strong basic sites that cause the catalyst deactivation [149].

Ferrierite zeolites, after preparation in the presence of non-ionic surfactants at low concentration of pyrrolidine template, were employed in the Beckmann's rearrangement at vapour phase [150]. The temperature study was realized in 300–450 °C range, increasing in oxime conversion but decreasing in selectivity towards the ϵ -caprolactam formation, due to decomposition of formed lactam in the catalyst surface. The space velocity in the fixed-bed down-flow reactor used, showed to be optimum to lactam selectivity at WHSV = 1, once increasing WHSV decreases oxime conversion and increase lactam selectivity. It was observed that lactam selectivity is highly influenced by solvent's dipolar moment, with polar solvents being preferred for the ferrierite catalysts, as so low oxime's concentration and a N_2 feed of 20 mL/min.

For the Beckmann's rearrangement in liquid phase, a novel methodology was developed using two bifunctional transition-metal-ion (framework)-substituted aluminophosphate molecular sieve, $\text{M}^{\text{II}}\text{M}^{\text{III}}\text{AlPO-36}$ ($\text{M} = \text{Co}, \text{Mn}$) catalyst using oxygen (air) and ammonia [151]. This process relies on formation of hydroxylamine in situ inside the pores, conversion of cyclohexanone with NH_2OH inside and outside the cavities, and isomerization of oxime inside the pore. Despite the big advantages of this process, relatively low yields and selectivity were obtained.

6. Conclusion

The preceding review illustrates the use of zeolites and other mesoporous materials as excellent catalysts in preparation of highly valuable heterocycles compounds. Their successful employment in industrial synthetic transformations can be attributed not only to their capacity of immobilize homogenous catalysts rendering them heterogeneous, but also to their thermal stability, the easy separation from the reaction products and their reuse facility in liquid and gas phase conditions. The importance of these materials can be exemplified by the great emphasis that has been attributed by the scientific community to understand and rationalize their properties in the last two decades. Among other topics, it was observed that their singular properties are not only

related to their pore size but more strictly to their Brønsted and Lewis acidity properties. However, some inconvenient can be described, for instance, the common deactivation of the zeolite surfaces, mostly in oxidative processes, that impose the need to calcinate the zeolite at high temperatures. In this topic resides one of the most defying challenges, that consists in develop smoother processes for the reactivation of the mesoporous material without the need to appeal to more expensive processes. The development of new zeolites and mesoporous materials containing other frameworks including the inclusion of complementary reactive metallic catalytic centres localized in specific positions will certainly promote new areas of application more diverse, clean, efficient and specific catalytic synthetic transformations.

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