

# 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

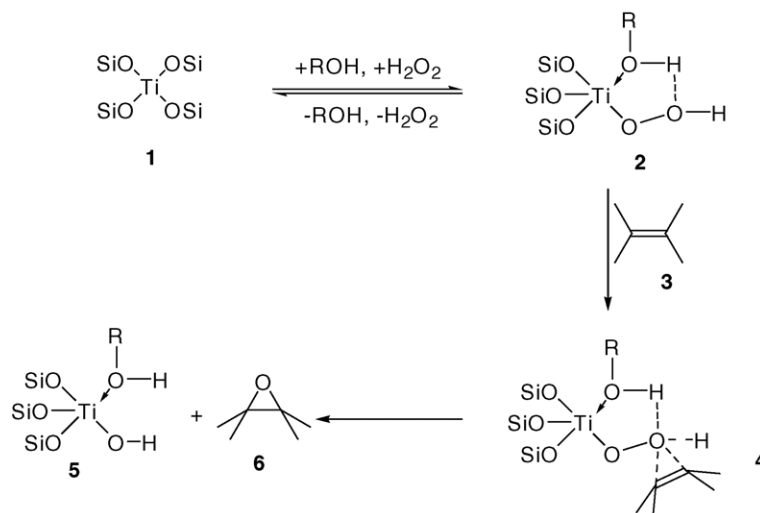
### 2.1. Epoxides

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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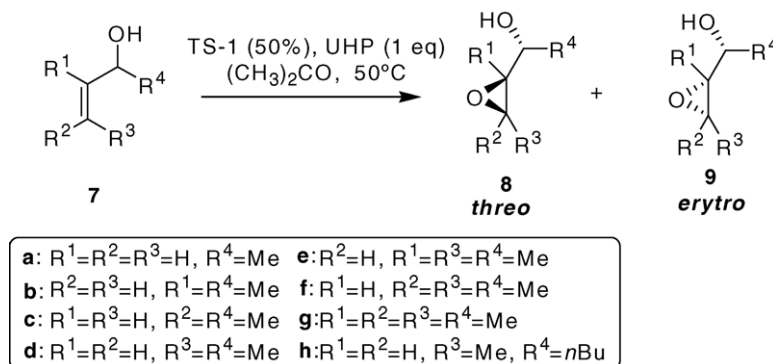
Scheme 1.

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% H<sub>2</sub>O<sub>2</sub> 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 R<sup>3</sup> and R<sup>4</sup>) was present in the substrate (**7**), and that R<sup>1</sup> substituent exerted no significant influence on this diastereoselectivity. In other words, despite that R<sup>1</sup>=R<sup>3</sup>=CH<sub>3</sub>, the *threo* isomer is still obtained in high diastereomer ratio (81:19).



Scheme 2.

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