

# Liquid phase epoxidation of allylic compounds with hydrogen peroxide over titanium silicalite catalysts

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## Abstract

The experimental results of the process of epoxidation of allylic compounds (allyl alcohol, methallyl alcohol and methallyl chloride) to corresponding epoxides with hydrogen peroxide over titanium silicalite: TS-1, TS-2, Ti-beta and Ti-MCM-41 have been presented. The epoxidation was carried out with a 30% hydrogen peroxide in methanol as solvent in an autoclave. The applied epoxidation system allowed to obtain glycidol,  $\beta$ -methylglycidol and  $\beta$ -methylepichlorohydrin with a good selectivity and conversion of allylic compounds in most cases. The major applications of glycidol,  $\beta$ -methylglycidol and  $\beta$ -methylepichlorohydrin have been also presented.

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## 1. Introduction

Olefin epoxidation is one of the main routes lead to the production of epoxides on both the laboratory and industrial scale [1]. Epoxides are very important intermediates for the manufacture of a range of important commercial products including pharmaceuticals and polymers. The epoxidation of allyl alcohol, methallyl alcohol and methallyl chloride with hydrogen peroxide using titanium silicalite catalysts leads to the formation of glycidol,  $\beta$ -methylglycidol and  $\beta$ -methylepichlorohydrin, respectively.

The presence of two functional groups causes that glycidol is a very reactive compound, capable to react both as 1,2-epoxide and as alcohol and due to bi-functionality the glycidol is a raw material in the production of both glycidol derivatives and glycerol. Glycerol is a compound with the hydrophilic properties that also finds the application in the manufacture of the surface-active compounds instead of ethylene oxide, which using requires the application of a high pressure. The surface-active compounds prepared with the

contribution of glycidol have the cleaning and emulsifiable properties, which are included in composition of protective colloids, washing and cleaning agents [2]. These compounds exhibit the disinfecting properties so they are used in the manufacture of cosmetics (shampoo, bath fluids, toothpastes, mouthwashes), pharmaceuticals and pesticides [3] as well as in the composition of electrostatic agents for plastics [4].

$\beta$ -Methylglycidol can be used for the synthesis of compounds having the application in medicine: D<sub>2</sub>- and D<sub>3</sub>-vitamins [5], antitumor products and other immunological disorders [6,7] and biologically active compounds [8].

$\beta$ -Methylepichlorohydrin is used predominantly for the synthesis of epoxy resins, which display the appropriate mechanical, chemical and dielectric properties and a good heat resistance. Obtained epoxy resins are used not only for the production of lacquers, laminates, glues, insulators and parts for chemical apparatus [9] but also for the synthesis of printing inks [10].

Titanium containing silicalites (zeolite catalyst) are the most efficient heterogeneous catalysts for epoxidation reactions and using hydrogen peroxide as an oxidant is an attractive method in the context of green chemistry. Hydrogen peroxide is cheap, readily available and gives water as the

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only by-product whereas heterogeneous catalysts are easily separated from the product mixture and can be recycled. Titanium silicalite can be used for the clean production of fine chemicals, which results in waste minimization, safe and simple operations. One additional advantage of using titanium silicalite catalysts which replaced more dangerous acid catalysts (HF, HCl and H<sub>2</sub>SO<sub>4</sub>) is associated with part elimination of the intermediate stage, which decreases the waste amounts and the other is a lack of corrosion of apparatus. As opposed from the amorphous materials molecular sieves of this type offer many advantages, because they have a uniform surrounding in the form channels and holes with an appropriate shape and magnitude. The location of the active sites on the inner surface of the molecular sieves creates the possibility of the formation of shape-selective catalyst as well as the dimension and a hydrophobic/hydrophilic character of the holes (spaces) redox may be a method for the selection of an appropriate catalyst.

The aim of this work is to determine the optimum parameters of the epoxidation of allylic compounds (allyl alcohol, methallyl alcohol and methallyl chloride) to corresponding epoxides over TS-1, TS-2, Ti-beta and Ti-MCM-41 catalysts. The following parameters were investigated: reaction temperature, the mole ratio allylic compound/H<sub>2</sub>O<sub>2</sub>, methanol concentration, catalyst concentration and reaction time. The values describing the process were: the selectivity of transformation to the epoxide in relation to allylic compound and conversion of allylic compound.

## 2. Experimental

### 2.1. Raw materials

The following raw materials were used in the epoxidation process of allylic compounds: allyl alcohol (>98 wt.%, Fluka), methallyl alcohol (>98 wt.%, Fluka), methallyl chloride (>97 wt.%, Fluka), hydrogen peroxide (30 wt.%, P.O.Ch. Gliwice, Poland) and methanol (Analytical grade, P.O.Ch. Gliwice, Poland).

The TS-1 catalyst was prepared by the method of Thangaraj et al. [11], TS-2 by the method of Reddy et al. [12], Ti-beta by the method of Cambor et al. [13] and Ti-MCM-41 by the method of Grün et al. [14].

### 2.2. Method of epoxidation

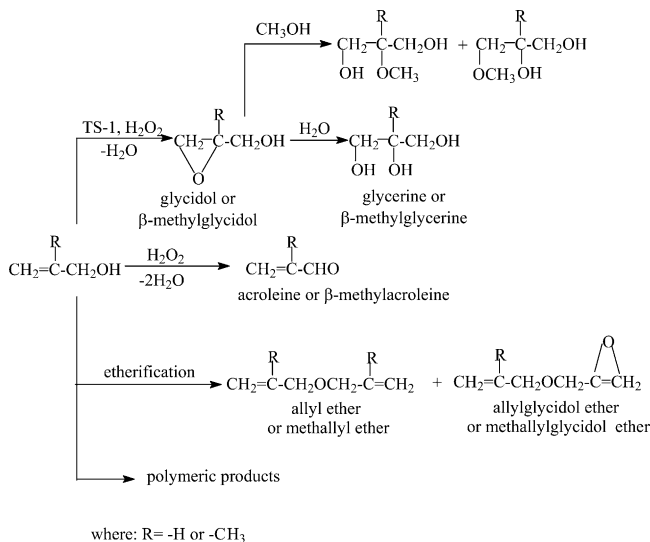
The reagents: allyl alcohol (AA) (methallyl alcohol (MAA) or methallyl chloride (MAC)), methanol, titanium silicalite catalyst and 30 wt.% hydrogen peroxide were placed in a stainless steel autoclave equipped with PTFE insert of 8 cm<sup>3</sup> capacity. The amounts of the reagents were selected in order to obtain the filling ratio of autoclave not exceeding 80%. The autoclave was placed in a shaker holder, fixed and the reaction was performed at the temperature controlled by a thermostat. After completing the reaction the post-reaction mixture was

analysed and the balance of organic mass was performed. The studies were performed over the following ranges of variations of process parameters: temperature 20–120 °C, the mole ratio allylic compound/H<sub>2</sub>O<sub>2</sub> 1–5:1, methanol concentration 5–80 wt.%, catalyst concentration 0.1–2.0 wt.% and reaction time 30–300 min. The starting parameters were the following: the mole ratio allylic compound/H<sub>2</sub>O<sub>2</sub> 1:1, methanol concentration 40 wt.%, catalyst concentration 1.0 wt.% and reaction time 120 min.

The products were quantitatively analyzed by GC method. The determinations were carried out on a Chrom 5 apparatus equipped with a flame ionization detector (FID) with the application of column packed with Chromosorb 101 60/80 mesh. The temperature of the injector amounted to 250 °C, the detector 250 °C and the oven: 170 °C for 14 min, followed by the increase to 200 °C at the rate of 10 °C/min, isothermally for 10 min, subsequently the increase to 220 °C at the rate of 20 °C/min and finally isothermally for 2 min. The quantitative calculations were carried out using a method of the external standard. Glycerol was determined by periodate method [15], whereas hydrogen peroxide consumption was measured by iodometric titration [16]. After the mass balance was performed, the parameters characterising the process (selectivity of transformation to the epoxide in relation to allylic compound and the conversion of allylic compound) were calculated.

## 3. Results and discussion

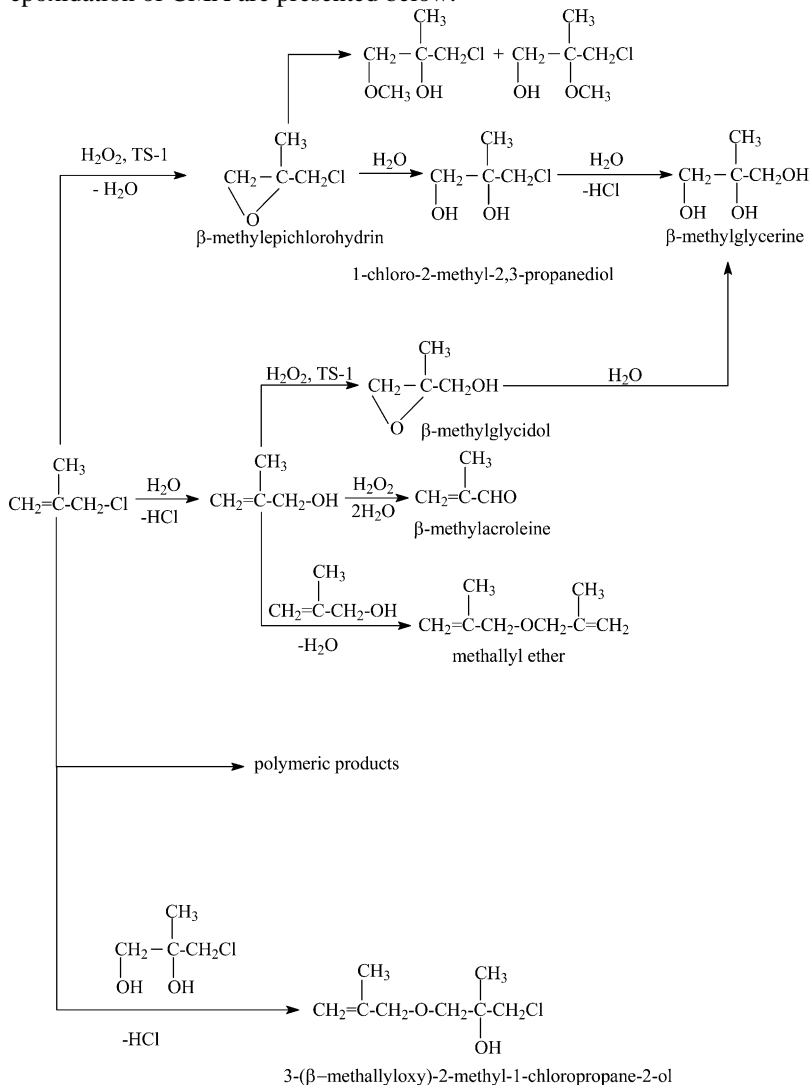
The principal and side reactions proceeding during the epoxidation of AA and MAA can be presented as follows:



Glycidol (epoxidation of AA) and β-methylglycidol (epoxidation of MAA) are the principle products in this process. Glycidol and β-methylglycidol may be secondarily hydrolyzed to glycerine and β-methylglycerine through the epoxide ring opening reaction. Glycidol and β-methylglycidol also undergo solvolysis to form glycerine and

$\beta$ -methylglycerine ethers and other products in insignificant amounts.

The principal and side reactions proceeding during the epoxidation of CMA are presented below:



As a result of the epoxidation of MAC with hydrogen peroxide  $\beta$ -methylepichlorohydrin and 1-chloro-2-methyl-2,3-propanediol were obtained as the major products. The other by-products are formed in insignificant amounts.

In Table 1 are presented optimum conditions of the epoxidation of allylic compounds using titanium silicalite catalysts (TS-1, TS-2, Ti-beta and Ti-MCM-41) and the function

Table 1  
Optimum conditions of the epoxidation of allylic compounds (AC) using titanium silicalite catalysts

	Allyl alcohol	Methallyl alcohol	Methallyl chloride
TS-1			
(a) Temperature ( $^{\circ}$ C)	20	20	20
(b) Allylic compound/ $\text{H}_2\text{O}_2$ molar ratio	1	2	1
(c) Methanol concentration (wt.%)	80	90	40
(d) Catalyst concentration (wt.%)	1	0.1	2
(e) Reaction time (h)	1	0.5	1 (5)
(f) Epoxide selectivity/allylic compound (%)	93.6	59.2	92.6 (75.6) <sup>a</sup>
(g) Conversion of allylic compound (%)	68.9	15.2	15.4 (47.1) <sup>a</sup>
TS-2			
(a) Temperature ( $^{\circ}$ C)	20	20	20
(b) Allylic compound/ $\text{H}_2\text{O}_2$ molar ratio	1	1	1

values, which the best describing this process: selectivity transformation of allylic compound to the epoxide and conversion of allylic compound.

Table 1 (Continued)

	Allyl alcohol	Methallyl alcohol	Methallyl chloride
(c) Methanol concentration (wt.%)	80	40	40
(d) Catalyst concentration (wt.%)	0.1	0.1	1
(e) Reaction time (h)	1	5	0.5
(f) Epoxide selectivity/allylic compound (%)	88.4	39.0	83.3
(g) Conversion of allylic compound (%)	97.7	7.30	13.6
<b>Ti-beta<sup>b</sup></b>			
(a) Temperature (°C)	20	80	–
(b) Allylic compound/H <sub>2</sub> O <sub>2</sub> molar ratio	1	1	–
(c) Methanol concentration (wt.%)	80	40	–
(d) Catalyst concentration (wt.%)	0.5	1.0	–
(e) Reaction time (h)	1	3	–
(f) Epoxide selectivity/allylic compound (%)	82.3	50.0	–
(g) Conversion of allylic compound (%)	87.7	6.7	–
<b>Ti-MCM-41<sup>b</sup></b>			
(a) Temperature (°C)	20	100	–
(b) Allylic compound/H <sub>2</sub> O <sub>2</sub> molar ratio	1	1	–
(c) Methanol concentration (wt.%)	40	5	–
(d) Catalyst concentration (wt.%)	1	1	–
(e) Reaction time (h)	0.5	2.0	–
(f) Epoxide selectivity/allylic compound (%)	10.0	61.70	–
(g) Conversion of allylic compound (%)	17.0	16.9	–

<sup>a</sup> The best results from the point of view of the conversion of methallyl chloride.

<sup>b</sup> Methallyl chloride do not react with H<sub>2</sub>O<sub>2</sub> over Ti-beta and Ti-MCM-41 catalysts.

The best results were obtained for titanium silicalite catalysts: TS-1 and TS-2 in case of all allylic compounds. Ti-beta and Ti-MCM-41 catalysts only catalyze epoxidation of allyl and methallyl alcohol. The results obtained over Ti-beta catalyst for allyl alcohol are close to that obtained for this allylic compound over TS-1 and TS-2 catalysts. Table 1 result that with the increase of pores diameter the catalysts selectivity transformation to epoxide and conversion of allylic compounds decreases. Probably, the presence of large quantity water and methanol molecules in the pore system causes that the active centres (Ti) are not easily accessible.

#### 4. Conclusions

The epoxidation of allylic compounds with hydrogen peroxide is an example of new trends in modern organic technologies. This is a low-tonnage technology (fine chemistry), fulfilling the requirements green chemistry. The advantages of this technology are associated with easy recovery and regeneration of the heterogenous zeolite catalyst. The employment of very mild conditions (low process temperature up to 120 °C, autogenic pressure) is very attractive. Organic reagents used in this process together with protic solvent (methanol) can be recovered by distillation and recycled to the process. A high selectivity of transformation in relation to

consumed organic reagents allows decreasing the quantity of by-products. Numerous applications of epoxides create the prospects of implementation of this technology.

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