

# The utilization of the mesoporous Ti-SBA-15 catalyst in the epoxidation of allyl alcohol to glycidol and diglycidyl ether in the water medium

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This work presents the studies on the optimization the process of allyl alcohol epoxidation over the Ti-SBA-15 catalyst. The optimization was carried out in an aqueous medium, wherein water was introduced into the reaction medium with an oxidizing agent (30 wt% aqueous solution of hydrogen peroxide) and it was formed in the reaction medium during the processes. The main investigated technological parameters were: the temperature, the molar ratio of allyl alcohol/hydrogen peroxide, the catalyst content and the reaction time. The main functions the process were: the selectivity of transformation to glycidol in relation to allyl alcohol consumed, the selectivity of transformation to diglycidyl ether in relation to allyl alcohol consumed, the conversion of allyl alcohol and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. The analysis of the layer drawings showed that in water solution it is best to conduct allyl alcohol epoxidation in direction of glycidol (selectivity of glycidol 54 mol%) at: the temperature of 10–17°C, the molar ratio of reactants 0.5–1.9, the catalyst content 2.9–4.0 wt%, the reaction time 2.7–3.0 h and in direction of diglycidyl ether (selectivity of diglycidyl ether 16 mol%) at: the temperature of 18–33°C, the molar ratio of reactants 0.9–1.65, the catalyst content 2.0–3.4 wt%, the reaction time 1.7–2.6 h. The presented method allows to obtain two very valuable intermediates for the organic industry.

**Keywords:** glycidol, diglycidyl ether, Ti-SBA-15 catalyst, allyl alcohol epoxidation, hydrogen peroxide.

## INTRODUCTION

The processes of allylic compounds epoxidation over titanium silicalite catalysts are very popular among researchers<sup>1–2</sup>. This is due to the fact that in the presence of titanium silicalite catalysts, these processes can be conducted in mild conditions (at a low temperature and at an atmospheric pressure) and using a cheap and easily accessible oxidizing agent - hydrogen peroxide. Moreover, another benefit associated with the use of hydrogen peroxide as an oxidizer is that the only product of this compound conversion is water. Until now, processes of allylic compounds epoxidation were performed over the following titanium silicalite catalysts: TS-1, TS-2, Ti-Beta, Ti-MWW, Ti-MCM-41 and Ti-MCM-48<sup>3–9</sup>. The epoxidation process over these catalysts was mainly conducted in methanol as a solvent. Water was not considered as an attractive medium for the epoxidation processes due to hydrolysis of the epoxide ring, which reduced selectivity of transformation into the epoxy compound and resulted in the formation of diol (for allyl alcohol it was glycerol) which is of much less practical importance. Furthermore, when it comes to mesoporous titanium silicalite catalysts (Ti-MCM-41 and Ti-MCM-48), the structure of these catalysts was disintegrated in the aqueous medium and at elevated temperature. Thus, researchers started looking for new titanium silicalite catalysts that would be stable (taking into account both the disintegration of the structure and the titanium leaching). This resulted in the discovery of the Ti-MWW and the Ti-SBA-15 materials. The latter material is a mesoporous catalyst with pore walls of greater thickness than Ti-MCM-41. What is more, the main channels in the structure of this catalyst

are connected to each other with additional ones, which reinforce the whole structure<sup>10–13</sup>. Taking into consideration the structure of the catalyst, it can be very active in epoxidation processes that are conducted in aqueous medium. Moreover, a large advantage associated with its use may be the fact that there will be a possibility to use it in this process longer when compared to older titanium silicalite catalysts. Our studies also show that the mesoporous material Ti-SBA-15 is much more stable, taking into account the leaching of titanium from its structure in the process of epoxidation. This is a great advantage considering the need to recover it from the reaction mixture and periodical regeneration.

The earlier studies on the epoxidation of allyl alcohol over TS-1, TS-2, Ti-Beta, Ti-MWW, Ti-MCM-41 and Ti-MCM-48 catalysts showed that diglycidyl ether was not present in the post-reaction mixtures, independent on used catalyst and solvent (methanol, acetonitrile or water). Our studies show that this compound is one of the main by-products in this process in the presence of water as a solvent when the epoxidation is performed over newest titanium silicalite catalyst Ti-SBA-15. Establishing the most beneficial conditions of glycidol and diglycidyl ether obtaining is very important problem because these compounds have a lot of applications in organic industry. Glycidol is used for the production of surface active agents which are included in the composition of: cosmetic formulation for moistening and cleaning of skin, shampoo and toothpaste. Other groups of glycidol applications include dispersive agents, plasticizers for resins and rubber and the detergents in petroleum industry<sup>14–18</sup>. Diglycidyl ether has utilization: in production of linear, branched and cyclic oligoglycerols

used in the production of surfactants<sup>19</sup>, in preparation of anti-arrhythmia agents<sup>20</sup>, in production of component of other pharmaceuticals and medicines, for example cryptands<sup>21-22</sup>, in preparation of lubricating oil additives<sup>23</sup>, in the synthesis of aminoethers<sup>24</sup>.

The aim of this work was the establishing of the most beneficial conditions for carrying out the process of allyl alcohol epoxidation over the Ti-SBA-15 catalyst and in aqueous medium, but water was only introduced into reaction medium with 30 wt% hydrogen peroxide or it was formed during the process. The established the most beneficial conditions should allow to obtain the most useful products of this process (glycidol and diglycidyl ether) with the highest selectivities.

## EXPERIMENTAL

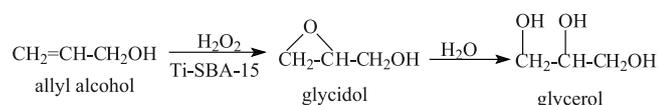
Catalyst Ti-SBA-15 was obtained by the method described in the literature<sup>13</sup>. The full description of the catalyst was presented in our previous work<sup>9</sup>.

In the epoxidation of allyl alcohol the following raw materials were used: allyl alcohol (98%, Fluka) and hydrogen peroxide (30 wt% water solution, POCH Gliwice). The process was carried out in a glass vial with the capacity of 12 cm<sup>3</sup> equipped with a rubber septum and a capillary. The vials were located in a shaker holder and immersed in a water bath.

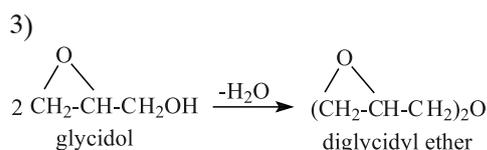
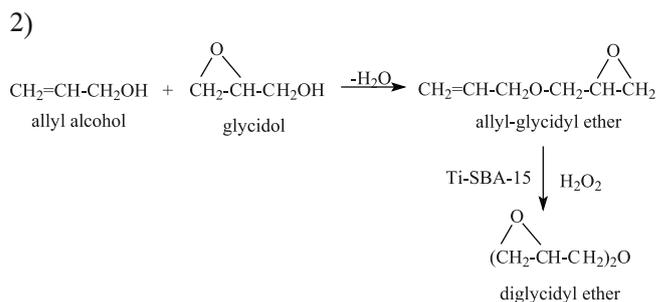
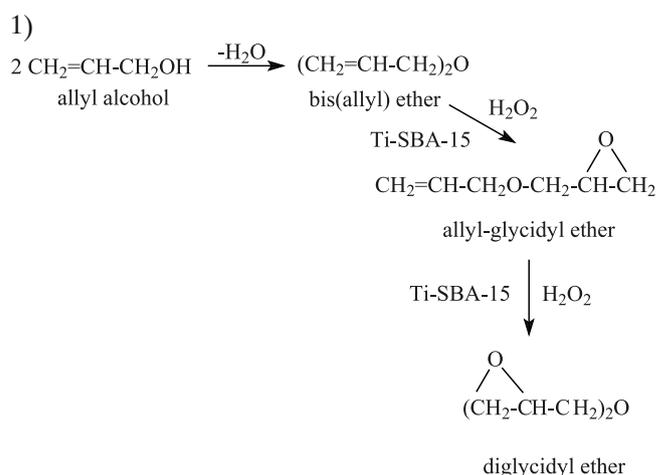
In order to calculate the mass balance, the post-reaction mixtures were analyzed in the following way: unreacted hydrogen peroxide was determined by means of iodometric method<sup>25</sup>, glycerol formed in the process was determined by means of potentiometric method<sup>26</sup>. The remaining products and the unreacted organic substrate were analyzed by means of gas chromatography. The chromatographic analyses were performed on the FOCUS apparatus with a flame-ionization detector (FID) fitted with Quadrex capillary columns filled with methyl-phenyl-siloxanes. The parameters of chromatographic separation were as follows: the pressure of helium 50 kPa, sensitivity 10, the temperature of the sample chamber 150°C, the detector temperature 250°C, the temperature of the thermostat was increasing according to the following program: isothermally at 40°C for 3 minutes, an increase to 250°C at the rate of 10°C/min, isothermally at 250°C for 5 minutes, cooling to 60°C.

## RESULTS AND DISCUSSION

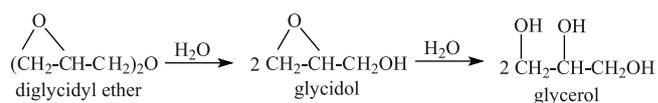
During the process of allyl alcohol epoxidation as a main product glycidol is formed. But this epoxide compound undergoes very easy a hydration in reaction conditions. These transformations can be described as follows:



One of the main by-products of this process is diglycidyl ether. Taking into account the results obtained in this work and in our previous works<sup>3, 9</sup>, the possible three ways of diglycidyl ether forming can be presented:



During the process also the decomposition of ethers undergoes, especially diglycidyl ether. The decomposition of this compound is probably also connected with hydration of epoxide rings and formation of glycerol. The reactions of diglycidyl ether decomposition and in the next step hydration are presented below:



The reactions presented above show that the studied process is very complicated and for its description very complex method should be used, for example mathematical optimization.

The optimization of the technological parameters of allyl alcohol epoxidation (AA) in the presence of water and over Ti-SBA-15 catalyst was conducted using a rotatable-uniform design<sup>27-30</sup>. Experiments were planned and calculations were made using computer software Cadex: Esdet 2.2.<sup>31</sup>. The design was carried out for four input values  $x_1-x_4$  (process parameters):  $x_1$  – temperature 10–40°C,  $x_2$  – molar ratio of AA/H<sub>2</sub>O<sub>2</sub> 0.5 – 2.0,  $x_3$  – content of catalyst Ti-SBA-15 2.0–4.0 wt% and  $x_4$  – reaction time of 1–3 h.

The total number of experiments was 31. The real values of the input values  $x_1-x_4$  were converted into the coded values (non-dimensional). Thanks to the normalization process, a universal design with values of the input values normalized in a non-dimensional interval [-2, 2] was obtained. Table 1 shows the input values and

**Table 1.** The levels of the examined variables for the process of AA epoxidation in the presence of water

| Level       | Coded variables | Temperature [°C] | Molar ratio AA/H <sub>2</sub> O <sub>2</sub> | Ti-SBA-15 content [wt%] | Reaction time [h] |
|-------------|-----------------|------------------|--|-------------------------|-------------------|
|             | X <sub>i</sub>  | x <sub>1</sub>   | x <sub>2</sub>                               | x <sub>3</sub>          | x <sub>4</sub>    |
| Basic       | 0               | 25               | 1.3  | 3.0                     | 2                 |
| Higher      | 1               | 33               | 1.6  | 3.5                     | 2.5               |
| Lower       | -1              | 18               | 0.9  | 2.5                     | 1.5               |
| Star higher | 2               | 40               | 2.0  | 4.0                     | 3                 |
| Star lower  | -2              | 10               | 0.5  | 2.0                     | 1                 |

the normalized input values at levels resulting from the rotatable-uniform design.

The following functions were accepted as response functions: z<sub>1</sub> – selectivity of transformation to glycidol in relation to AA consumed (S<sub>gly/AA</sub>), z<sub>2</sub> – selectivity of transformation to diglycidyl ether in relation to AA consumed (S<sub>DGE/AA</sub>), the conversion of AA (C<sub>AA</sub>) and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (S<sub>org. com./H<sub>2</sub>O<sub>2</sub></sub>).

Table 2 shows a design matrix in a form of normalized values and the real values of response functions z<sub>1</sub>-z<sub>4</sub> obtained experimentally.

The influence of normalized independent factors (X<sub>1</sub>:X<sub>4</sub>) in the process of allyl alcohol epoxidation on the value of the response function is presented with the second-degree algebraic polynomial:

$$Z = Z(X_k) = b_0 + b_1 * X_1 + \dots + b_i * X_i + b_{11} * X_1^2 + \dots + b_{ii} * X_i^2 + b_{12} * X_1 * X_2 + \dots + b_{i-1,i} * X_{i-1} * X_i$$

for X<sub>k</sub> ∈ [-2, 2], where: b<sub>i</sub> – normalized coefficient of the approximation function;

N<sub>b</sub> – the number of polynomial coefficients; N<sub>b</sub> = 0,5 \* (i + 1) \* (i + 2), i – the number of the input variables X<sub>k</sub>; k=1,2,...,i

To obtain response functions containing the real factors of an approximating function and the real input variables x<sub>k</sub> (technological parameters), normalized values of input variables X<sub>k</sub> were converted into real using the following formulas: X<sub>1</sub> = 0.13\*(x<sub>1</sub>-10)-2, X<sub>2</sub> = 2.67\*(x<sub>2</sub>-0.5)-2, X<sub>3</sub> = 2\*(x<sub>3</sub>-2)-2, X<sub>4</sub> = 2\*(x<sub>4</sub>-1)-2.

The factors of regression equations for normalized input variables were determined over the least squares method, using the matrix analysis (Table 3). After determining the function that approximated the results of measurements, the adequacy of the obtained function was verified based on the Fisher-Snedecor test by comparing them with the critical value of F (0.05) read from the tables<sup>32</sup>. Moreover, relative errors of approximation and multidimensional correlation coefficients (R) were calculated for each function. Table 3 shows the values of factor R and Δz<sub>max</sub> – the maximum error of approximation. In Table 3 are also given the values of: S<sup>2</sup><sub>repeat</sub> – variance of inaccuracy, f<sub>repeat</sub> – freedom degrees number of variance of inaccuracy, S<sup>2</sup><sub>adeq</sub> – variance of adequacy and f<sub>adeq</sub> – freedom degrees number of variance of adequacy.

The maxima of the obtained regression equations were determined mathematically using computer software Cadex Esdet 2.2<sup>33</sup>. The calculations included the methods

**Table 2.** Design matrix and experimental results (for the response functions z1-z2)

|    | X <sub>1</sub> | X <sub>2</sub> | X <sub>3</sub> | X <sub>4</sub> | S <sub>gly/AA</sub> | S <sub>DGE/AA</sub> | C <sub>AA</sub> | S <sub>org. com./H<sub>2</sub>O<sub>2</sub></sub> |
|----|----------------|----------------|----------------|----------------|---------------------|---------------------|-----------------|---|
|    |                |                |                |                | [mol%]              |                     |                 |   |
| 1  | 1              | -1             | -1             | -1             | 10                  | 0                   | 60              | 53  |
| 2  | 1              | -1             | -1             | -1             | 20                  | 0                   | 55              | 51  |
| 3  | -1             | 1              | -1             | -1             | 15                  | 0                   | 28              | 46  |
| 4  | 1              | -1             | -1             | 1              | 22                  | 0                   | 31              | 55  |
| 5  | 1              | 1              | -1             | -1             | 9                   | 0                   | 59              | 55  |
| 6  | 1              | -1             | 1              | -1             | 11                  | 0                   | 56              | 54  |
| 7  | -1             | 1              | 1              | -1             | 10                  | 0                   | 37              | 51  |
| 8  | 1              | 1              | 1              | -1             | 17                  | 0                   | 31              | 51  |
| 9  | -1             | -1             | -1             | 1              | 15                  | 11                  | 71              | 68  |
| 10 | 1              | -1             | -1             | 1              | 9                   | 0                   | 53              | 48  |
| 11 | -1             | 1              | -1             | 1              | 20                  | 0                   | 39              | 58  |
| 12 | 1              | 1              | -1             | -1             | 11                  | 0                   | 32              | 49  |
| 13 | -1             | -1             | 1              | 1              | 18                  | 0                   | 53              | 58  |
| 14 | 1              | -1             | 1              | 1              | 8                   | 0                   | 52              | 48  |
| 15 | -1             | 1              | 1              | 1              | 24                  | 0                   | 36              | 50  |
| 16 | 1              | 1              | 1              | 1              | 13                  | 0                   | 25              | 42  |
| 17 | -2             | 0              | 0              | 0              | 22                  | 0                   | 40              | 58  |
| 18 | 2              | 0              | 0              | 0              | 9                   | 18                  | 38              | 49  |
| 19 | 0              | -2             | 0              | 0              | 17                  | 0                   | 96              | 52  |
| 20 | 0              | 2              | 0              | 0              | 18                  | 19                  | 30              | 61  |
| 21 | 0              | 0              | -2             | 0              | 15                  | 0                   | 44              | 51  |
| 22 | 0              | 0              | 2              | 0              | 10                  | 15                  | 47              | 58  |
| 23 | 0              | 0              | 0              | -2             | 12                  | 0                   | 37              | 49  |
| 24 | 0              | 0              | 0              | 2              | 10                  | 15                  | 45              | 59  |
| 25 | 0              | 0              | 0              | 0              | 9                   | 15                  | 44              | 59  |
| 26 | 0              | 0              | 0              | 0              | 9                   | 17                  | 40              | 57  |
| 27 | 0              | 0              | 0              | 0              | 8                   | 16                  | 44              | 58  |
| 28 | 0              | 0              | 0              | 0              | 9                   | 17                  | 44              | 59  |
| 29 | 0              | 0              | 0              | 0              | 8                   | 16                  | 44              | 58  |
| 30 | 0              | 0              | 0              | 0              | 8                   | 16                  | 41              | 60  |
| 31 | 0              | 0              | 0              | 0              | 8                   | 16                  | 41              | 60  |

**Table 3.** Coefficients of the regression equations Z1-Z2 and results of statistical analyses

|                                  | Z <sub>1</sub> | Z <sub>2</sub> | Z <sub>3</sub> | Z <sub>4</sub> |
|----------------------------------|----------------|----------------|----------------|----------------|
| b <sub>00</sub>                  | 8.43*          | 16.14          | 42.57*         | 58,710*        |
| b <sub>01</sub>                  | -1.46*         | 1.00*          | -2.17*         | -2,380*        |
| b <sub>02</sub>                  | 1.38*          | 1.08*          | -13.83         | -0,630*        |
| b <sub>03</sub>                  | -0.88*         | 0.75*          | -0.58          | -0,290         |
| b <sub>04</sub>                  | 0.04           | 1.75*          | 0.83           | 1,040*         |
| b <sub>11</sub>                  | 1.84*          | -3.06*         | -1.26*         | -1,610*        |
| b <sub>12</sub>                  | -0.19          | 0.75*          | 0.38           | 1,560*         |
| b <sub>13</sub>                  | -0.81*         | 0.75*          | 0.38           | 0,190          |
| b <sub>14</sub>                  | -3.81*         | -0.75*         | -1.63*         | -3,310*        |
| b <sub>22</sub>                  | 2.34*          | -2.93*         | 4.73*          | -0,980*        |
| b <sub>23</sub>                  | -0.19          | 0.75*          | 1.13*          | -0,560         |
| b <sub>24</sub>                  | 0.19           | -0.75*         | 0.38           | -0,810*        |
| b <sub>33</sub>                  | 1.09*          | -3.43*         | 0.36           | -1,360*        |
| b <sub>34</sub>                  | 0.81*          | -0.75*         | -2.38*         | -1,940*        |
| b <sub>44</sub>                  | 0.71*          | -3.43*         | -0.77          | -1,610*        |
| S <sup>2</sup> <sub>repeat</sub> | 0.29           | 0.48           | 3.29           | 1,24           |
| F <sub>repeat</sub>              | 6.00           | 6.00           | 6.00           | 6,00           |
| S <sup>2</sup> <sub>adeq</sub>   | 4.82           | 54.63          | 18.64          | 16,35          |
| F <sub>adeq</sub>                | 15.00          | 15,00          | 15.00          | 15,00          |
| R                                | 0.95           | 0.76           | 0.97           | 0,85           |
| Δz <sub>max</sub>                | 3.88           | 12.42          | 6.83           | 7,46           |

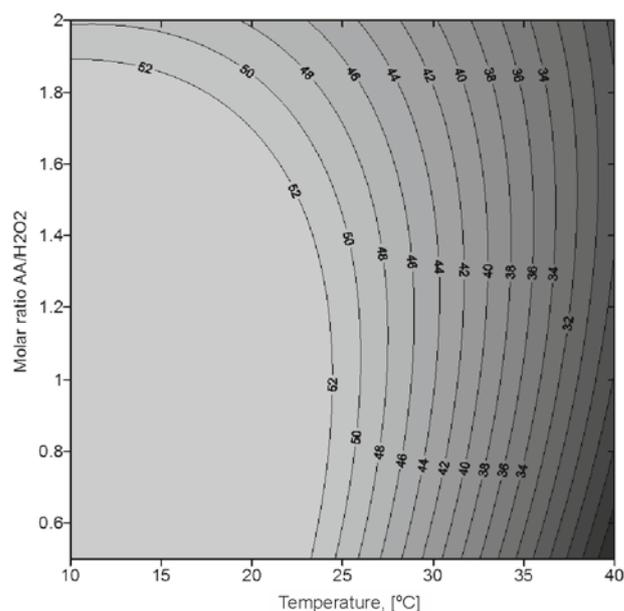
\*essentials coefficients

by Hooke-Jeeves and Gauss-Seidel. The maximum values of independent variables for a given regression function marked using these methods were identical. Table 4 shows maximum values of response functions z<sub>1</sub>-z<sub>2</sub> and the corresponding real values of independent variables.

#### The selectivity of transformation to glycidol in relation to AA consumed (z<sub>1</sub>)

The influence of changes of two selected parameters on the selectivity of transformation to glycidol in relation to AA consumed (z<sub>1</sub>) at optimal values of the remaining parameters that allow obtaining the maximum value of the tested function is shown in Figures 1–3 (contour drawings).

Table 4 shows that the optimal parameters that allow achieving the highest value of the selectivity of glycidol (54 mol%) are as follows: temperature of 11°C, molar ratio of reactants of 1.8, catalyst content of 3.9 wt% and reaction time of 2.9 h. A detailed analysis of Figure 1 shows that for the temperatures in the range of 10–23°C, it is the best to operate within the range of molar ratios of reactants ranging from about 0.5 to 1.9. At these low temperatures and within this range of molar ratios of reactants the glycidol molecules are probably more stable in reaction medium and resistant to the reaction with water molecules. Additionally, for the molar ratios of AA/H<sub>2</sub>O<sub>2</sub> above 1.0 to 1.9, the excess of AA molecules causes that the molecules of glycidol can be surrounded by AA molecules and probably because of this phenomenon the epoxide rings are not opened so fast. On the other hand, the increasing of temperature causes that the tendency of the opening of the epoxide ring raises and at the temperatures above about 25°C, the selectivity of glycidol decreases practically independent



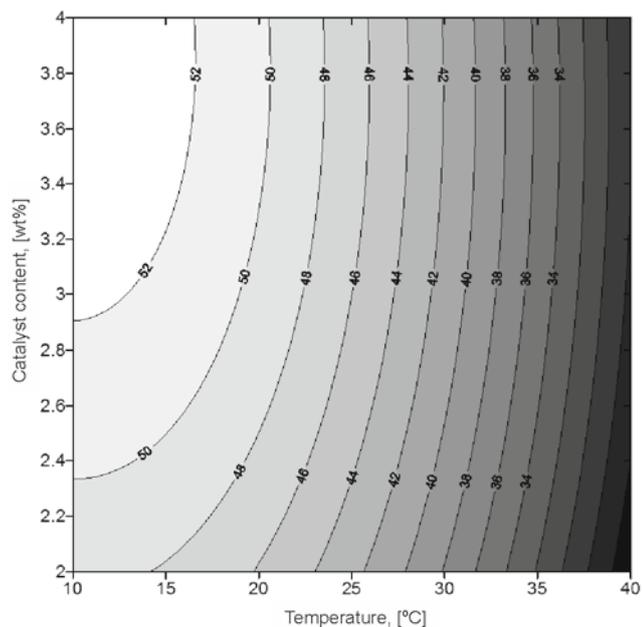
**Figure 1.** The influence of the technological parameters on the selectivity of transformation to glycidol in relation to AA consumed – the dependence of temperature and molar ratio of AA/hydrogen peroxide (the content of Ti-SBA-15 3.9 wt%, reaction time 2.9 h)

on the molar ratio of AA/hydrogen peroxide. It shows that at higher temperatures, the utilization of the molar ratios of AA/hydrogen peroxide above 1 has probably a slighter influence on the stability of glycidol molecules and thus water molecules have easy access to epoxide ring of glycidol. As a result of this situation glycerol is formed in higher amount in post-reaction mixtures.

**Table 4.** Parameters determining maximum values of the response functions

| Functions                                    |        | S <sub>glyl/AA</sub> | S <sub>DGE/AA</sub> | C <sub>AA</sub> | S <sub>org.com./H<sub>2</sub>O<sub>2</sub></sub> |
|--|--------|----------------------|---------------------|-----------------|--|
| Maximum values of the response function      | [mol%] | 54                   | 16                  | 100             | 73   |
| Temperature                                  | [°C]   | 11                   | 28                  | 19              | 11   |
| Molar ratio AA/H <sub>2</sub> O <sub>2</sub> |        | 1.8                  | 1.4                 | 0.5             | 0.7  |
| Ti-SBA-15 content                            | [wt%]  | 3.9                  | 3.1                 | 2.0             | 2.3  |
| Reaction time                                | [h]    | 2.9                  | 2.0                 | 2.9             | 3.0  |

Figure 2 shows that at the temperature range of 10–17°C, when conducting the process with a content of catalyst Ti-SBA-15 from 2.9–4.0 wt%, we should always get the selectivity of glycidol of about 54 mol%. The rising of temperature to 40°C decreases the selectivity of glycidol to about 25 mol%, practically independent on the content of the Ti-SBA-15 catalyst. The performing the process of AA epoxidation at the temperature of 20°C allows to achieve a little lower value of the selectivity of glycidol – about 47 mol%.

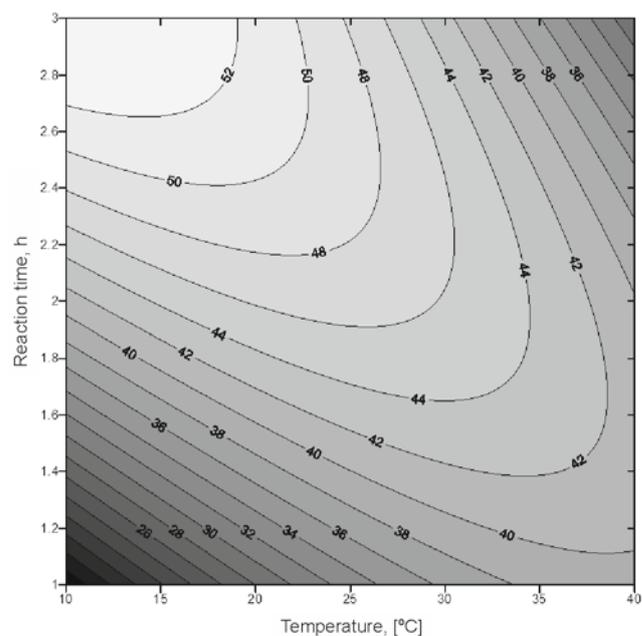


**Figure 2.** The influence of the technological parameters on the selectivity of transformation to glycidol in relation to AA consumed – the dependence of temperature and the content of Ti-SBA-15 (the molar ratio AA/hydrogen peroxide 1.8, reaction time 2.9 h)

Figure 3 shows that at the temperatures from 10°C to about 18°C, when we conduct the process at the reaction time 2.7 up to 3.0 h, we can obtain the highest value of selectivity of glycidol – 54 mol%. The raising of the temperature from 18°C to 25°C for the reaction time above 2 h causes slight changes in values of the selectivity of glycidol (from 54 mol% to 44–46 mol%). The performing the process at the temperatures of 10–25°C for the reaction time 1–2 h allows to obtain the selectivity of glycidol from 16 mol% to 46 mol%. For the temperatures from 25°C to 40°C and the reaction time to 2 h the changes in values of the selectivity of glycidol are lower (from 34 to 46 mol%). For the higher temperatures (25°C to 40°C) and for longer reaction time (from 2 h to 3 h) the changes of the selectivity of glycidol are similar. Generally, the lower temperatures and the reaction time above 2 h is the most beneficial to perform the process of epoxidation, because at lower temperatures the hydration of epoxide ring proceeds slower.

#### The selectivity of transformation to diglycidyl ether in relation to AA consumed ( $z_2$ )

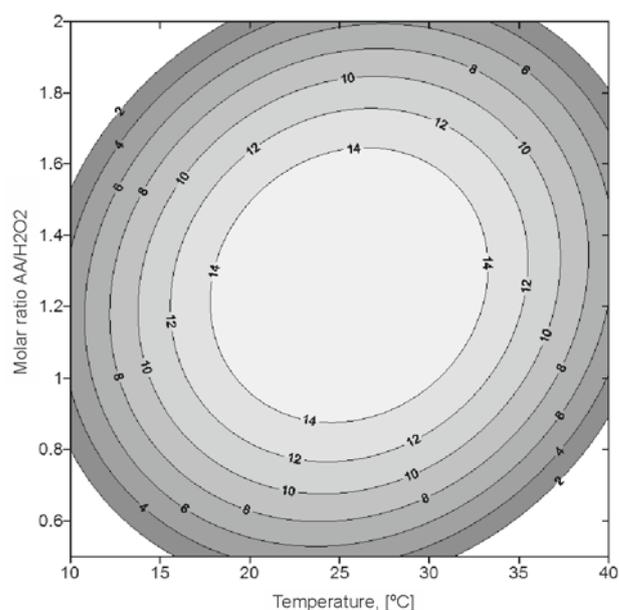
The influence of changes of two chosen parameters on the selectivity of diglycidyl ether ( $z_2$ ) at optimal values of the remaining parameters that allow obtaining the



**Figure 3.** The influence of the technological parameters on the selectivity of transformation to glycidol in relation to AA consumed – the dependence of temperature and reaction time (the molar ratio AA/hydrogen peroxide 1.8, the content of Ti-SBA-15 3.9 wt%)

maximum value of the tested function is presented in Figures 4–6.

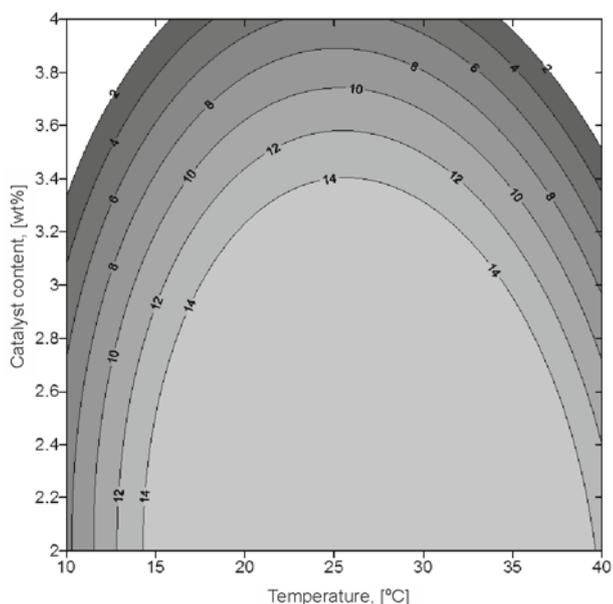
Table 4 shows that the most favorable conditions for the epoxidation of allyl alcohol in the direction of diglycidyl ether were as follows (maximum selectivity of diglycidyl ether is 16 mol%): the temperature of 28°C, the molar ratio of reactants of 1.4, the content of the catalyst of 3.1 and reaction time of 2 h. Figure 4 shows that the epoxidation of AA at temperatures ranging from 18 up to 33°C, and molar ratios of reactants from 0.9 up to 1.65, also allows obtaining optimal values of



**Figure 4.** The influence of the technological parameters on the selectivity of transformation to diglycidyl ether in relation to AA consumed – the dependence of temperature and molar ratio of AA/hydrogen peroxide (the content of Ti-SBA-15 3.1 wt%, reaction time 2.0 h)

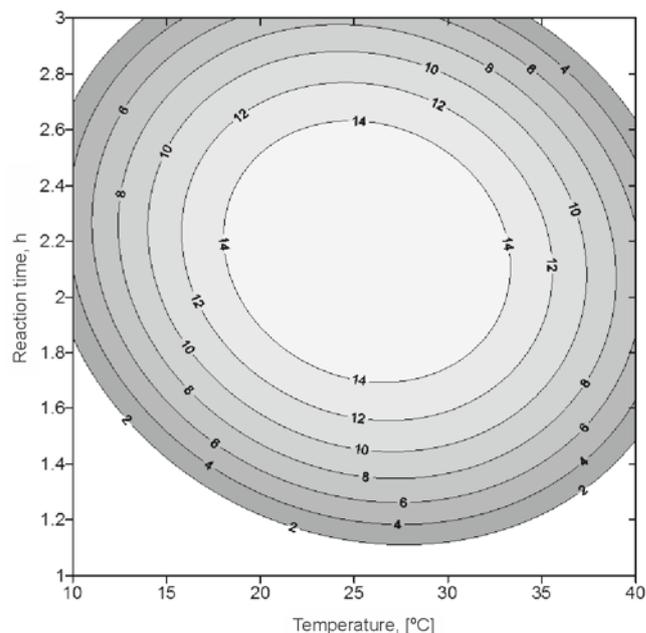
the function of the process (16 mol%). At temperatures below 10°C for the whole range of the investigated molar ratios of reactants the processes of the etherification is inhibited, whereas at temperatures above 33°C, probably the decomposition of diglycidyl ether and hydration of the epoxide rings occurs, what reduces the amount of diglycidyl ether formed in the process.

Figure 5 shows that the highest selectivity of diglycidyl ether (16 mol%) can be obtained at temperatures of 14–39°C and at the catalyst content ranging from 2.0 up to 3.4 wt%. At lower temperatures (10–14°C) and for the catalyst content above 3.4 wt% the etherification process is inhibited. Moreover, at temperatures above 35°C and for catalyst content 3.5 wt% also diglycidyl ether is also not formed, but in this case probably the decomposition of the diglycidyl ether took place and this product is not detected in the post-reaction mixtures.



**Figure 5.** The influence of the technological parameters on the selectivity of transformation to diglycidyl ether in relation to AA consumed – the dependence of temperature and the content of Ti-SBA-15 (the molar ratio AA/hydrogen peroxide 1.4, reaction time 2.0 h)

Figure 6 shows that at temperatures ranging from 18–34°C it is best to carry out the process at time intervals from 1.7 up to 2.65 h. For the reaction time to about 1.15 h independent on the temperature of the process performing the etherification process takes no place or the decomposition the diglycidyl ether molecules (for higher temperatures) can perform, thus the diglycidyl ether is not present in the post-reaction mixtures. The same phenomenon is observed for low temperatures (10–11°C) independent on the used reaction time. For higher temperatures and for short reaction time (to 1.4 h) diglycidyl ether is also not present in the post-reaction mixtures. It is possible that these reaction times are not enough to formation this product or the decomposition of this product proceeds. On the other hand, for highest temperatures and for longest time (2.65–3 h) this compound is also not detected. It is possible that at these conditions the molecule of diglycidyl ether is not stable and in the consequence of its breakdown glycidol and glycerol molecules are formed.

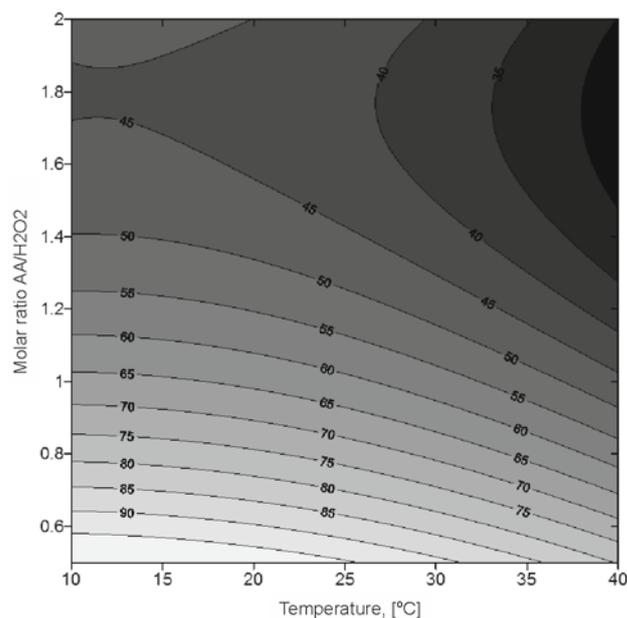


**Figure 6.** The influence of the technological parameters on the selectivity of transformation to diglycidyl ether in relation to AA consumed – the dependence of temperature and reaction time (the molar ratio AA/hydrogen peroxide 1.4, the content of Ti-SBA-15 3.1 wt%)

### The conversion of AA ( $z_3$ )

The influence of changes of two chosen parameters on the conversion of AA ( $z_3$ ) at optimal values of the remaining parameters that allow obtaining the maximum value of the tested function is presented in Figures 7–9.

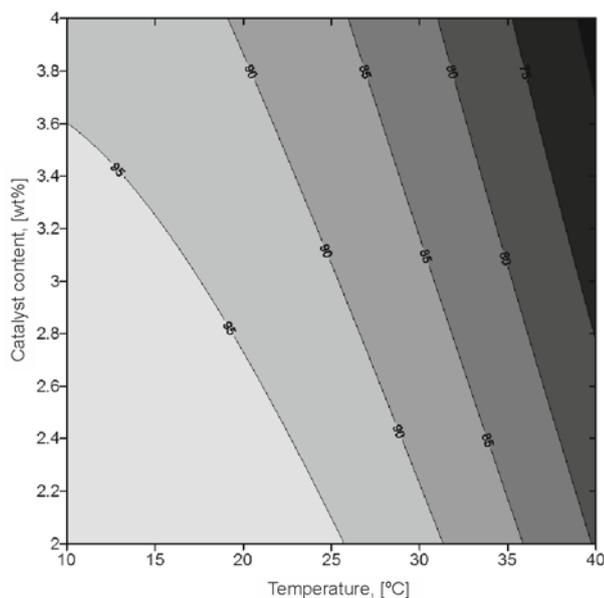
Table 4 shows that the most favorable conditions for obtaining of 100 mol% conversion of AA were as follows: the temperature of 19°C, the molar ratio of reactants of 0.5, the content of the catalyst of 2.0 and reaction time of 2.9 h. Figure 7 shows that for the temperature range of 10–25°C and for the molar ratio of reactants 0.5 to



**Figure 7.** The influence of the technological parameters on the conversion of AA – the dependence of temperature and molar ratio of AA/hydrogen peroxide (the content of Ti-SBA-15 2.0 wt%, reaction time 2.9 h)

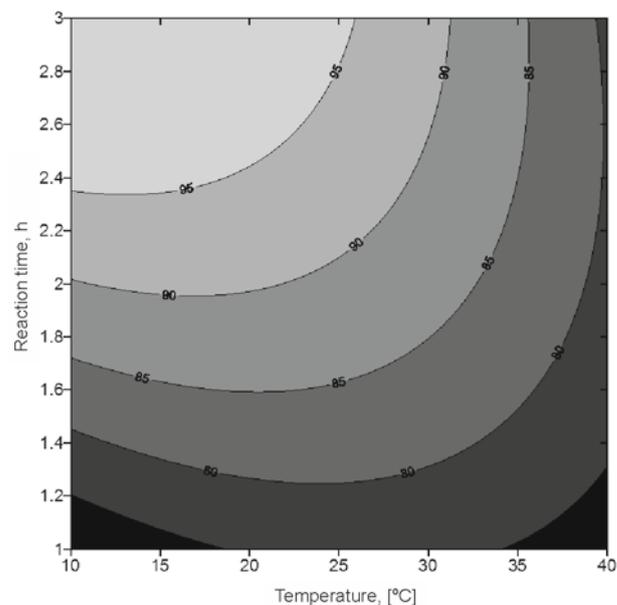
about 0.6 it is possible to achieve the highest conversion of AA. The raising of the molar ratio of reactants at the lowest temperatures (10–25°C) causes that the conversion of AA decreases to 40 mol%. It is possible that the AA molecules take part in stabilization of epoxide compounds, thus do not react with hydrogen peroxide or do not take part in etherification reactions. At higher temperatures for higher molar ratios of reactants also a decrease of the conversion of AA is observed. This phenomenon is connected with the excess of AA in reaction medium.

Figure 8 shows that at temperature range of 10 to about 26°C and for catalyst content from 2.0 to 3.6 wt% it is possible to obtain the highest values the conversion of AA. At the lowest temperatures (to 20°C) the increase the catalyst content above 3.6 wt% does not cause significant changes in values this investigated function of the process (the decrease to 90 mol%). The increase the temperature in the range of 20–40°C for the catalyst content above 3.6 wt% causes a notable decrease in values of AA conversion to 70 mol%. Generally, it can be claimed that the lowest temperatures and low catalyst content are the most beneficial to obtain high values of AA conversion.



**Figure 8.** The influence of the technological parameters on the conversion of AA – the dependence of temperature and the content of Ti-SBA-15 (the molar ratio AA/hydrogen peroxide 0.5, reaction time 2.9 h)

Figure 9 shows that it is the most beneficial to carry out the process at the temperatures from 10°C to about 26°C and for the reaction time in the range from about 2.35 to 3 h. The reducing the reaction time and increasing the temperature of the process decrease only slightly the conversion of AA. Probably for the longer time the secondary reactions, for example the decomposition of diglycidyl ether, proceed in reaction mixture and the transformations of AA are restricted.

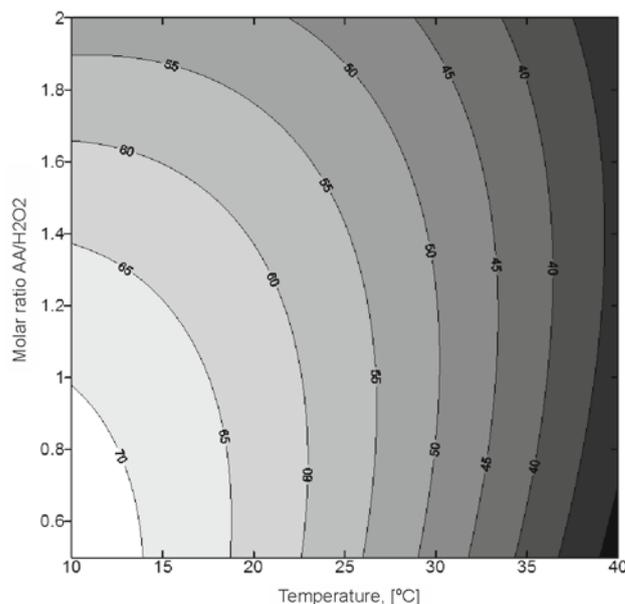


**Figure 9.** The influence of the technological parameters on the conversion of AA – the dependence of temperature and reaction time (the molar ratio AA/hydrogen peroxide 0.5, the content of Ti-SBA-15 2.0 wt%)

#### The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed ( $z_4$ )

The influence of changes of two chosen parameters on the selectivity of transformation to organic compounds in relation to consumed hydrogen peroxide ( $z_4$ ) at optimal values of the remaining parameters that allow obtaining the maximum value of the tested function is presented in Figures 10–12.

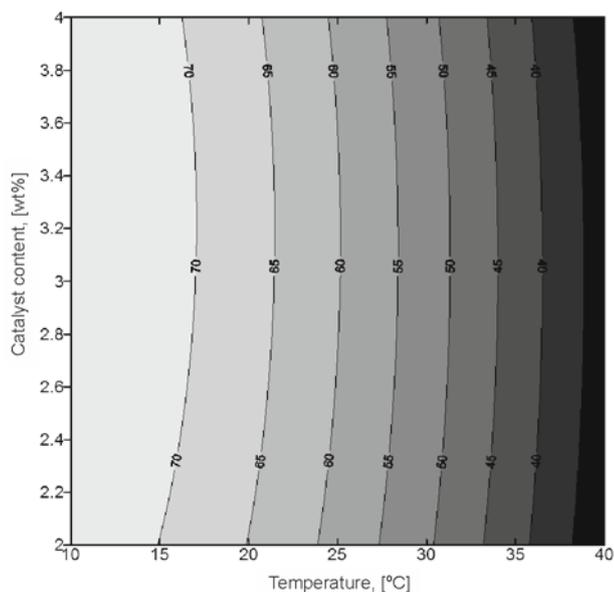
Figure 10 presents that the highest selectivity of transformation to organic compounds in relation to hydrogen peroxide (73 mol%) can be achieved for the temperature range of 10°C to 14°C and for the molar ratio of reactants from 0.5 to about 1.0. Probably, at lower temperatures the hydrogen peroxide molecules



**Figure 10.** The influence of the technological parameters on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed – the dependence of temperature and molar ratio of AA/hydrogen peroxide (the content of Ti-SBA-15 2.3 wt%, reaction time 3.0 h)

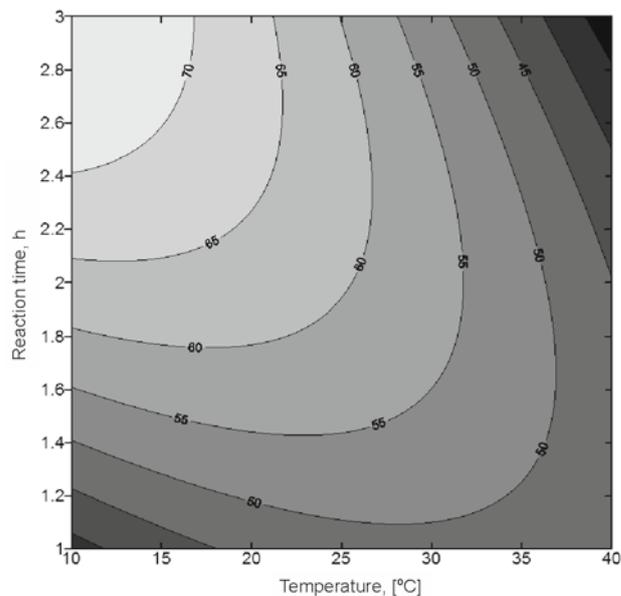
are more stable and thus are not so susceptible to the decomposition at the active centres of Ti or under the influence of temperature. The increase of temperature from 25°C to 40°C, practically independent on the molar ratio of AA/hydrogen peroxide, significantly changes the values the investigated function from about 58 mol% to about 30 mol%. On the other hand, the increase of temperature from 10°C to 25°C has also influence on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (it changes from 73 to 58 mol%) but in this case the molar ratio of reactants has an important influence on the value of the investigated function (it changes from 73 mol% to about 53 mol%). At low temperatures and for the molar ratio of reactants above 1 the tendency to etherification reaction raised, the hydrogen peroxide molecules have a difficult access to active centres and thus ineffective decomposition of hydrogen peroxide takes place.

Figure 11 shows that at the temperature range of 10–15°C and independent on the content of the catalyst, the value 73 mol% for the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed can be reached. The raising of the temperatures from 15°C to 40°C changes significantly the values of this function from 70 mol% to 30 mol% – ineffective decomposition of hydrogen peroxide takes place. As shows Figure 11 this phenomenon is independent on the molar ratio of reactants.



**Figure 11.** The influence of the technological parameters on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed – the dependence of temperature and the content of Ti-SBA-15 (the molar ratio AA/hydrogen peroxide 0.7, reaction time 3.0 h)

Figure 12 shows that in the range of temperatures 10–17°C and for the reaction time 2.4–3.0 h it is possible to obtain the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed – 73 mol%. For the reaction time from 1.0 to 1.4 h, the changes of the temperatures from 10°C to 40°C do not change significantly the value of this function, it amounts to still about 54 mol%. For longer reaction time (1.4 to 3.0 h) the increase the temperature of the reaction cases



**Figure 12.** The influence of the technological parameters on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed – the dependence of temperature and reaction time (the molar ratio AA/hydrogen peroxide 0.7, the content of Ti-SBA-15 2.3 wt%)

significant changes in values the studied function (from 70 mol% to about 30 mol%). This decrease is connected with the phenomenon of ineffective decomposition of hydrogen peroxide.

## CONCLUSIONS

The results obtained during the epoxidation of AA in the direction of glycidol show that at low temperatures (10°C) it is possible to obtain high selectivity of glycidol, amounting to 54 mol%. Therefore, aqueous medium is also a suitable environment for the course of the process. At low temperatures, and with a molar excess of allyl alcohol in relation to hydrogen peroxide, the surrounding AA molecules can stabilize glycidol molecules. This prevents hydration and limits the formation of glycerol.

Moreover, the obtained results show that short reaction times are not in favor of the etherification process at ambient temperature or slightly higher temperature. As in the case of other mesoporous titanium silicalite catalysts, the content of the catalyst in the reaction mixture has to be quite high (above 2.9 wt%) for the epoxidation and etherification processes to occur.

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