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Chapter 5

Studies on Obtaining Diglycidyl Ether from Allyl-Glycidyl Ether over the Mesoporous Ti-SBA-15 Catalyst

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/61881

Abstract

The work presents the studies on the epoxidation of allyl-glycidyl ether (AGE) to diglycidyl ether (DGE) over the mesoporous Ti-SBA-15 catalyst and with 60 wt% hydrogen peroxide. The influence of the following parameters was studied: the temperature 0–100°C, the molar ratio of AGE/H_2O_2 = 0.03:1 – 4:1, the content of Ti-SBA-15 catalyst 0.0–0.5 wt%, and the reaction time 15–240 min. The studies showed that it is possible to obtain DGE with the selectivity of 100 mol% (for reaction time below 60 min) but at low conversion of AGE – about 4 mol%. The prolongation of the reaction time decreases the selectivity of DGE because the following competitive reactions take place: (1) hydration of the epoxide ring in AGE and 3A12PD formation, (2) collapsing of the ethers by hydrolysis of the ether groups, and (3) the epoxidation and the hydration of the products of collapsing and obtaining glycerol. The explanation of the very high ineffective decomposition of hydrogen peroxide and possible ways of increasing its efficiency of conversion are also presented.

Keywords: Epoxidation, allyl-glycidyl ether, diglycidyl ether, hydrogen peroxide, Ti-SBA-15

1. Introduction

1.1. Epoxidation of allylic compounds, especially diallyl ether and allyl-glycidyl ether, and applications of allyl-glycidyl ether epoxidation product

Research on the epoxidation of allylic compounds: propylene [1–5], allyl chloride [6–12], allyl alcohol [13–17], methallyl alcohol, crotyl alcohol, and 1-butene-3-ol [18] with hydrogen peroxide over the titanium silicate catalysts have been carried out for over 10 years. There are not many reports concerning the epoxidation of allyl-glycidyl ether (AGE) or diallyl ether

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(DAE) [19] with hydrogen peroxide over these catalysts. It can be caused by the fact that the epoxidation of AGE and DAE is very complicated, as in addition to the epoxidized ether derivatives, by-products formed by the decomposition of these ethers and their epoxidized derivatives, as well as products of further transformations of these decomposed products, i.e. glycidol and glycerol, are received. Moreover, during epoxidation, the epoxy rings may be opened and diols can be formed. However, due to numerous applications of diglycidyl ether – DGE (production of linear, branched, and cyclic oligoglycerols used in the production of surfactants, preparation of anti-arrhythmia agents, production of components of other pharmaceuticals and medicines, for example, cryptands, preparation of lubricating oil additives, and synthesis of aminoethers), the epoxidation of AGE with hydrogen peroxide over Ti-SBA-15 is very interesting and worth further examinations. The simultaneous utilization of Ti-SBA-15 and a low-cost, environment friendly oxidant - hydrogen peroxide in the epoxidation of AGE, makes this method of DGE production a modern and environment friendly as the only product of hydrogen peroxide transformation is water and Ti-SBA-15 can be easily recovered from reaction mixtures, recycled into the process, and regenerated if it loses its activity [20]. An additional advantage is this process can be carried out in an aqueous medium also.

2. The titanium silicate materials used for diallyl ether and allyl-glycidyl ether epoxidation [19]

Until now, only the TS-1 and Ti-MWW titanium silicate materials have been used in the epoxidation of DAE and AGE – with hydrogen peroxide. In the studies performed by Wu et al. [19], AGE was the semi-product which was formed during DAE epoxidation and it underwent among others further transformation to DGE. In the above mentioned research, at the first stage, the epoxidation of DAE with hydrogen peroxide was performed under vigorous stirring in a 20 ml glass flask, connected to a condenser. In the typical run, the appropriate amounts of DAE, solvent (acetonitrile, acetone, water, methanol, ethanol, dioxane), and the catalyst were mixed in the flask and heated to the desired temperature under the agitation. Next, aqueous hydrogen peroxide (30 wt%) was added to the mixture to start the reaction. The reaction was carried out at the temperature of 60°C for 0.5 h in case of Ti-MWW and for 1.5 h in case of TS-1. Both Ti-MWW and TS-1 materials showed different solvent effect. During the examinations over Ti-MWW catalyst, the highest conversion of DAE was obtained for acetonitrile (about 40 mol%) and acetone (about 39 mol%) as the solvents. The selectivity of AGE was the highest for acetonitrile, methanol, ethanol, and dioxane and amounted to about 71–79 mol%. The selectivity of DGE, which was formed as the product of AGE transformation (epoxidation of the next double bond), was the highest for water as the solvent (about 40 mol %). High values of the selectivity of this product also allow to obtain such solvents as: acetonitrile (about 29 mol%) and acetone (about 25 mol%). The efficiency of hydrogen peroxide conversion was the highest for examinations in acetonitrile (about 95 mol%), acetone (about 92 mol%), and dioxane (about 94 mol%). In methanol and in water, the efficiency of hydrogen peroxide conversion amounted to about 82–87 mol%. The lowest value of this function of the

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process was obtained for ethanol (61 mol%). The total conversion of hydrogen peroxide was the highest in acetonitrile and acetone (about 99–100 mol%). These studies showed that the Ti-MWW catalyst favoured aprotic solvents such as acetonitrile or acetone. A little worse results were obtained for water as the solvent.

During the studies over the TS-1 catalyst, the highest conversion of DAE was obtained in acetone, methanol, and ethanol as the solvents. The selectivity of AGE was usually high and amounted to about 61–89 mol%. This function was the highest for dioxane. The highest values of DGE selectivity were obtained for acetone and methanol: about 22 and 21mol%, respectively. Efficiency of hydrogen peroxide conversion was the highest for acetone and amounted to 70 mol%. The studies over the TS-1 material showed that methanol and acetone were the most effective solvents in this process. The comparison of the results of DAE epoxidation present that Ti-MWW material was more efficient than TS-1 material in catalytic activity, epoxide selectivity, and hydrogen peroxide conversion when choosing acetonitrile or acetone as the solvent [19].

At the second stage, in which only Ti-MWW material was used, also the influence of temperature from 0 to 67°C was tested in the epoxidation of DAE over the Ti-SBA-15 material. The studies were performed in acetone and at the same conditions as in the first stage of these studies. The examinations showed that the selectivities of AGE and DGE changed of about 10 mol% during the rising of temperature (the selectivity of AGE from about 80 to about 70 mol %, and the selectivity of DGE from about 20 to 30 mol%). Conversion of DAE reached 40 mol % above the temperature of 60°C. The efficiency of hydrogen peroxide conversion slightly decreased with increasing temperature as a result of the thermal decomposition of hydrogen peroxide, but the value of this function was higher than 95 mol% [19].

At the third stage, the influence of the Ti-MWW amount and reaction time were studied. The examinations were performed in acetonitrile and at the temperature of 60°C. The studies showed that the more the catalyst was used, the higher the catalytic activity of Ti-MWW material. The DAE conversion raised rapidly within 30 min and then gradually with the time. The decrease in the reaction rate for longer time was mainly caused by the pore blocking by heavy organic species [19].

The comparison of the results obtained for Ti-MWW and TS-1 catalysts show that Ti-MWW material exhibited more benefits in catalytic activity using less harsh reaction conditions [19].

3. The Ti-SBA-15 – titanium silicate mesoporous material, its synthesis and characteristic

One of the newer titanium silicate catalysts is Ti-SBA-15. It is a mesoporous material, which is much more durable than Ti-MCM-41 catalyst [20, 21]. Greater durability of this catalyst is likely due to its construction – a honeycomb structure, wherein unlike Ti-MCM-41, in Ti-SBA-15 the main cylindrical channels are connected together by transverse channels which introduces additional porosity and, at the same time, strengthens the structure. Furthermore, Ti-SBA-15

is characterized by thicker pore walls, and its synthesis is carried out in the presence of a biodegradable template – Pluronic P123, as opposed to Ti-MCM-41 whose synthesis is carried out in the presence of an ammonium compound (hexadecyltrimethylammonium bromide) and is uncomfortable to the environment due to formation of amines during calcination of this catalyst [22–31]. Our studies on the epoxidation of allylic alcohols over the Ti-SBA-15 catalyst showed that this catalyst is very active in this process and these compounds can be effectively converted to epoxides [18]. This is the main reason why this catalyst has been chosen to conduct the epoxidation of AGE.

Ti-SBA-15 was obtained by the method of Berube et al. [30] and the following raw materials were used in its synthesis: Pluronic P123 (Aldrich, MW = 5800) as structure-directing agent, tetraethylortosilicalite (TEOS 98%, Aldrich) as a silicon source, and tetraisopropyl orthotitanate (TiPOT >98%, Merck) as a titanium precursor. The characterization of Ti-SBA-15 was performed with the following instrumental methods: XRD (X'Pert PRO Philips diffractometer, Co Kα radiation), IR (Shimadzu FTIR-8100 spectrometer, KBr pellet technique), UV-vis (SPECORD M40 type V-530 with the attachment for solid materials measurements), X-ray microanalysis (Oxford X-ray analyzer ISIS 300), SEM (JOEL JSM-6100 instrument), and porosimetric analysis (porosimetry analyzer ASAP Micromeritics).

The XRD pattern of the obtained Ti-SBA-15 catalyst was similar to the literature data [28, 32–33]. For the SBA-15 material are typical: one characteristic very intensive diffraction peak at 2 Theta angle of 1.01° and two weak peaks at 2 Theta angle of 1.75° and 2.05°, corresponding to the (100), (110), and (200) Bragg reflections. These reflections confirm the 2-d hexagonal symmetry (P6mm) of the SBA-15. The IR spectrum of the obtained Ti-SBA-15 was also similar to the literature data [23, 34–35]. To the main bands characterized, this kind of materials belong to: the band at 800 cm^{-1} which is assigned to symmetric stretching vibrations of Si-O-Si in SiO4 units the same as the band at 1, 000–1, 300 cm^{-1}, the band at 1625-1650 cm^{-1} which is assigned to adsorbed water molecules, the band at 3, 000–3, 700 cm^{-1} which is characteristic for surface Si-OH groups and adsorbed water molecules, and the band 957 cm^{-1} which is associated with Ti=O or Si-O-Ti vibrations. The UV-VIS spectrum of the obtained Ti-SBA-15 catalyst showed an intense absorption band at 211 nm, associated with ligand-to-metal charge transfer from oxygen to Ti of an isolated tetrahedral Ti species. This band is direct evidence for titanium atoms incorporated into the framework of the silica [36]. In this spectrum also a shoulder with a maximum around of 290 nm was present. This band is connected with the presence of Ti atoms in fivefold and sixfold coordination. This fivefold and sixfold coordination is generated through hydration by one or two water molecules of the tetrahedral titanium ion in the first coordination sphere [36]. Moreover, in the spectra was visible a weak band at 340 nm, which is assigned to the presence of anatase in the sample. The obtained UV-VIS spectrum is similar to the literature data [32, 36].

An X-ray microanalysis showed that the amount of Ti in the sample after calcination was 2.9 wt%. According to the porosimetric analysis, the specific surface area of the obtained catalyst amounted to 620 m^2/g, the size of the pores achieved was 5.0 nm, and the pore volume was 0.6 cm^3/g. The SEM analyses showed that the Ti-SBA-15 catalyst consisted of large and long, branched, pipe-like structures with diameter of about 4 μm. These structures consisted of

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smaller particles with diameter of about 0.3–0.6 μm and length about 1–2 μm. This morphology is typical for structures such as SBA-15 [28, 37].

4. The studies on the epoxidation of AGE over the Ti-SBA-15 catalyst and the comparison of the results obtained with the previous results obtained for Ti-MWW and TS-1 catalysts

In the epoxidation of AGE, the following raw materials were used: AGE (99%, Aldrich), hydrogen peroxide (60 wt% water solution, Chempur), and Ti-SBA-15 catalyst. The initial technological parameters were as follows: the molar ratio of AGE/H_2O_2 = 1:1, catalyst content 3 wt%, the reaction time 2 h, and intensity of stirring 500 rpm.

The process of AGE epoxidation was carried out in glass vials with the capacity of 12 cm^3 equipped with a rubber septum and a capillary. The raw materials were introduced into the vials at the ambient temperature and in the following order: hydrogen peroxide, catalyst, and AGE. Then the vials were closed with the rubber equipped with the capillary, located in a shaker holder and immersed in a water bath having the appropriate temperature. In order to calculate the mass balance, the unreacted hydrogen peroxide was determined by iodometric method and the remaining products and the unreacted AGE were analyzed by the GC method. The analyses were performed on the FOCUS apparatus with a flame-ionization detector fitted with Quadrex capillary columns filled with methyl-phenyl-siloxanes. After calculating the mass balance, the main functions describing the process were determined: the selectivity of transformation to DGE in relation to AGE consumed and also selectivities of the by-products in relation to AGE consumed, the conversion of AGE, and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (effective conversion of H_2O_2).

The studies on the epoxidation of AGE to DGE was carried out by one-variable method, changing the values of the following parameters: temperature 0–100°C, molar ratio of AGE/H_2O_2 0.03:1–4:1, content of the Ti-SBA-15 catalyst (0–5 wt%), and reaction time 15–240 min. The main results of the studies on the influence of temperature on the course of AGE epoxidation were presented in Figure 1.

During the studies on the influence of temperature, only three products were obtained: DGE, 3-allyloxy-1, 2-propanediol (3A12PD), and glycerol. The selectivity of transformation of AGE to the product of epoxidation of the unsaturated bond – DGE, increases during the increase of the temperature from 0 mol% (the temperature of 0°C) to 38 mol% (the temperature of 20°C) and then decreases to 9 mol% (the temperature of 100°C). Figure 1 shows that DGE is not the main product of this process, because for all investigated temperatures the main product of the process is 3A12PD (with exception at the temperature of 0°C at which the reaction does not proceed). The selectivity of this products changes from about 53–54 mol% (the temperatures 10–20°C) to 80–90 mol% (the temperatures 40–100°C).. The selectivity of glycerol amounts to 13 mol% for the temperature of 10°C, and then decreases to about 2 mol% (for the temperatures of 40–100°C). For the description of the process of AGE epoxidation, the reactions presented in Figure 2 can be proposed.

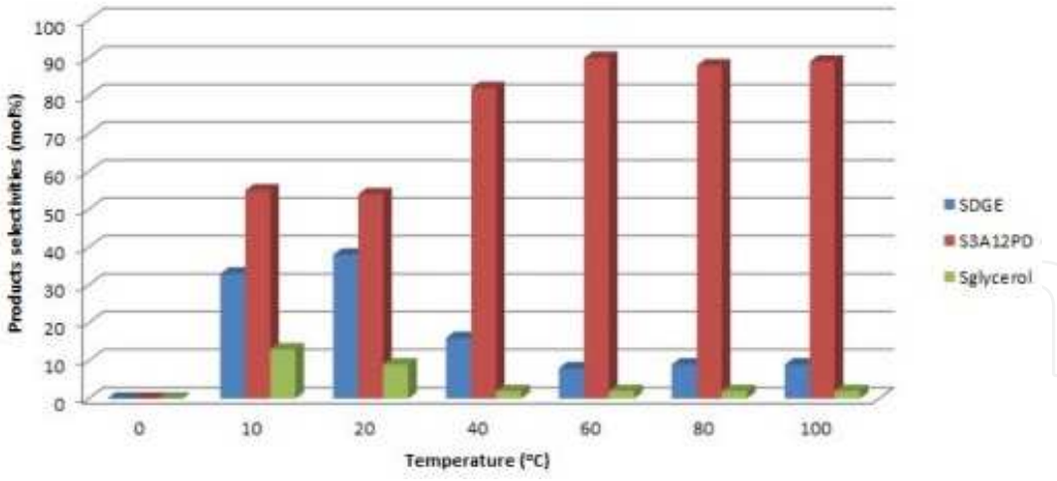


Figure 1. The influence of temperature on the selectivities of the products of AGE epoxidation process: S_{DGE} – the selectivity of DGE, S_{3A12PD} – the selectivity of 3-allyloxy-1, 2-propanediol, and $S_{glycerol}$ – the selectivity of glycerol (the molar ratio of AGE/H_2O_2 = 1:1, the content of the catalyst 3 wt%, and the reaction time 120 min).

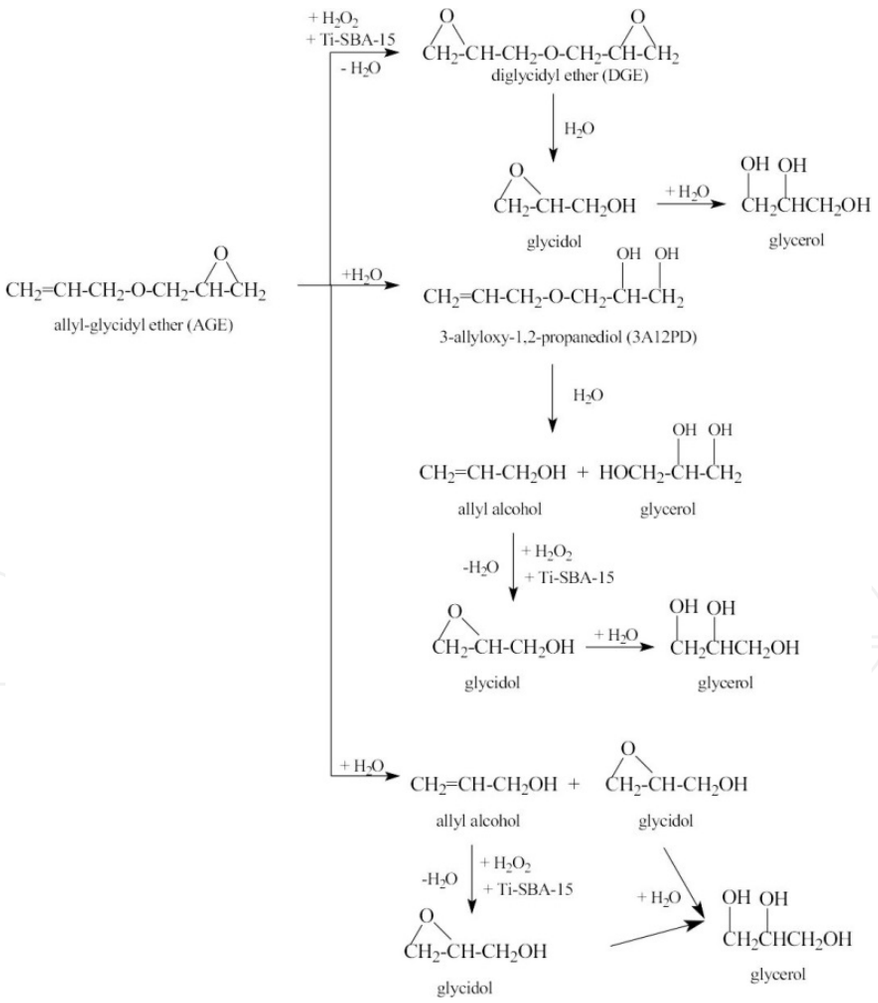


Figure 2. The main reactions of the process of AGE epoxidation.

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Figure 2 shows that the process can proceed in the three directions: (1) the epoxidation of allylic group in AGE and formation of DGE, (2) the hydration of the epoxide ring in AGE and formation of 3A12PD, and (3) the formation of glycerol. Moreover, the two first directions are the main directions of the process in low temperatures. The glycerol formation is a very complicated process and this product can be formed as a product of hydrolysis of the ether groups of AGE, DGE, 3A12PD, and, simultaneously, as a result of the secondary reactions of the products of the hydrolysis of these ethers (epoxidation of allylic group in allyl alcohol to glycidol and next hydration of the epoxide ring in glycidol to glycerol). Allyl alcohol and glycidol were not detected in post-reaction mixtures. It shows that these compounds were very reactive at the investigated conditions and right away underwent secondary reactions. The tendency towards the formation of 3A12PD rises during increasing the temperature of the performing process. On the other hand, the selectivities of the DGE and glycerol decrease. It shows that at higher temperatures the epoxidation of AGE to DGE is hindered and the hydrolysis of the ether groups in AGE, DAE, and 3A12PD is stepped or it proceeds very slowly. The main reaction is hydration of the epoxide ring in AGE and formation of 3A12PD. The formation of 3A12PD as the main product in this process can be explained taking into account the acidic character of the mesoporous Ti-SBA-15 material. This character is mainly connected with: (1) the silanol groups located on the surface of this catalyst [19, 38], (2) the species of Ti present on the surface of the catalyst – tetrahedral Ti(IV) active sites, titanium-containing species in the form of dimmers or very small oligomers [38–41], and (3) the active species of titanium with hydrogen peroxide which are formed during the oxidation process, for example, five-membered active complexes – titanium hydroperoxo species with the specific structure, which are formed from tetrahedral Ti(IV) active sites, protic solvent (for example, methanol or water), and hydrogen peroxide and are present on the surface of the catalyst [42].

Among others, the formation of 3A12PD can also be under influence of the active species of titanium with hydrogen peroxide which are formed during the oxidation process and some of them can have the acidic character. A few structures have been proposed until now for explanations of the structures of these active species. Among these structures are: the peroxide structure, the hydroperoxide structure, and superoxide structures (radical species) [40, 42–49]. Indeed, mainly the hydroperoxide structure was described as the structure responsible for the epoxidation of olefinic compounds [45, 47]. It exists in equilibrium with the peroxide structure, which is a dominant structure in the water solution because it is stabilized by water molecules [45]. In the medium in which epoxidation takes place, the excess of olefins causes that the peroxide structure is converted to hydroperoxide structure [45]. Hydroperoxide structures in the presence of protic solvent create the five-membered active complexes – titanium hydroperoxo species which are composed from tetrahedral Ti(IV) active sites, protic solvent (in case of these studies, from water), and hydrogen peroxide[40, 42, 50, 51].

Bhaumik et al. [42] described that under the influence of the titanium hydroperoxo species undergoes acid-catalyzed cleavage of the oxirane rings in the epoxide compounds; this reaction has considerable SN1 character and the nucleophilic attack is easy to occur at the more crowded carbon atom that can best accommodate the positive charge. Taking into account that this data can be propose the possible way of 3A12PD formation from the AGE presented in Figure 3.

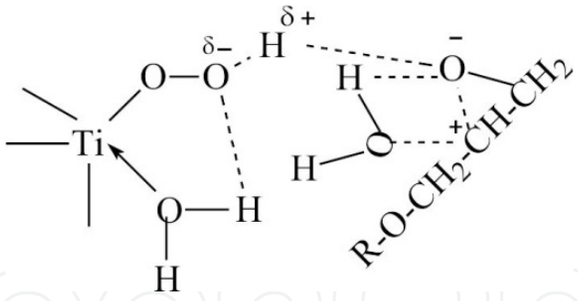


Figure 3. The possible way of 3A12PD formation from the AGE, where: R = CH_2=CH-CH_2-.

Also the hydration of the ether groups in AGE, DGE, and 3A12PD can be explained taking into account the acidic character of various species which are present in the mesoporous Ti-SBA-15 material (silanol groups, species of Ti and titanium hydroperoxo species).

During the studies on the influence of temperature, the conversion of AGE was very low and it changes from 0 mol% (the temperature of 0°C) to about 4–5 mol% for the highest temperatures. The changes of the effective conversion of H_2O_2 are very similar. Very low values of this function show that at the studied conditions the catalyst was very active in the ineffective decomposition of hydrogen peroxide to water and oxygen, which takes place at the active centres of Ti in the catalyst even at very low temperatures (the total conversion of hydrogen peroxide changed from 83–90 mol%). The ineffective decomposition of hydrogen peroxide over titanium silicate catalysts has been described in a great number of works [52–57], and this phenomenon is typical for these catalysts, for example, it was shown in the literature that titanium hydroperoxo species can decompose hydrogen peroxide molecules via formation of Ti-O* radical and hydroperoxo radical (HOO*) [52]. As the results presented in this work showed, the Ti-SBA-15 catalyst was very active in the decomposition of hydrogen peroxide. The epoxidation of olefinic bonds undergoes slower than the ineffective decomposition of hydrogen peroxide at the five-membered active species. Probably, very small reactivity of the AGE is connected with the steric hindrances connected with the structure of this ether when the molecules of AGE are close to the active species of Ti with hydrogen peroxide. These steric hindrances cause that the decomposition of AGE molecules also takes place. The increased, ineffective decomposition of hydrogen peroxide can be also caused by the presence of TiO_2 domains in the structure of the Ti-SBA-15 catalyst. Taking into account the UV-VIS spectrum of the Ti-SBA-15 catalyst used in this work, the broad absorption peak at the 211 cm^{-1} and the shoulder at the 290 cm^{-1}, which is not only connected with the presence of Ti atoms in fivefold and sixfold coordination [36] but also can be assigned to the oligomerized titanium-oxygen species – formation of Ti-O-Ti bonds by clusterization of octahedrally coordinated titanium ions [46, 58] or to octahedral titanium species in the form of highly dispersed TiO_2 particles with the particle size smaller than 5 nm [48]), and the results of the X-Ray microanalysis (amount of Ti 2.9 wt%), it can be assumed that the Ti-SBA-15 catalyst contains the titanium-oxygen species in the form of dimmers or very small oligomers (TiO_2 domains, Ti aggregates) [53, 55].

A lot of works present the strategies to increase the oxidant efficiency. The hydrogen peroxide decomposition is strongly dependent on the pH of the reaction mixtures and on the surface concentration of the hydroxyl groups of the catalytic material [52]. The improving of the

efficiency of the hydrogen peroxide conversion can be done by: (1) addition of additives such as for example: CH_3COOH, $KHSO_4$, KH_2PO_4, KHF_2, Na_2SO_4, $NaHCO_3$, K_2CO_3, K_3PO_4, K_2HPO_4, or KH_2PO_4 [52]; (2) slow addition of hydrogen peroxide [52, 55, 57]; (3) choosing of the appropriate solvent for the epoxidation process – the most beneficial are methanol, acetonitrile, and acetone [44, 54, 55] or co-solvent, for example, sulfolane [59]; (4) increasing of the acidity of the catalyst by the addition of metal oxide, for example, of TiO_2, and utilization of the appropriate temperature of the calcination [56]; and (5) the surface hydrophobization of mesoporous titanium silicates [46]. We would like to test in our future work some of the ways of improving the efficiency of hydrogen peroxide conversion: choosing the appropriate solvent, additives, and slow addition of hydrogen peroxide.

Taking into account the results of the studies on the influence of temperature on the course of AGE epoxidation, the temperature of 20°C was taken as the most beneficial for the next studies.

The main results of the studies on the influence of the molar ratio of AGE/H_2O_2 on the course of AGE epoxidation were presented in Figure 4. The studies were performed at the range of molar ratios of AGE/H_2O_2 0.03:1 – 4:1. The other parameters were as follows: the temperature of 20°C, the content of the catalyst 3 wt%, and the reaction time 120 min.

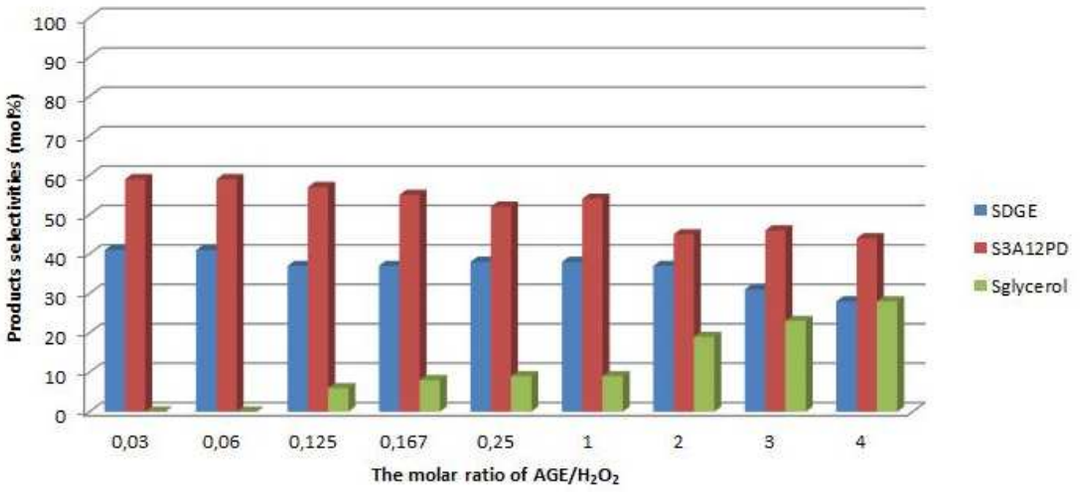


Figure 4. The influence of molar ratio of AGE/H_2O_2 on the selectivities of the products of AGE epoxidation process: S_{DGE} – the selectivity of DGE, S_{3A12PD} – the selectivity of 3-allyloxy-1, 2-propanediol, and $S_{glycerol}$ – the selectivity of glycerol (the temperature 20°C, the content of the catalyst 3 wt%, and the reaction time 120 min).

The studies show that the conversion of AGE was the highest for the lowest molar ratio of reactants and amounted of 11 mol% and next it decreased to 1 mol% for the molar ratio of AGE/H_2O_2 = 4:1. The effective conversion of H_2O_2 had very low values independent of the studied molar ratios, even for the molar ratios of AGE/H_2O_2 > 1. Figure 4 shows that independent of the molar ratio of reactants the main product of the process was 3A12PD, but its selectivity decreased during increasing the molar ratio of reactants. It shows that the excess of hydrogen peroxide or AGE molecules in the reaction mixture does not cause that the epoxidation of AGE is intensified and the hindering of the hydration of epoxide ring in AGE is not

observed. The ethers molecules are unstable in reaction medium and underwent decomposition by the hydration of the ether groups. Simultaneously, the results obtained show that the surface of the catalyst independent of the molar ratio of reactants was very active in the reactions of hydration of epoxide rings and ether groups. Also the formed allyl alcohol and glycidol undergo secondary reactions (epoxidation and hydration of the epoxide ring) very easily. On the basis of the results obtained, the molar ratio of AGE/H_2O_2 = 0.03 was taken as the most beneficial for the next stages of the studies.

The main results of the studies on the influence of the Ti-SBA-15 catalyst content on the course of AGE epoxidation were presented in Figure 5. These studies were performed for the following parameters: the temperature 20°C, the molar ratio AGE/H_2O_2 = 0.03, and the reaction time of 120 min.

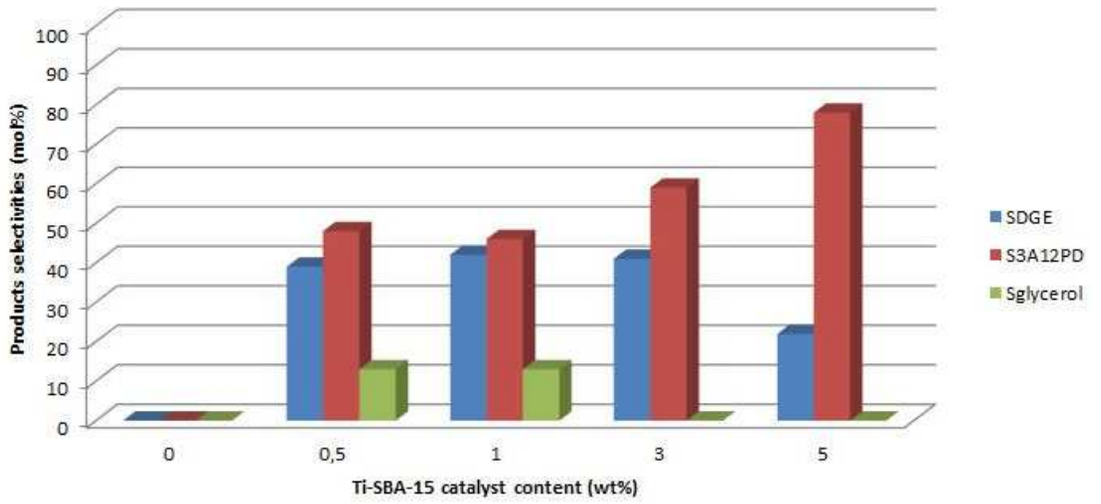


Figure 5. The influence of the Ti-SBA-15 catalyst content on the selectivities of the products of AGE epoxidation process: S_{DGE} – the selectivity of DGE, S_{3A12PD} – the selectivity of 3-allyloxy-1, 2-propanediol, and $S_{glycerol}$ – the selectivity of glycerol (the temperature 20°C, the molar ratio of AGE/H_2O_2 = 0.03, and the reaction time 120 min).

The studies show that for the amount of the catalyst of 0 wt% no one reaction proceeded. The conversion of AGE raised from 0 mol% (for 0 wt% of Ti-SBA-15) to 11 mol% (for 3 wt% of Ti-SBA-15) and next did not change. The effective conversion of H_2O_2 was very low and amounted to about 1 mol%, independent of the studied Ti-SBA-15 content.

Figure 5 shows that during the rising of the content of the catalyst the selectivity of 3A12PD increased from 0 mol% (the Ti-SBA-15 content 0 wt%) to 78 mol% (the Ti-SBA-15 content 5 wt %). It presents that with the increase of the Ti-SBA-15 content, the hydration of the epoxide ring in AGE was intensified, but the hydrolysis at the ether group of AGE, DGE, and 3A12PD was hindered. Only for the Ti-SBA-15 content of 0.5 and 1 wt%, glycerol was present in the post-reaction mixtures. On the other hand, at higher catalyst content, the phenomenon of ineffective decomposition of hydrogen peroxide at the active centers of Ti in the catalyst was intensified and the water molecules obtained during ineffective decomposition of hydrogen

http://dx.doi.org/10.5772/61881

peroxide could probably take part in hydration of the epoxide ring in AGE. The content of the catalyst amounting to 3 wt% was chosen as the most beneficial for the last stage of the studies.

The main results of the studies on the influence of the reaction time on the course of AGE epoxidation were presented in Figure 6. These studies were performed for the following parameters: the temperature 20°C, the molar ratio AGE/H_2O_2 = 0.03, and the Ti-SBA-15 catalyst content 3 wt%.

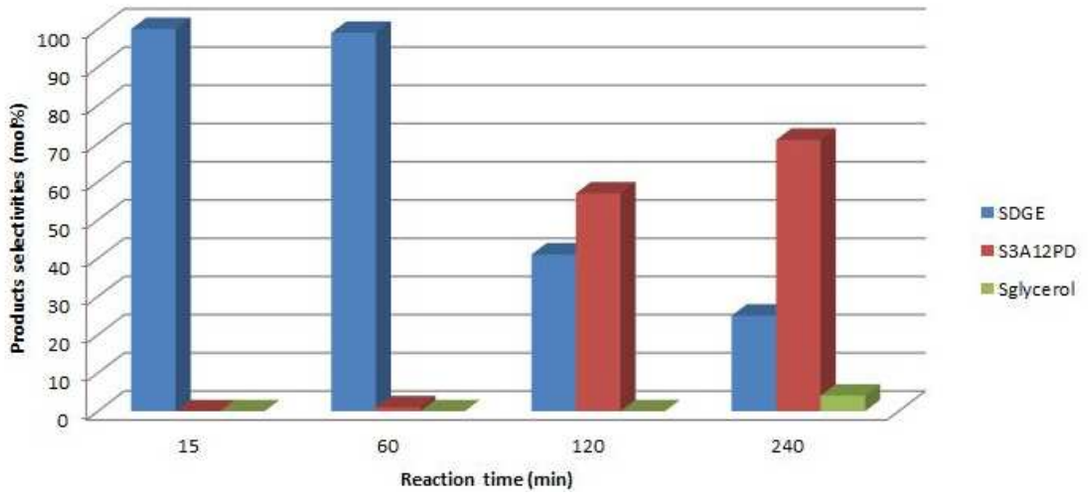


Figure 6. The influence of the reaction time on the selectivities of the products of AGE epoxidation process: S_{DGE} – the selectivity of DGE, S_{3A12PD} – the selectivity of 3-allyloxy-1, 2-propanediol, and $S_{glycerol}$ – the selectivity of glycerol (the temperature 20°C, the molar ratio of AGE/H_2O_2 = 0.03, and the Ti-SBA-15 catalyst content 3 wt%).

The results show that with the prolongation of the reaction time from 15 min to 240 min, the selectivity of DGE decreased from 100 mol% to 25 mol%. Only for the reaction time of 15 min and 50 min, it was possible to obtain only DGE as the product in the post-reaction mixtures. The conversion of AGE increased in the range of the studied reaction time from 3 mol% to 18 mol%, but the effective conversion of H_2O_2 was very low and amounted to about 1 mol%. Figure 6 presents that for the reaction time of 120 min the second product of this process was established – 3A12PD. Glycerol – the third product of this process appeared in the post-reaction mixture for the reaction time of 240 min. It shows that it is possible to obtain only one product in the post-reaction mixture – DGE (very desirable) only for short reaction time – 15 min. and 60 min. At this reaction time, it is only possible to stop the hydration of the epoxide ring and formation of 3A12PD.

The comparison of our results obtained for the Ti-SBA-15 material with the results obtained previously by Wu et al. for the Ti-MWW and TS-1 materials [19] shows that the main difference between the epoxidation of AGE over Ti-SBA-15 and the epoxidation of DAE and AGE over Ti-MWW and TS-1 is formation of the considerable amounts of 3-allyloxy-1, 2-propanediol over Ti-SBA-15 and low efficiency of hydrogen peroxide conversion for this catalyst. It is probably connected with the pore size of the Ti-SBA-15 mesoporous material and the structure of the surface of this catalyst, especially with the presence of various species of Ti and hydroxyl groups.

5. Conclusions and future possibilities

The results presented in these studies show that the best conditions established for the epoxidation of AGE to DGE on the Ti-SBA-15 catalyst in water solution are as follows: the temperature of 20°C, the molar ratio of AGE/H_2O_2 = 0.03:1, the content of the catalyst 3 wt%, and the reaction time of 60 min. At these mild and relatively safe conditions, the selectivity of DGE amounts to 100 mol%; the conversion of AGE and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed amount to 4 mol% and 1 mol %, respectively. These studies also show that this process is very complicated because of the secondary reactions which proceed in reaction medium – hydration of epoxide ring in AGE (formation of 3A12PD), hydrolysis at the epoxide group in AGE, DGE, 3A12PD, epoxidation of the formed allyl alcohol, and hydration of the epoxide ring in glycidol and formation of glycerol. However, it is possible to choose such a way of carrying up this process in which only one product – DGE (the most desirable) – is obtained. The process of obtaining DGE is performed at very mild conditions, thus the danger of the explosive decomposition of hydrogen peroxide or compounds with epoxide group is very little, mainly taking into account the very low temperature of this process which amounts 20°C. Hydrogen peroxide used in this process is a relative cheap oxidizing agent and moreover, the methods of production of hydrogen peroxide are still developed and modernized. The method of AGE epoxidation with hydrogen peroxide is also ecologically friendly because only one product of its transformation is water. The presented studies showed that for this process hydrogen peroxide should be used in excess in relation to AGE. Mainly, it is connected with the phenomenon of ineffective decomposition of hydrogen peroxide (not explosive decomposition) at the active centers of Ti in the structure of the catalyst. This phenomenon causes that only a little amount of hydrogen peroxide takes part in epoxidation process and utilization of the excess of hydrogen peroxide in relation to AGE improves effective utilization of hydrogen peroxide molecules in the process of epoxidation. On the other hand, hydrogen peroxide undergoes very easy ineffective decomposition, thus even at the excess of hydrogen peroxide its concentration in reaction mixtures is low. The main cause of this situation is high content of the Ti-SBA-15 catalyst in reaction mixture (3 wt%). There are some possible ways of improving the hydrogen peroxide conversion efficiency by, for example, (1) addition of additives (CH_3COOH, $KHSO_4$, KH_2PO_4, KHF_2, Na_2SO_4, $NaHCO_3$, K_2CO_3, K_3PO_4, K_2HPO_4, or KH_2PO_4); (2) the changing of the way of hydrogen peroxide addition; (3) choosing the appropriate solvent (methanol, acetonitrile or acetone), or co-solvent (sulfolane); (4) increasing the acidity of the catalyst by the addition of metal oxide, for example, of TiO_2, and utilization of the appropriate temperature of the calcination; and 5) the surface hydrophobization of mesoporous titanium silicates. We would like to test in our future works some of the ways of improving the efficiency of hydrogen peroxide conversion: choosing of the appropriate solvent, additives, and slow addition of hydrogen peroxide. A large advantage of the presented process is also performing the process of epoxidation in water solution without any other solvents. Moreover, water was not additionally introduced in the reactor, only with the solution of the oxidizing agent it was formed during the process. Water is now regarded as a very ecological solvent for organic processes.

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