Epoxidation of allyl-glycidyl ether with hydrogen peroxide over Ti-SBA-15 catalyst and in methanol medium

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This work presents the studies on the epoxidation of allyl-glycidyl ether (AGE) over the Ti-SBA-15 catalyst. In these studies an aqueous hydrogen peroxide was used as an oxidizing agent and as a solvent methanol was applied. The studies on the influence the following parameters: temperature (20–80°C), molar ratio of AGE/H_2O_2 (1:1.5–5:1), methanol concentration (10–90 wt%), catalyst content (1–9 wt%) and reaction time (15–240 min.) were carried out and the most favourable values of these parameters were chosen (temperature 80°C, molar ratio of AGE/H_2O_2 = 5:1, methanol concentration 30 wt%, catalyst content 3 wt% and the reaction time 240 min.). At these conditions the functions describing the process reached the following values: the selectivity of diglycidyl ether (DGE) 9.2 mol%, the conversion of AGE 13.9 mol% and the efficiency of H_2O_2 conversion 89.9 mol%.

Keywords: diglycidyl ether, allyl-glycidyl ether, Ti-SBA-15, epoxidation.

INTRODUCTION

Diglycidyl ether (DGE) belongs to the group of epoxides (oxiranes). In the structure of this compound two epoxide rings are present, which may react with compounds containing an active hydrogen atom[1] – Figure 1. DGE can polymerize in the presence of an appropriate catalyst or under the influence of heat. Its ability to link a polymer chains has been used extensively in: pharmaceutical[2, 3], cosmetic[4] or fuel industry[5]. DGE can form a polymeric film at temperatures lower than 80°C and in a short time, thus it can find applications in production of reactive ink for ink jet printing[6]. Furthermore, DGE can be used in a cationization of cotton[7] in a textile industry, as a component of an electrolyte liquid inactivator in disassembling and recycling of batteries[8], as a diluent for epoxy resins[9] or as a component for adhesives[10]. Along with other epoxy compounds, DGE may form the epoxy coating which is an effective protection layer against adverse effects of corrosion, oxidation and other undesirable reactions[11].
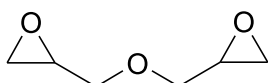

Figure 1. The structure of diglycidyl ether

Until know, there are only few methods of DGE synthesis. These methods can be divided into two groups. The first group includes oxidation of the unsaturated bond in allyl-glycidyl ether (AGE) using peroxyacids such as m-CPBA (m-chloroperoxybenzoic acid)[12, 13] or H_2O_2 solution as oxidizing agents and in the presence of divanadium-substituted phosphotungstate[14, 15] or titanium silicate catalysts: Ti-MWW[16], TS-1[16] and T-SBA-15[17]. The second group involves condensation of glycidol and epichlorohydrin catalyzed by TBAHS-MB (tetrabutylammonium hydrosulfate)[18].

In the presented studies 30 wt% H_2O_2 was used as the oxidizing agent. H_2O_2 is one of the strongest oxidants and the only by-products of its ineffective decomposition are oxygen and water. Moreover, it is widely available and relatively cheap oxidizing agent. All of these features make it an excellent oxidant for the epoxidation processes. The process of AGE epoxidation was catalyzed by the Ti-SBA-15 catalyst. This material is a mesoporous titanium silicate material, which is an effective catalyst in processes of olefinic compounds oxidation or in hydroxylation of aromatic compounds. It is obtained in the presence of a biodegradable copolymer – Pluronic P123 (template), which is a copolymer of ethylene oxide and propylene oxide. In comparison to the mesoporous Ti-MCM-41 and Ti-MCM-48 titanium silicate catalysts, in which synthesis hexadecyltrimethylammonium bromide is used, the process of Ti-SBA-15 preparation does not involve ammonium compounds in the crystallization stage, thus its synthesis is environmentally friendly (taking into account the smell and toxicity of amines, which are formed during calcination process of Ti-MCM-41 and Ti-MCM-48 materials as a result of the decomposition of hexadecyltrimethylammonium bromide)[19]. The combination of titanium silicate catalyst with a solution of hydrogen peroxide allowed to design process, which is very advantageous from the point of view of clean technologies because it can be carried out at mild conditions and at a high selectivity of the main product (which is calculated on the organic raw material). The problem is only a low conversion of the organic raw material.

The aim of this work were the studies on the course of the epoxidation of AGE with hydrogen peroxide over the Ti-SBA-15 catalyst in methanol as the solvent. In our previous studies[17] we presented the epoxidation of AGE in similar conditions but without of any additional solvents, only in water which was introduced with hydrogen peroxide and which was formed during the process. The studies were performed at the following ranges process 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. Performed studies showed, that the most beneficial conditions for the epoxidation of AGE over the Ti-SBA-15 catalyst and in aqueous solution were as follows: temperature of 20°C, molar ratio of AGE/H_2O_2 = 0.03:1, catalyst content 3 wt% and reaction time 60 min. At these mild and relatively safe conditions, the selectivity of DGE amounted to 100 mol%, but the conversion of

AGE and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (efficiency of hydrogen peroxide conversion) amounted to: 4 mol% and 1 mol%, respectively. These studies also showed that the process of AGE epoxidation was very complicated – Figure 2. It was connected with the secondary reactions, which proceed in reaction medium – hydration of the epoxide ring in AGE (formation of 3-allyloxy-1,2-propanediol – 3A12PD), hydrolysis at the epoxide group in AGE, DGE, 3A12PD, epoxidation of the formed allyl alcohol, hydration of the epoxide ring in glycidol and formation of glycerol. However, it is possible to establish such way of performing of this process in which only one product – DGE (the most desired) is obtained. The main problem connected with the process of AGE epoxidation is the phenomenon of an ineffective decomposition of hydrogen peroxide (not explosive decomposition) at the active centres of Ti in the structure of the catalyst. This phenomenon causes that only a little amount of hydrogen peroxide takes part in the epoxidation process. The utilization of the excess of hydrogen peroxide in relation to AGE improves the effective utilization of hydrogen peroxide molecules in the epoxidation process. On the other hand, hydrogen peroxide undergoes very easy the ineffective decomposition, thus even at the excess of hydrogen peroxide its concentration in the reaction mixtures is low. The main cause of this situation is high content of the Ti-SBA-15 catalyst in the reaction mixture (3 wt%). In our previous work[17] we also presented some possible ways of the improving the efficiency of hydrogen peroxide conversion which

we would like to test in future: 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) changing 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 calcination or 5) surface hydrophobisation of the mesoporous titanium silicates. Thus, we decided to test in this work the influence of: the addition of methanol as the solvent and the changes of the concentration of this solvent in the reaction mixture (10–90 wt%) on the course of AGE epoxidation. Moreover, we changed the apparatus for epoxidation - we extended volume of the glass reactor, inserted reflux condenser to this apparatus and temperature adjuster. Also the manner of stirring was changed – we used magnetic stirring. It can allow us to better control temperature and mass transfer, and also to maintain the reproducibility of the reaction conditions and the obtained results.

MATERIAL AND METHODS

In the process of AGE epoxidation the following raw materials were used: AGE ($\geq$99%, Sigma-Aldrich), hydrogen peroxide (min. 30 wt% aqueous solution, Chempur), methanol (min. 99.8%, Chempur) and the Ti-SBA-15 catalyst, previously synthesized by using the method described by Berube et al.[20]. The molar ratio of Si/Ti in the gel before crystallization (in the starting titanium silicate gel) was 40:1. The Ti content in this catalyst was 2.46 wt%, the specific surface area amounted to 622 m^2/g, the size of the pores achieved 5.0 nm and the particles of this catalyst had shape of the rods with the width of about 3–4 mm and the length of 15 mm and were composed with smaller particles with the width of 0.54 mm and the length of 0.76 mm. The detailed description of this catalyst was presented in our previous works[17, 21–23].

All epoxidations were carried out in the glass reactors with the capacity of 50 ml, equipped with the reflux condenser. The temperature of the reaction was kept with help of the water bath, and the reaction was carried out under the vigorous stirring (500 rpm). The influence of the following parameters was studied: temperature (20–80°C), molar ratio of AGE/H_2O_2 (1:1.5–5:1), methanol concentration (10–90 wt%), catalyst content (1–9 wt%) and reaction time (15–240 min).

For the establishing the amount of the unreacted hydrogen peroxide, unreacted AGE and the amounts of the products of this process, the following analytical methods were used: the iodometric titration (unreacted hydrogen peroxide), the $NaJO_4$ method (potentiometric determination of glycerine) and the gas chromatography method. On the basis of these methods quantitative and qualitative analysis's of products were performed. The most important functions describing the process were: the selectivities of the products, the conversion of AGE (C_{AGE}), the conversion of hydrogen peroxide (C_{H2O2}) and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (the efficiency of hydrogen peroxide conversion – E_{H2O2}). These
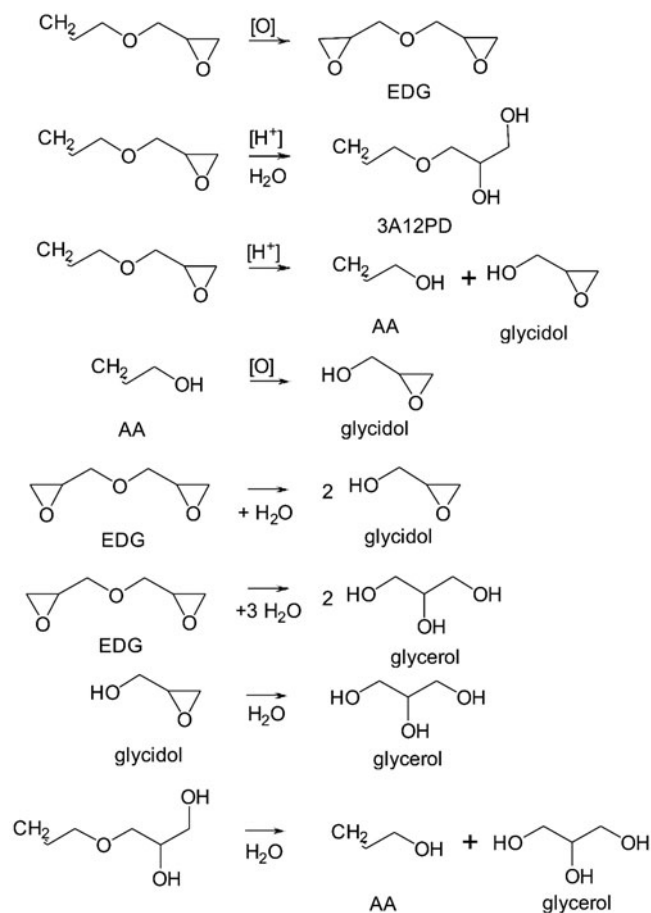

Figure 2. Main reaction and side reactions occurring during the epoxidation of allyl-glycidyl ether process with hydrogen peroxide over the Ti-SBA-15 catalyst

functions were taken into account during choosing the most beneficial conditions of AGE epoxidation process.

RESULTS AND DISCUSSION

The influence of temperature

The influence of temperature was studied for the following values of the remaining parameters (starting parameters): molar ratio of AGE/H_2O_2 = 1:1, methanol concentration 50 wt% and catalyst content 3 wt%. The reaction time was 120 min. The obtained post-reaction mixtures had different colours, depending on the temperature at which the reaction was conducted. At the temperature range of 20–40°C – yellow colour of mixtures was observed, but when the epoxidation was carried out at 50°C, the colour was less intense, and at the temperature 80°C the mixture was almost clear. The yellow-orange colour can be related with the formation of the complex $[TiO.H_2O_2]^{2+}$, which are formed from titanium ions and hydrogen peroxide in the reaction environment[24]. It is connected with the phenomenon of leaching of titanium from the catalyst structure in the presence hydrogen peroxide and diols[21, 25–30].

The studies on the influence of temperature on the course of AGE epoxidation showed that temperature influenced on the selectivities of the products and also but not so significantly on the conversion of AGE – Figures 3–4. Depending on the temperature the main pro-
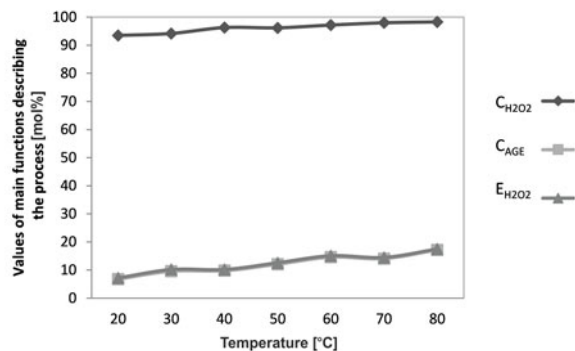
duct of the process was glycerol (temperatures 20–60°C) or 3A12PD (temperatures 70–80°C). DAE was formed with very small selectivity (1–2% mol), independent of the temperature. Probable, DGE could formed during our studies but it was so unstable that it underwent very fast collapsing to glycidol, and next the hydration to glycerol. Also the decomposition of AGE to AA and glycidol, the epoxidation AA to glycidol, and next the hydration glycidol to glycerol was possible. 3A12PD also could decompose to AA and glycerol, and next AA could be converted to glycerol (by the stage of glycidol). It is impossible on this stage of our studies to answer, which from these three ethers (AGE, DGE or 3A12PD) is the most instable at the conditions at which the reaction is performed. As the most beneficial temperature was taken the temperature of 80°C – mainly the values of conversion of AGE and efficiency of hydrogen peroxide conversion were taken into account during selection this the most beneficial temperature. At this temperature the selectivities of the products were as follows: DGE 1.9 mol%, 3A12PD 62.7 mol%, glycidol 4.0 mol%, glycerol 28.7 mol% and AA 28.7 mol%. The conversion of AGE reached 17.2 mol%, the conversion of H_2O_2 was 98.3 mol% and efficiency of hydrogen peroxide conversion amounted to 17.5 mol%.

The formation of 3A12PD during our studies can be explained by the following derivative formed in the structure of the catalyst[17]:
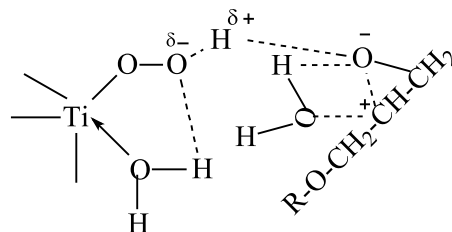
Acid-catalyzed cleavage of the oxirane rings in this epoxide compounds has considerable S_N1 character and the nucleofilic attack is easy to occur at the more crowded carbon atom that can best accommodate the positive charge. On the basis this derivative also the formation of glycerol can be explained.

Moreover, the collapsing of ethers by the cleavage of the etheric bond can be explained by the following derivative which is also formed in the structure of the Ti-SBA-15 catalyst but in this reaction take part Si atoms:

The formation of the negative charge on the oxygen atom from the ether group can be a result of shifting electrons from the epoxide group or the allylic double bound, depending on the investigate ether (AGE, DGE or 3A12PD).

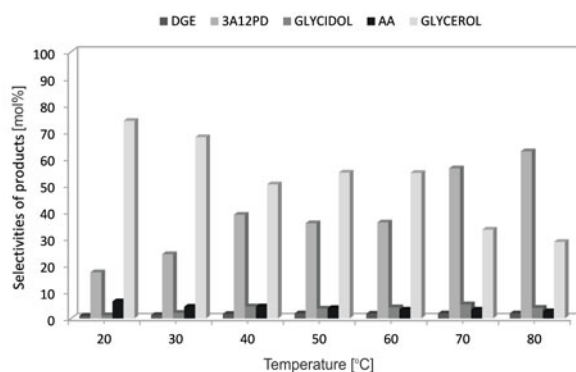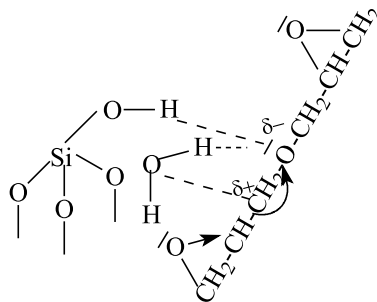**Figure 3.** Values of the main functions describing the process of AGE epoxidation for the studied temperatures

Figure 4. Values of the selectivities of DGE, 3A12PD, glycidol, AA and glycerol for the studied temperatures

The influence of the molar ratio of AGE/H₂O₂

The influence of molar ratio of AGE/H₂O₂ was studied at the temperature of 80°C, while the other parameters were the same as in the previous stage of our studies.

The results of the studies on the influence of the molar ratio of AGE/H₂O₂ on the course of AGE epoxidation were presented on Figures 5–6. The main products of the epoxidation process were 3A12PD and glycerol. The selectivity of 3A12PD raised during the increasing the molar ratio of reactants from 44.8 mol% to 61.7 mol%, and the selectivity of glycerol decreased from 50.3 to 17.8 mol%. It was observed, that the selectivity of DGE increased with the increasing of the molar ratio of reactants and achieved the maximum value (11.6 mol%) for the highest molar ratio of reactants (EAG/H₂O₂ = 5:1). This value of the selectivity of DGE was the basis the selection the most favourable molar ratio of reactants, and therefore the molar ratio of AGE/H₂O₂ =5:1 has been chosen as the most beneficial. For this molar ratio of reactants the following values of the main functions describing the process were achieved: the selectivity of DGE 11.6 mol%, the selectivity of 3A12PD 61.7 mol%, the selectivity of glycidol 1.8 mol%, the selectivity of AA 7.1 mol%, the selectivity of glycerol 17.8 mol%, the conversion of AGE 3.8 mol%, the conversion of H₂O₂ 91.9 mol%, and the efficiency of hydrogen peroxide conversion 20.7 mol%.
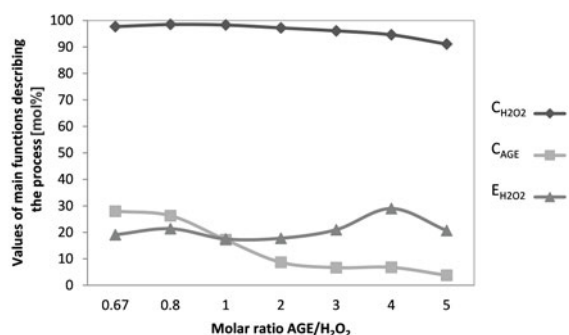

Figure 5. Values of the main functions describing the process of AGE epoxidation for the studied molar ratios of AGE/H₂O₂
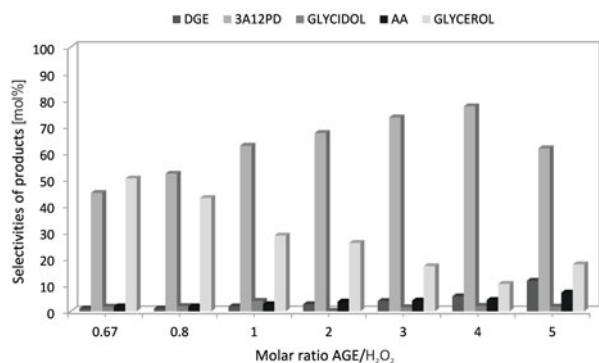

Figure 6. Values of the selectivities of DGE, 3A12PD, glycidol, AA and glycerol for the studied molar ratios of AGE/H₂O₂

The influence of methanol concentration

The studies on the influence of methanol concentration were carried out at the same starting conditions and for the molar ratio of AGE/H₂O₂ = 5:1 (Figs. 7–8). The stu-
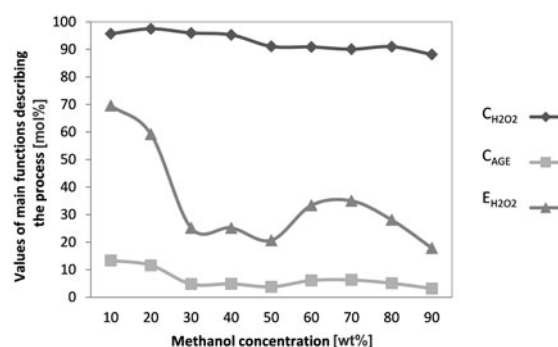

Figure 7. Values of the main functions describing the process of AGE epoxidation for the studied methanol concentrations
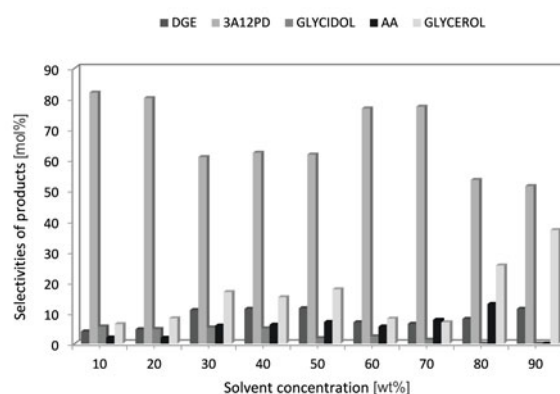

Figure 8. Values of the selectivities of DGE, 3A12PD, glycidol, AA and glycerol for the studied methanol concentrations

died methanol concentration were as follows: 10, 20, 30, 40, 50, 60, 70, 80 and 90 wt%. Also at this stage of studies 3A12PD and glycerol were the main products. During the increase of methanol concentration the selectivity of 3A12PD decreased from 82.0 mol% to 51.4 mol%, and the selectivity of glycerol raised from 6.4 mol% to 37.2 mol%. The selectivity of DGE achieved very small values in the whole range of methanol concentration. As the most beneficial concentration of methanol the concentration of 30 wt% was taken – because the further increase in the methanol concentration did not cause any significant changes in the values of the main function describing the process. At this methanol concentration, the main functions describing the process achieved the following values: the selectivity of DAE 11.0 mol%, the selectivity of 2A12PD 60.9 mol%, the selectivity of glycidol 5.3 mol%, the selectivity of AA 5.9 mol%, the selectivity of glycerol 16.9 mol%, the conversion of AGE 4.8 mol%, the conversion of H₂O₂ 96 mol% and the efficiency of hydrogen peroxide conversion 25.7 mol%.

The influence of the catalyst content

The studies on influence of catalyst Ti-SBA-15 content were carried out at the same conditions as in the previous stage and for methanol concentration 30 wt% (Figs. 9–10). The influence of Ti-SBA-15 catalyst content was studied in the range of 1–9 wt%. The studies showed that the main product was 3A12PD, independent of the catalyst content. The selectivity of this compound raised from 67.3 mol% to 83.3 mol%. The selectivity of DGE was the highest for the catalyst content amounted to 3 wt%. For the next contents of the catalyst (5, 7 and 9 wt%)
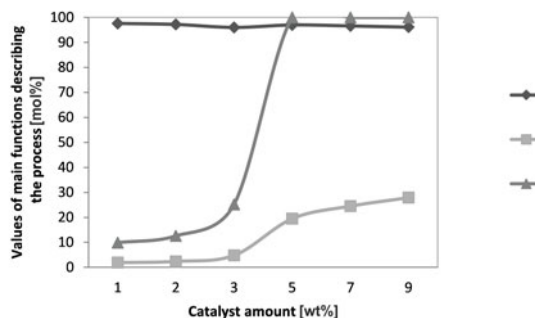
Figure 9. Values of the main functions describing the process of AGE epoxidation for the studied Ti-SBA-15 catalyst contents
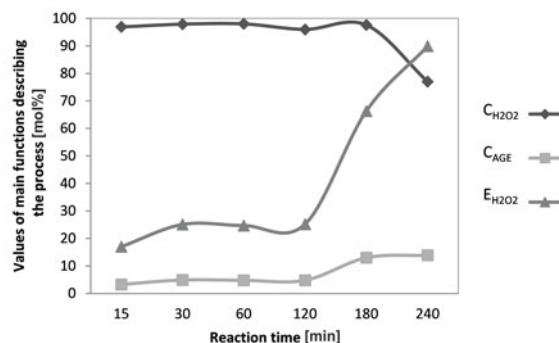

Figure 11. Values of the main functions describing the process of AGE epoxidation for the studied reaction time
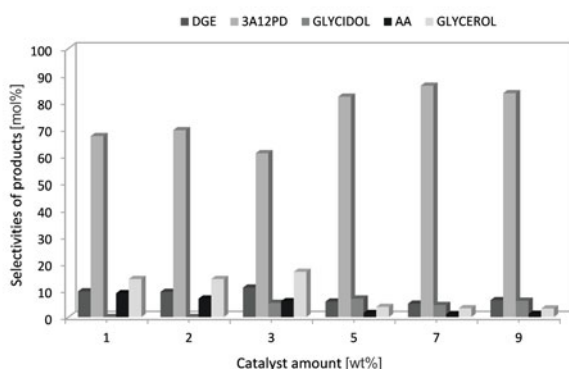

Figure 10. Values of the selectivities of DGE, 3A12PD, glycidol, AA and glycerol for the studied Ti-SBA-15 catalyst contents
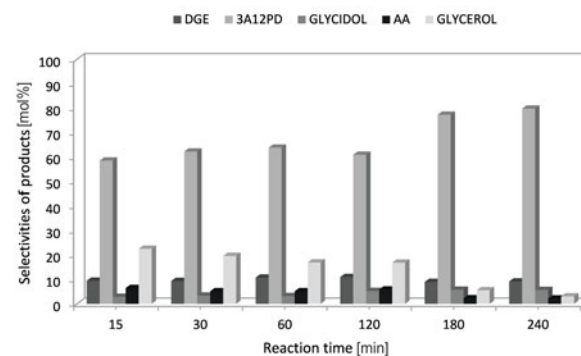

Figure 12. Values of the selectivities of DGE, 3A12PD, glycidol, AA and glycerol for the studied reaction time

this function showed decreasing tendency. As the most beneficial the catalyst content 3 wt% was taken. At this content of the catalyst the main functions of the process achieved the following values: the selectivity of DGE 11.0 mol%, the selectivity of 3A12PD 60.9 mol%, the selectivity of glycidol 5.3 mol%, the selectivity of AA 5.9 mol%, the selectivity of glycerol 16.9 mol%, the conversion of AGE 4.8 mol%, the conversion of H_2O_2 96.0 mol% and the efficiency of hydrogen peroxide conversion 25.2 mol%.

The influence of reaction time

Studies on the influence of the reaction time were carried out at the parameters described as the most beneficial in the previous stages of our examinations (Figs. 11–12). The reaction time was changed in the range of 15–240 min. The analysis of the obtained results showed, that the DGE selectivity was practically constant over the whole range of the tested reaction time (9.2–11.0 mol%). The conversion of AGE increased with the increasing of the reaction time from 3.3 to 13.9 mol%, the same as the efficiency of hydrogen peroxide conversion (from 17.0 mol% to 89.9 mol%). Taking into account the above results, as the most favourable time for this process was taken time 240 min. For this reaction time the following values of the main functions describing the process were obtained: the selectivity of DGE 9.2 mol%, the selectivity of 3A12PD 79.8 mol%, the selectivity of glycidol 5.7 mol%, the selectivity of AA 2.2 mol%, the selectivity of glycerol 3.1 mol%, the conversion of AGE 13.9 mol%, the conversion of H_2O_2 77.0 mol% and the efficiency of hydrogen peroxide conversion 89.9 mol%.

CONCLUSIONS

The analysis of the influence such parameters as: temperature, molar ratio of AGE/H_2O_2, the methanol concentration, the Ti-SBA-15 catalyst content and the reaction time on the course of EAG epoxidation showed that these parameters have significant effect on the course of this process. The most beneficial were the following values of the studied parameters: the temperature 80°C, the molar ratio of AGE/H_2O_2 = 5:1, the methanol concentration 30 wt%, the catalyst content 3 wt% and the reaction time 240 minutes. These studies showed that it was impossible to obtain EDG as the only product in this process. At all conditions the hydration of the epoxide ring in AGE and the decomposition of ethers (AGE, DGE and 3A12PD) were observed, which caused the formation of AA, glycidol and glycerol. From these additional products, 3A12PD and glycerol were formed preferably. The comparison the results presented in this work with our previous work[17] shows that the addition of methanol changed the way of the AGE epoxidation, because the most beneficial conditions obtained for epoxidation AGE in water medium were different from obtained in this work. The addition of methanol as the solvent caused the increase in values of the AGE conversion (at the most beneficial conditions it amounted to 13.9 mol% and this function increased above 3 times in comparison to our previous studies[17]) and the efficiency of hydrogen peroxide conversion (90 times – from 1 mol% to 89.9 mol%). Especially, the increase in the values of the second function (the efficiency of hydrogen peroxide conversion) is important from the point of view of the utilization of hydrogen peroxide. Studies also showed that this process still needs further

examinations on the increase of the selectivity of DAE and the conversion of AGE, and also on the decrease the amount of the by-products of this process – products of the hydration of the epoxide rings and products of the collapsing of the etheric compounds. Probably, the other ways presented in our previous work[17] should be tested and it can help in future to optimize this process.

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