

Acetonitrile and water as solvents for the epoxidation of allylic compounds over the Ti-SBA-15 catalyst

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Abstract Research studies on the epoxidation of allyl alcohol, methallyl alcohol, crotyl alcohol and 1-butene-3-ol over the titanosilicate catalysts—Ti-SBA-15 have been conducted. The studies were carried out in an acetonitrile medium and in water. However, water was introduced only with an oxidizing agent, which was a 30 wt% aqueous solution of hydrogen peroxide. When investigating the influence of chosen technological parameters, the most favorable conditions for conducting epoxidation for each of the allylic alcohols, both in the acetonitrile medium and in water, were determined. The obtained results were compared. The comparison showed that water may be a good solvent for the epoxidation of allylic alcohols. The phenomenon of epoxy ring hydration can be limited by choosing appropriate reaction conditions, when the reaction is performed only in an aqueous medium.

Keywords Ti-SBA-15 · Allylic alcohols · Epoxide compounds · Liquid phase epoxidation

Introduction

Epoxy compounds obtained from the epoxidation of allyl alcohol (AA), methallyl alcohol (MAA), crotyl alcohol (CA), and 1-butene-3-ol (1B3O) find numerous applications in the cosmetic industry (cleansing and moisturizing cosmetics), household chemistry (shampoos, toothpastes, washing agents and disinfectants), drug production (HIV drugs, antibiotics) and in the polymer industry (plasticizers, paint and varnish coatings) [1–10]. Therefore, it is crucial to develop an environmentally friendly method for their preparation.

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The process of the epoxidation of allylic compounds over titanium silicalite and titanosilicates catalysts has been investigated for more than ten years. Until now, the following catalysts have been used in this process: TS-1, TS-2, Ti-Beta, Ti-MCM-41, Ti-MCM-48 and Ti-SBA-15—tests were carried out mainly in methanol as a solvent. Unfortunately, there are many inconveniences associated with this process. The first includes a loss of catalytic activity that is connected with leaching of titanium from the catalyst, disintegration of the catalyst structure, and occlusion of polymer products within catalyst pores [11–16]. The second inconvenience is the need to use a large amount of a polar solvent (methanol) in the process, even 80 wt%. Such amounts of the solvent have to be recovered, regenerated and reused in the process. Another disadvantage of using methanol as a solvent is its high volatility. This results in a loss of this compound during the epoxidation process at higher temperatures [17, 18]. A beneficial alternative for the epoxidation of allylic compounds would be to conduct epoxidation in acetonitrile or water, if the latter would not be additionally introduced into the reaction medium. Instead, it would come from the aqueous solution of hydrogen peroxide (30 wt% aqueous solution of hydrogen peroxide), which is used as the oxidant in this process. The second solvent seems particularly interesting if the epoxidation process conditions could be chosen in a way as to reduce the hydration process of the epoxy ring. The titanosilicate catalysts are particularly attractive as catalysts for the epoxidation process of allylic compounds. One of the latest titanosilicate catalysts is Ti-SBA-15. Compared to the previous titanosilicate catalysts, its synthesis is friendlier to the environment, because ammonium compounds that convert into amines during calcination are not used as a “structure-directing agent”, which, as a result, can be very cumbersome in terms of smell. The triblock copolymer of ethylene oxide and propylene oxide—Pluronic P123 is used for the synthesis of Ti-SBA-15 as a “structure-directing agent”. Ti-SBA-15 catalyst has a specific surface from 600 up to 1,000 m²/g and the size of pores from 5 up to 30 nm. Its structure resembles a honeycomb, wherein transverse channels are formed between the main ones—this creates additional porosity in this material. Moreover, the pore walls of Ti-SBA-15 material are much thicker, which should increase the durability of the material during epoxidation conducted at higher temperatures [19–28]. A disadvantage of the previous titanium silicalite materials, such as TS-1, was poor recurrence of synthesis. In the case of Ti-SBA-15, our preliminary studies had shown that it is much more stable and can be effectively used in the epoxidation process [17].

The aim of this paper was to conduct research studies on the process of epoxidation of allylic compounds over the Ti-SBA-15 catalyst in acetonitrile and water as the solvents. Water was used only with an aqueous solution of an oxidizer (30 % aqueous solution of hydrogen peroxide) and it was not introduced into the reaction mixture additionally. The influence of chosen technological parameters on the course of epoxidation of allylic compounds in acetonitrile and water was investigated. The results obtained for these two solvents were compared. Based on the comparison, the most beneficial solvent for carrying out this process was chosen.

Experimental

The Ti-SBA-15 material was synthesized by the method of Berube et al. [27]. The following raw materials were used in the synthesis: Pluronic P123 (Aldrich, MW = 5,800) as structure-directing agent, tetraethylorthosilicate (TEOS 98 %, Aldrich) as a silicon source and tetraisopropyl orthotitanate (TiPOT > 98 %, Merc) as a titanium precursor. The detailed characteristics of the obtained Ti-SBA-15 catalyst were presented in our previous article [29].

In the epoxidation of allylic compounds, the following raw materials were used: AA (98 %, Fluka), MAA (98 %, Fluka), CA (95 %, Fluka), 1B3O (97 %, Merck), hydrogen peroxide (30 wt % water solution, POCH Gliwice) and acetonitrile (analytical grade, POCH Gliwice). The research studies in acetonitrile were conducted with the following parameters: molar ratio of the allylic compound/hydrogen peroxide = 1, acetonitrile concentration 40 wt%, catalyst content 3 wt%, reaction time 2 h, and intensity of stirring 500 rpm. The studies in water were conducted under very similar conditions. The only difference was that the reaction medium did not include any additional water apart from the amount which derived from the hydrogen peroxide solution (30 wt% aqueous solution) and formed in the reaction medium during the process. During the studies on the influence of the molar ratio of reactants on the course of epoxidation, the appropriate amount of the raw materials were calculated in the following way: the calculations were started from the appropriate amount of allylic compound, and the next reactants were calculated on the basis of the initial amount of this allylic compound (this amount of allylic compound was the same for all molar ratio of reactants). The process was carried out in a glass vial with the volume of 12 cm³ equipped with a rubber septum and a capillary. The vials were located in a shaker holder and immersed in a water bath. After the process, the post-reaction mixtures were cooled down and the catalyst was separated from these mixtures. All post-reaction solutions obtained in this way were clear and one-phase. In order to calculate the mass balance, the post-reaction solutions were analyzed in the following way: unreacted hydrogen peroxide was determined by iodometry [30], and glycerol formed in the process was determined by potentiometry [31]. The remaining products and the unreacted organic substrate were analyzed quantitatively by means of gas chromatography. For the post-reaction solutions obtained after AA epoxidation, the method of external standard and for the post-reaction solutions of the next three allylic compounds, the method of internal standardization was applied. The chromatographic analysis was performed on the FOCUS apparatus with a flame ionization detector (FID) fitted with Quadrex capillary columns filled with methyl-phenylsiloxanes. 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 min, an increase to 250 °C at the rate of 10 °C/min, isothermally at 250 °C for 5 min, cooling to 60 °C. The qualitative analyses were performed on a Hewlett Packard 6890 apparatus equipped with a mass detector HP 5973 and using a capillary column HP 5MS (30 m × 0.25 mm × 0.25 μm).

After calculating the mass balance, the main functions describing the process were determined: the selectivity of epoxide compound in relation to allylic compound consumed, also the selectivities of by-products were the same calculated ($S_{\text{product/allylic compound}}$), the conversion of allylic compound ($C_{\text{allylic compound}}$) and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed $S_{\text{org. comp/H}_2\text{O}_2}$:

$$S_{\text{product/allylic compound}} = \frac{\text{Amount of moles of product}}{\text{Amount of moles of allylic compound consumed}} \times 100 (\text{mol}\%)$$

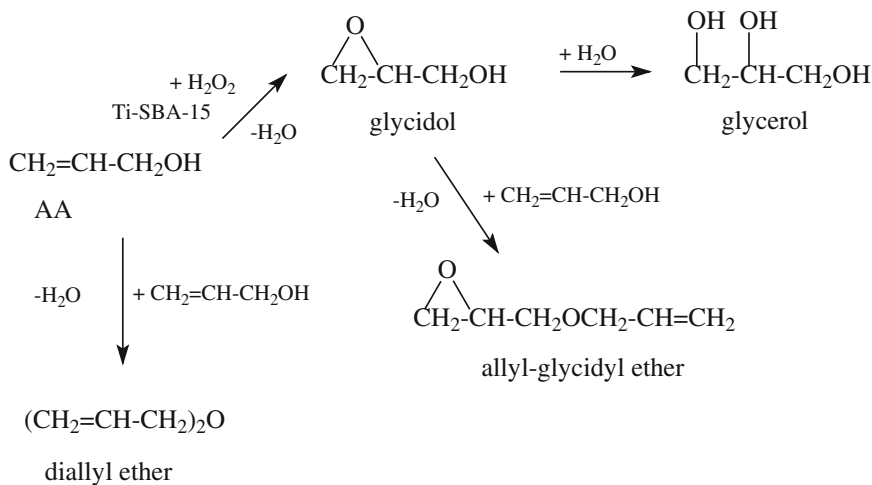
$$C_{\text{allylic compound}} = \frac{\text{Amount of moles of allylic compound consumed}}{\text{Amount of moles of allylic compound introduced into reactor}} \times 100 (\text{mol}\%)$$

$$S_{\text{org. comp/H}_2\text{O}_2} = \frac{\text{Amount of moles of organic compounds for information of which H}_2\text{O}_2 \text{ is needed}}{\text{Amount of moles of H}_2\text{O}_2 \text{ consumed}} \times 100 (\text{mol}\%)$$

For the last function in the whole text, the abbreviation of “efficiency of H_2O_2 ” will be used.

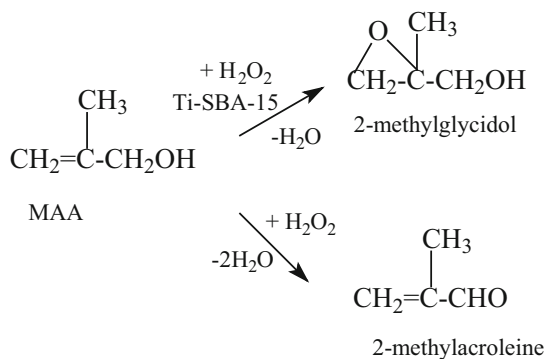
Results and discussion

The studies showed that during the process of AA epoxidation in acetonitrile and in water solution, the following products were formed:



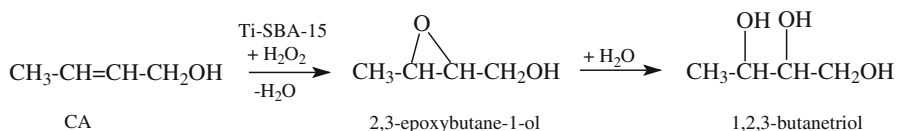
The main product of AA epoxidation is glycidol, and the by-products are glycerol, diallyl ether and allyl-glycidyl ether.

During the process of MAA epoxidation in acetonitrile and in water solution, the following products were formed:

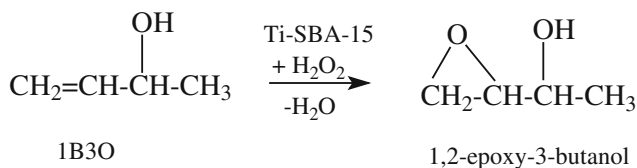


The main product of MAA epoxidation is 2-methylglycidol and the only by-product of this process is 2-methylacroleine.

The studies on the epoxidation of CA showed that the only product of this process was 1,2,3-butanetriol. This compound was formed as a result of hydration of epoxide ring in 2,3-epoxybutane-1-ol:



During the process of 1B3O epoxidation the only product was the epoxide compound 1,2-epoxy-3-butanol:



Studies on epoxidation of allylic compounds in acetonitrile

The results of the studies of the effect of temperature on selectivity of epoxy compounds for the epoxidation of 4 chosen allylic compounds in acetonitrile are shown in Fig. 1 and in Table 1.

Fig. 1 shows that glycidol selectivity increases from 49 mol% (20 °C) up to 73 mol% (40 °C) and then decreases to 33 mol% (80 °C) under the studied conditions. At the same time, at low temperatures (20 and 30 °C), the only by-product is glycerol with the selectivity of 51 and 47 % mol. This means that a half of the glycidol formed at the lowest temperatures is hydrolyzed to glycerol. At a temperature of 40 °C only 27 % of the obtained glycidol is converted to glycerol,

and at temperatures from 50 up to 80 °C, the second by-product starts appearing in the post-reaction mixture: diallyl ether (its selectivity increases from 5 up to 12 mol%). At the highest temperatures of the study (70 and 80 °C), glycidol hydrolysis to glycerol and etherification of the organic substrate (glycerol selectivity of 55–56 mol% and diallyl ether of 11–12 mol%) take place.

AA conversion decreases with temperature rising from 36 up to 19 mol% (almost 50 %) as shown in Table 1. This is probably due to the inefficient decomposition of hydrogen peroxide occurring at higher temperatures, as indicated by the reduction of value of the third main function describing the process, efficiency of H₂O₂ from 38 mol% (20 °C) up to 20 mol% (80 °C) as shown in Table 1. The most favorable temperature for the process of AA epoxidation in acetonitrile was 30 °C. The selection of this temperature was determined by the maximum value of the conversion of AA (62 mol%) and the efficiency of H₂O₂ (65 mol%) and a relatively high selectivity of glycidol 53 mol%.

In the case of the epoxidation of MAA, the selectivity of transformation to 2-methylglycidol increases in the temperature range of 20–80 °C from 27 up to 45 mol% (Fig. 1). Additional studies carried out at higher temperatures have shown that the value of this function decreases to 37 mol% for the temperatures of 90 and 100 °C. It is worth noting that a competitive reaction for the process of the epoxidation of the double bond taking place in the tested conditions is the oxidation of the OH- group of MAA to an aldehyde group. The selectivity of 2-methylacrolein under the studied conditions decreases slightly from 73 mol% (20 °C) to 61 mol% (30 °C), and then it is practically the same (under the studied conditions, 2-methylacrolein is the main product of the process). Changes in the temperature of the process from 20 up to 80 °C do not cause significant changes in the values of MAA conversion and efficiency of H₂O₂ (Table 1). Both functions of the process are as follows: about 43–49 and 14–15 mol%. The temperature of 80 °C is the most advantageous for the epoxidation process of MAA (considering the fact that the highest selectivity of epoxy compound is obtained at this temperature).

Studies on CA epoxidation in acetonitrile have shown that regardless of the temperature of the process, the whole content of the epoxy compound formed underwent hydration to 1,2,3-butanetriol thus the selectivity of the epoxy compound was 0 mol% (Fig. 1) and the selectivity of 1,2,3-butanetriol was 100 mol%. The same phenomenon was observed for CA in the case of all other parameters studied in this work. The CA conversion in the temperature range of 20–40 °C increased from 58 up to 73 mol% (Table 1). Later, it remained the same. The efficiency of H₂O₂ changed in a similar way. The temperature of 40 °C was considered the most advantageous for the epoxidation of CA. Taking into account that at the next stages of the studies on CA epoxidation, the selectivity of 1,2,3-butanetriol was always 100 mol%, only the values of conversion of CA and efficiency of H₂O₂ will be taken for choosing the best parameters.

The studies on the effect of temperature on the course of epoxidation of 1B3O showed that the selectivity of the epoxy compound was 100 mol% (Fig. 1) regardless of the temperature of the process. In the studied temperature range, the values of the conversion of 1B3O and the efficiency of H₂O₂ did not change and amounted to about 53 mol% (Table 1). The temperature of 20 °C was considered

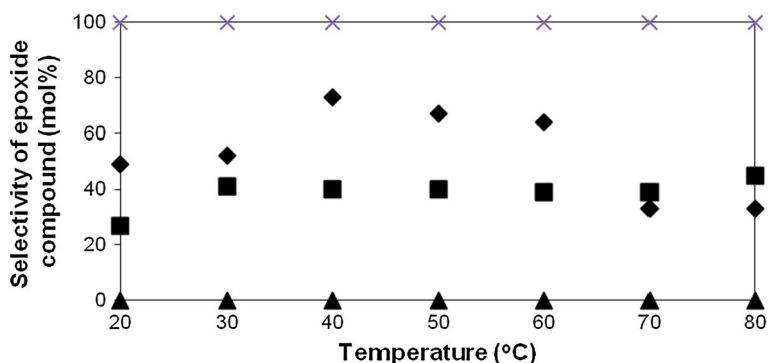


Fig. 1 The influence of temperature on the course of allylic compounds epoxidation in acetonitrile: *black diamond* suit glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (molar ratio allylic compound/hydrogen peroxide 1:1, acetonitrile concentration 40 wt%, Ti-SBA-15 catalyst content 3 wt%, reaction time 2 h, intensity of stirring 500 rpm)

Table 1 The influence of temperature on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in acetonitrile)

Temperature (°C)	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
20	36	43	58	55
30	62	43	62	53
40	50	45	73	52
50	30	47	72	50
60	26	46	72	50
70	20	47	72	49
80	19	49	72	50

Temperature (°C)	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
20	38	14	58	56
30	65	14	63	54
40	53	14	74	54
50	29	14	72	53
60	27	14	72	54
70	21	14	72	52
80	20	15	72	53

the most favorable temperature for the epoxidation process of 1B3O. The same as above, taking into account that at next stages of the studies on 1B3O epoxidation the selectivity of 1,2-epoxybutane-3-ol was always 100 mol%, only the values of conversion of 1B3O and the efficiency of H₂O₂ will be taken for choosing the best parameters.

Studies of the influence of the molar ratio of reactants on the epoxidation process of various alcohols were carried out at the most favorable temperatures chosen for these alcohols and with parameters taken as initial at the beginning of the study (Fig. 2; Table 2).

Research studies on the influence of molar ratio of reactants on the course of AA epoxidation have shown that a change in the molar ratio of reactants from 1 to 5 increases the selectivity of glycidol from 53 mol% (molar ratio of AA/H₂O₂ = 1) up to 73 mol% (molar ratio of AA/H₂O₂ = 5) as shown in Fig. 2. With equimolar ratio of reactants, a half of the glycidol formed is hydrated to glycerol. However, with increasing amounts of AA in the reaction mixture, water molecules have more difficulty in accessing glycidol molecules. As a result, the hydration of epoxy rings in glycidol molecules is slowed down (the selectivity of glycerol at a molar ratio of reactants amounting to 5:1 is only 22 mol%). Simultaneously, at a molar ratio of AA/hydrogen peroxide = 2, the third product appears in the reaction mixture, which is diallyl ether. Regardless of the increasing molar ratio, its selectivity is about 5 mol%. In the investigated range of molar ratios of reactants, the conversion of AA decreases from 62 to 16 mol% and the efficiency of H₂O₂ increases from 65 up to 83 mol% (Table 2). The increase in the value of the second function indicates that the larger amount of AA in the reaction mixture results in the stabilization of hydrogen peroxide molecules and prevents their inefficient decomposition. The most favorable molar ratio at this stage of the studies was the molar ratio of AA/H₂O₂ that equaled 1:1 (taking into account AA conversion and selectivity of glycidol).

Studies of the influence of the molar ratio of reactants on the course of MAA epoxidation have shown that the selectivity of the epoxy compound increases with the increase in the molar ratio of reactants from 45 mol% (equimolar ratio of reactants) up to 73 mol% (molar ratio of MAA/hydrogen peroxide = 5:1) as shown in Fig. 2. However, the selectivity of the second product in this process (2-methylacrolein) decreased from 54 to 27 mol%. The MAA conversion decreases in the studied range of molar ratios from 49 to 20 mol%, and the efficiency of H₂O₂ increases from 15 up to 32 mol% (Table 2). The stability of peroxide increases with the increasing concentration of MAA in the reaction mixture. Further investigation included molar ratio of reactants that equaled 5.

Studies on the influence of the molar ratio of reactants on the course of CA and 1B3O epoxidation have shown that the equimolecular ratio of reactants can be considered as the most favorable (Table 2).

Studies on the influence of acetonitrile concentration (solvent) on the course of the epoxidation process of particular alcohols were conducted at temperatures and molar ratios of reactants considered for these alcohols as the most favorable. Other initial parameters were also applied (Fig. 3; Table 3).

Studies on the influence of acetonitrile concentration on the course of AA epoxidation have shown that with increasing the acetonitrile concentration in the reaction mixture, the selectivity of glycidol increases from 0 mol% (acetonitrile concentration: 5 wt%) up to 79 mol% (acetonitrile concentration: 80 wt%). Then it decreases to 52 mol% (acetonitrile concentration: 90 wt%) as shown in Fig. 3. Simultaneously, the hydration process of glycidol to glycerol is stopped (glycerol

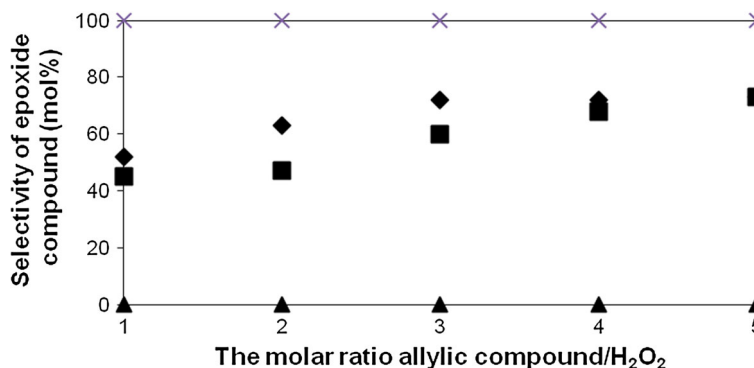


Fig. 2 The influence of the molar ratio of reactants on the course of allylic compounds epoxidation: *black diamond* suit glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 30 °C for AA, 80 °C for MAA, 40 °C for CA and 20 °C for 1B3O, acetonitrile concentration 40 wt%, Ti-SBA-15 catalyst content 3 wt%, reaction time 2 h, intensity of stirring 500 rpm)

Table 2 The influence of the molar ratio of reactants on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in acetonitrile)

Molar ratio of reactants	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
1	62	49	73	55
2	35	48	48	36
3	27	32	30	22
4	23	24	25	20
5	16	20	17	8

Molar ratio of reactants	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
1	65	15	74	56
2	72	31	49	37
3	87	30	30	22
4	97	30	25	20
5	83	32	18	8

selectivity decreases from 100 to 9 mol%). Two additional by-products appear in the reaction mixture as a result of acetonitrile concentration of 60 wt% utilization, which are ethers: diallyl ether (selectivity of 4 mol%) and allyl-glycidyl ether (selectivity of 4 mol%). Their selectivity increases with the increasing acetonitrile concentration in the reaction mixture to 19 and 20 mol%, at a concentration of acetonitrile of 90 wt%. AA conversion decreases from 97 to 62 mol% with the increasing acetonitrile concentration in the reaction mixture from 5 to 40 wt% and next raises to 76–79 mol% (acetonitrile concentration 80–90 wt%) as shown in Table 3. Moreover, the efficiency of H₂O₂ decreases from 100 to 79 mol%

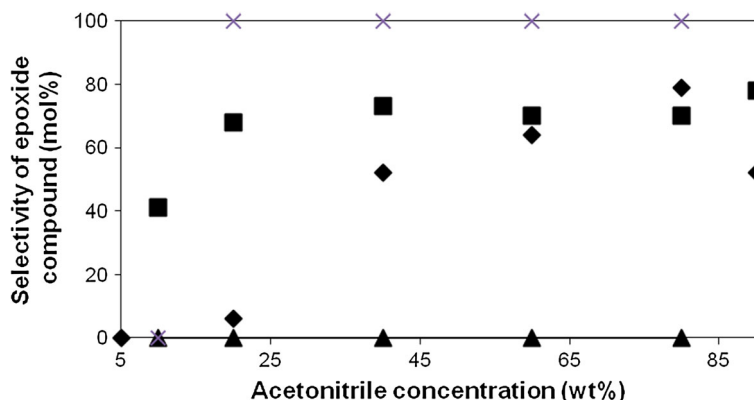


Fig. 3 The influence of acetonitrile concentration on the course of allylic compounds epoxidation: *black diamond suit* glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 30 °C for AA, 80 °C for MAA, 40 °C for CA and 20 °C for 1B3O, molar ratio allylic compound/hydrogen peroxide 1:1 for AA, CA, 1B3O and 5:1 for MAA, Ti-SBA-15 catalyst content 3 wt%, reaction time 2 h, intensity of stirring 500 rpm)

Table 3 The influence of acetonitrile concentration on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in acetonitrile)

Acetonitrile concentration	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
5	97			
10		15	68	0
20	85	19	70	25
40	62	20	73	55
60	69	19	66	46
80	79	19	57	46
90	76	17		

Acetonitrile concentration	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
5	100			
10		9	68	0
20	89	19	71	25
40	65	23	74	56
60	74	21	68	47
80	88	20	67	47
90	79	20		

(Table 3). The acetonitrile concentration that was considered the most favorable was 80 wt%.

Studies on the influence of acetonitrile concentration on the course of MAA epoxidation have shown that the selectivity of epoxy compound increases from

41 mol% (acetonitrile concentration: 10 wt%) up to 73 mol% (acetonitrile concentration: 40 wt%) and then remains practically unchanged. The only by-product of the process is 2-methylacrolein, which selectivity decreases with the increasing acetonitrile concentration in the reaction mixture. The MAA alcohol conversion increases slightly over the studied range of acetonitrile concentration from 15 up to about 17–20 mol%, as does the efficiency of H_2O_2 from 9 up to about 20–23 mol% (Table 3). Acetonitrile concentration of 40 wt% was considered the most favorable.

Studies of the influence of acetonitrile concentration on the course of CA and 1B3O epoxidation have shown that the acetonitrile concentration of 40 wt% can be considered as the most favorable (Table 3).

Studies of the influence of the catalyst content on the process of epoxidation of various alcohols were carried out at temperatures, molar ratios of reactants and acetonitrile concentration chosen for these alcohols as the most favorable and with other initial parameters (Fig. 4; Table 4).

Studies on AA epoxidation have shown that with the increasing content of the catalyst in the reaction mixture from 0.5 up to 2 wt%, the selectivity of glycidol increases from 0 up to 79 mol% as shown in Fig. 4. A further increase in the amount of the catalyst up to 4 and 5 wt% results in a decrease of the selectivity of this compound to about 60 mol%. A similar situation occurs in the conversion of AA and the efficiency of H_2O_2 . Both functions increase from 5 up to 79 and 88 mol%, and then decrease to 61 and 65 mol% (Table 4). This shows that when the content of the catalyst is more than 3 wt%, the inefficient decomposition process of hydrogen peroxide over the catalyst becomes more important. This, in turn, leads to a decrease in the conversion of the organic substrate (AA). Two by-products appear in the post-reaction mixture as a result of the catalyst content that amounts to 3 wt%, which are ethers: diallyl ether and allyl-glycidyl ether which are formed with selectivity from 12–14 mol%. At this stage of the studies, the catalyst content at the level of 3 wt% was considered the most favorable.

Studies on the influence of the catalyst content on the course of MAA epoxidation have shown that with increasing the content of the catalyst in the reaction mixture, the selectivity of the epoxy compound increases from 0 mol% (catalyst content: 0.5 wt%) up to about 72 mol% (catalyst content: 3 wt%), and then remains the same (Fig. 4). The selectivity of 2-methylacrolein decreases from 99 to 28 mol% in the range of the catalyst content from 0.5 to 3 wt%, and then remains the same. The formation of a small amount of bis(methallyl) ether (about 1 mol%) was observed at the lowest content of the catalyst (0.5 and 1 wt%). The conversion of MAA and efficiency of H_2O_2 hardly depended on the catalyst content in the reaction mixture and amounted to 16–20 and 25–32 mol%, respectively (Table 4). At this stage of the studies, the catalyst content that amounted to 3 wt% was considered the most favorable.

Studies of the influence of the catalyst content on the course of CA and 1B3O epoxidation have shown that the catalyst content that amounts to 3 wt% can be taken as the most favorable (Table 4).

Studies of the influence of reaction time on the course of the epoxidation process of various alcohols were carried out at temperatures, molar ratios of reactants,

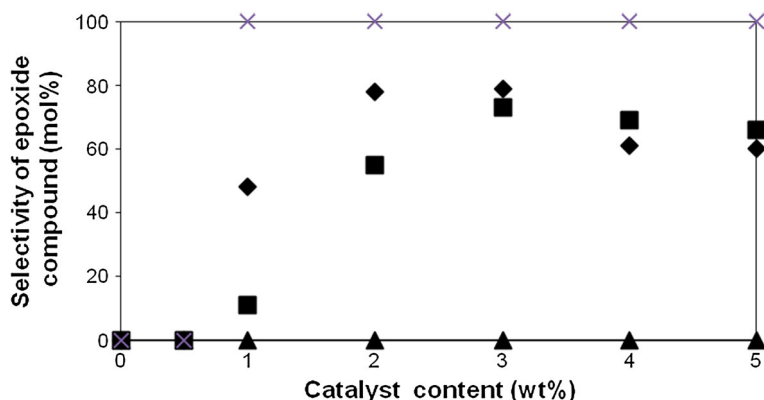


Fig. 4 The influence of catalyst content on the course of allylic compounds epoxidation in acetonitrile: *black diamond suit* glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 30 °C for AA, 80 °C for MAA, 40 °C for CA and 20 °C for 1B3O, molar ratio allylic compound/hydrogen peroxide 1:1 for AA, CA, 1B3O and 5:1 for MAA, acetonitrile concentration 80 wt% for AA and 40 wt% for MAA, CA and 1B3O, reaction time 2 h, intensity of stirring 500 rpm)

Table 4 The influence of catalyst content on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in acetonitrile)

Catalyst content (wt%)	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
0	0	0	0	0
0.5	5	16	34	0
1	35	14	50	14
2	74	17	54	44
3	79	20	73	55
4	56	18	73	43
5	61	16	72	26

Catalyst content (wt%)	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
0	0	0	0	0
0.5	5	25	36	0
1	39	22	53	16
2	83	26	55	48
3	88	32	74	56
4	70	27	74	44
5	65	25	73	26

acetonitrile concentration, and the catalyst content that were chosen for these alcohols to be the most favorable (Fig. 5; Table 5).

Studies of the influence of reaction time on the course of AA epoxidation have shown that with the prolongation of the reaction time from 15 up to 180 min, the

selectivity of glycidol increases from 55 up to 80 mol%, and then remains the same despite the extended reaction time (Fig. 5). This shows that for short reaction time (13 and 30 min), a half of the glycidol formed in the process is hydrolyzed to glycerol. Then, the glycidol hydrolysis process is stopped. The extended reaction time leads to etherification of glycidol and organic substrate molecules, and formation of allyl-glycidyl as well as diallyl ether with selectivity of about 9–13 mol% for a reaction time of more than 30 min. The results also show that the yield of glycerol decreases during prolongation the time of the reaction. This decrease of glycerol yield in the process of AA epoxidation during the prolongation of the reaction time can be caused by the phenomenon of a better stability of glycidol molecules in reaction medium for longer reaction time. Probably, ethers (diallyl ether and allyl-glycidyl ether) established in the reaction mixtures for the reaction time of 60 min and also for longer reaction time, hinder the water molecules from accessing the epoxide ring in glycidol molecules and hydration process is slower. It is visible in the increase in the yield of glycidol. The functions AA conversion and efficiency of H_2O_2 increase in the studied range of reaction time from 24 up to 77 mol% (reaction time 180 min) and from 29 up to 78 mol% (reaction time 180 min), and next decrease to 60 and 70 mol%, respectively (Table 5). Studies on AA epoxidation have shown that the most favorable reaction time is 3 h.

Studies on the course of MAA epoxidation (Fig. 5) have shown that the selectivity of the epoxy compound is about 100 mol% for short reaction times (15 up to 60 min). Extending the reaction time up to 120 min reduces the value of this function to about 70 mol%. Further reaction time extension has no influence on the values of this function. Extending the reaction time over 60 min results in an increase in the selectivity of 2-methylacrolein from 28 up to 30 mol%. In the studied reaction time, the conversion of MAA is doubled (from 10 up to 20 mol%) (Table 5). The efficiency of H_2O_2 is almost doubled as well, but from 16 up to 31 mol% (Table 5). At this stage of the studies, the reaction time that amounted to 30 min was considered the most favorable.

Studies on the course of CA and 1B3O epoxidation have shown that the reaction time of 2 h can be considered as the most favorable for CA epoxidation and for 1B3O epoxidation the reaction time of 3 h is the most favorable (Table 5).

Studies of the influence of intensity of stirring on the course of epoxidation in the range of 450 up to 700 rpm have not shown significant changes in the values of the functions that describe the process in relation to the results obtained at 500 rpm.

Studies on the epoxidation of allylic compounds in water

The results of the studies of the influence of temperature on the selectivity of epoxy compounds for epoxidation of 4 chosen allylic compounds in water are shown in Fig. 6 and Table 6.

Studies on the course of AA epoxidation (Fig. 6) in an aqueous medium have shown that with the increasing process temperature from 20 up to 60 °C, the selectivity of the epoxy compound decreases from 73 to 56 mol%. Compared to studies conducted in acetonitrile, it can be seen here that the decrease of the selectivity of glycidol in the highest temperature is lower (to 56 mol%, in

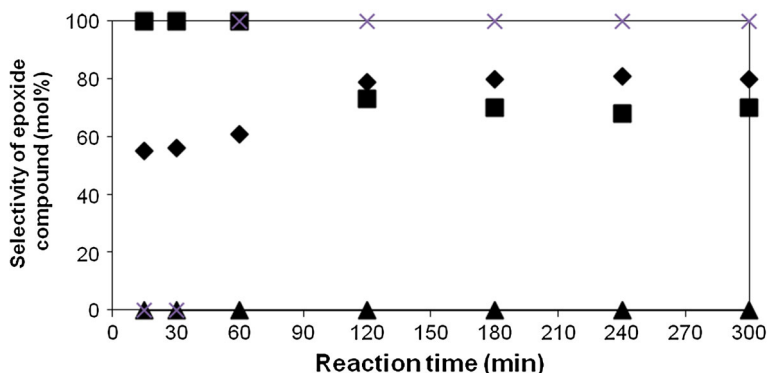


Fig. 5 The influence of reaction time on the course of allylic compounds epoxidation in acetonitrile: *black diamond* suit glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 30 °C for AA, 80 °C for MAA, 40 °C for CA and 20 °C for 1B3O, molar ratio allylic compound/hydrogen peroxide 1:1 for AA, CA, 1B3O and 5:1 for MAA, acetonitrile concentration 80 wt% for AA and 40 wt% for MAA, CA and 1B3O, Ti-SBA-15 catalyst content 3 wt% for all investigated allylic compounds, intensity of stirring 500 rpm)

Table 5 The influence of the reaction time on the conversion of allylic compounds and the efficiency of H_2O_2 (studies in acetonitrile)

Reaction time (min)	C_{AA} (mol%)	C_{MAA} (mol%)	C_{CA} (mol%)	C_{1B3O} (mol%)
15	24	10	42	0
30	32	19	51	35
60	56	18	61	44
120	79	20	73	55
180	77	20	73	58
240	64	20	73	57
300	60	20	73	57

Reaction time (min)	Efficiency of H_2O_2 (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
15	29	16	50	0
30	40	29	58	36
60	67	28	64	44
120	88	32	74	56
180	90	32	74	59
240	78	29	74	57
300	70	31	74	57

acetonitrile: to 33 mol%). The conversion of AA during the epoxidation in an aqueous medium decreased with the increasing temperature from 83 up to 63 mol% (Table 6). The conversions of AA obtained during studies in an aqueous medium

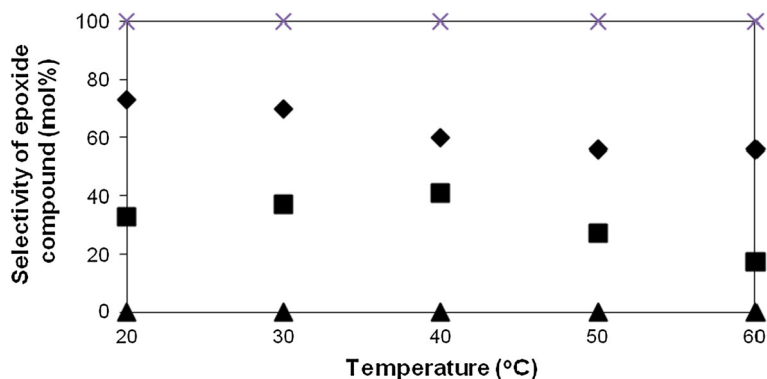


Fig. 6 The influence of temperature on the course of allylic compounds epoxidation in water: *black diamond suit glycidol*, *Black square 2-methylglycidol*, *Black up-pointing triangle 2,3-epoxybutane-1-ol*, *times symbol 1,2-epoxybutane-3-ol* (molar ratio allylic compound/hydrogen peroxide 1:1, Ti-SBA-15 catalyst content 3 wt%, reaction time 2 h, intensity of stirring 500 rpm)

Table 6 The influence of temperature on the conversion of allylic compounds and the efficiency of H_2O_2 (studies in water)

Temperature (°C)	C_{AA} (mol%)	C_{MAA} (mol%)	C_{CA} (mol%)	C_{1B3O} (mol%)
20	83	36	60	37
30	80	36	61	42
40	80	38	62	54
50	72	38	58	50
60	63	37	59	44

Temperature (°C)	Efficiency of H_2O_2 (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
20	100	14	61	45
30	96	14	62	52
40	93	14	63	63
50	87	15	59	62
60	74	14	59	52

were much higher than in acetonitrile (e.g. at 60 °C the conversion of AA in acetonitrile was 26 mol%). During studies on the epoxidation of AA in an aqueous medium, the efficiency of H_2O_2 decreased from 100 to 74 mol% (Table 6). When it comes to this function, much higher values were obtained in water than in acetonitrile (at 60 °C in acetonitrile, the efficiency of H_2O_2 was 27 mol%). The higher conversion of AA and efficiency of H_2O_2 in an aqueous medium is most likely associated with an easier access of water molecules to active centers, when the reaction is carried out only in water. This facilitates the formation of five-member active connections and thus initiates the process of epoxidation. It should

also be noted that in an aqueous medium, regardless of the process temperature, diallyl ether and allyl-glycidyl ether were not formed. The most favorable temperature for further studies was 20 °C.

Studies on the course of MAA epoxidation have shown that as the temperature increases, the selectivity of 2-methylglycidol increases from 33 up to 41 mol% (40 °C) and then decreases to 17 mol% (60 °C) as shown in Fig. 6. In the investigated temperature range, changes in the selectivity of 2-methylglycidol were similar to those observed during studies in acetonitrile. The conversion of MAA maintained practically the same level with the increasing temperature and amounted to 36–38 mol% (Table 6). It was about 10 mol% lower than during studies in acetonitrile (where it also practically did not change with the increasing temperature). The efficiency of H₂O₂ did not change over the studied range of temperatures and amounted to 14–15 mol% (Table 6), similar to the studies in acetonitrile. At this stage of the studies, the temperature of 40 °C was chosen the most favorable.

Studies on the process of CA and 1B3O epoxidation have shown that the temperature of 40 °C can be chosen as the most favorable (Table 6).

Studies of the influence of the molar ratio of allylic compound/hydrogen peroxide were conducted at temperatures that were considered the best for particular allylic compounds while maintaining other initial parameters (Fig. 7; Table 7).

Studies of the influence of molar ratio of reactants on the course of AA epoxidation have shown that with the increasing molar ratio of reactants from 1 up to 4, the selectivity of glycidol increases from 73 up to 85 mol%, and then remains the same (Fig. 7). During studies carried out in water, higher selectivity values of glycidol were obtained as compared to the studies carried out in acetonitrile at the lowest molar ratio of 20 mol%, and at higher by about 13 mol%. Simultaneously, during studies on the influence molar ratio on the course of epoxidation in water, there were no ether products formed (diallyl ether, allyl-glycidyl ether). The only by-product was glycerol. The AA conversion decreased with the increasing molar ratio of reactants from 84 to 20 mol% (Table 7). The efficiency of H₂O₂ increased from 64 up to 100 mol% (Table 7). At this stage of the studies, the equimolar ratio of reactants was considered the most favorable.

Studies of the influence of the molar ratio of reactants on the course of MAA epoxidation have shown that the highest value of selectivity of 2-methylglycidol is achieved at an equimolar ratio of reactants (41 mol%). Then, the value of this function is almost the same, about 34–39 mol% (Fig. 7). During studies in acetonitrile, the selectivity of the epoxy compound changed in a different manner, i.e. increased with the increasing molar ratio of reactants from 46 up to 73 mol%. The conversion of MAA decreased with the increase of molar ratio of reactants from 38 to 18 mol% and the efficiency of H₂O₂ increased from 14 up to 36 mol% (Table 7). Similar changes in the values of these functions were observed during the studies conducted in acetonitrile. At this stage of the studies, the equimolar ratio of reactants was considered the most favorable (as opposed to the research studies conducted in acetonitrile, where the most favorable molar ratio of reactants was 5:1).

Studies of the influence of molar ratio of reactants on the course of CA and 1B3O epoxidation have shown that the equimolecular ratio of reactants can be considered as the most favorable (Table 7).

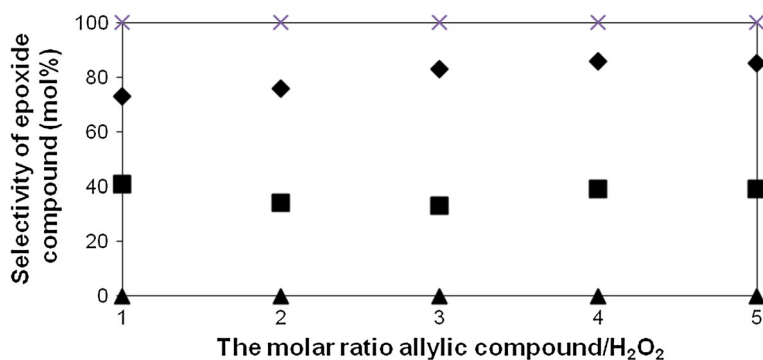


Fig. 7 The influence of the molar ratio of reactants on the course of allylic compounds epoxidation in water: *black diamond suit* glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 20 °C for AA and 40 °C for MAA, CA and 1B3O, Ti-SBA-15 catalyst content 3 wt%, reaction time 2 h, intensity of stirring 500 rpm)

Table 7 The influence of the molar ratio of reactants on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in water)

Molar ratio of reactants	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
1	84	38	62	54
2	32	27	44	30
3	25	27	32	26
4	23	25	22	26
5	20	18	18	20

Molar ratio of reactants	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
1	64	14	63	63
2	64	22	44	39
3	76	32	32	36
4	93	38	23	38
5	100	36	18	27

Studies of the influence of the catalyst content on the course of epoxidation of allylic compounds were conducted at the temperatures and molar ratios considered to be the most favorable for particular compounds. Other initial parameters were also maintained (Fig. 8; Table 8).

Studies of the influence of the catalyst content on the course of AA epoxidation have shown that with the increase in the amount of the catalyst from 0.5 up to 3 wt%, the selectivity of glycidol increases from 41 up to 73 mol%. Then, despite the increase in the content of the catalyst, the selectivity of glycidol remains at the same level (Fig. 8). During the research studies carried out in water, it was observed that no by-products, apart from glycerol, were formed at higher contents of the

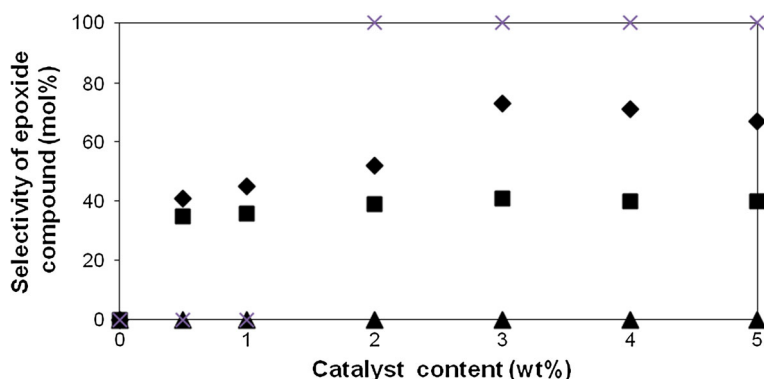


Fig. 8 The influence of catalyst content on the course of allylic compounds epoxidation in water: *black diamond suit* glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 20 °C for AA and 40 °C for MAA, CA and 1B3O, molar ratio allylic compound/hydrogen peroxide 1:1 for all allylic compounds, reaction time 2 h, intensity of stirring 500 rpm)

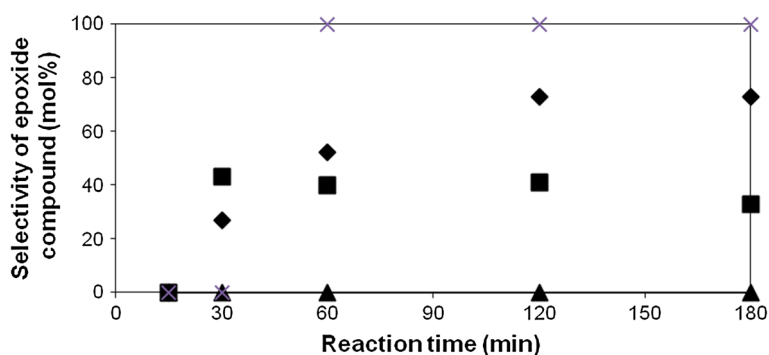
catalyst, as it happened during the studies in acetonitrile (the catalyst content was 3–5 wt% in the reaction mixture; by-products diallyl ether, allyl-glycidyl ether). The occurrence of ether products during the studies in acetonitrile decreased the selectivity of glycidol (20 mol%) for the content of the catalyst that amounted to 4 and 5 wt%. The AA conversion increases with the increasing content of the catalyst from 60 up to 87 mol% (Table 8). The efficiency of H_2O_2 changes from 73 mol% (catalyst content: 0.5–2 wt%) up to 100 mol% (catalyst content: 3–5 wt%) (Table 8). Such high efficiency of H_2O_2 for the highest content of the catalyst was not observed during the studies in acetonitrile, where an inefficient decomposition of hydrogen peroxide (20–30 % of the converted hydrogen peroxide) was observed for this content of the catalyst. At this stage of the studies, the content of the catalyst that amounted to 3 wt% was considered the most favorable.

Studies on the course of MAA epoxidation in an aqueous medium have shown that the selectivity of 2-methylglycidol does not change with the increasing content of the catalyst and amounts to 35–40 mol% (Fig. 8). A different situation occurred for the selectivity of 2-methylglycidol during the studies in acetonitrile. This function increased from 0 up to 73 mol%, and then remained at the same level. The MAA conversion increased to the content of the catalyst that amounted to 3 wt% (from 20 up to 38 mol%), and then decreased slightly to 30 mol% (Table 8). The slight decrease in the MAA conversion was associated with the inefficient decomposition of hydrogen peroxide. This phenomenon was intensified at higher contents of the catalyst. The efficiency of H_2O_2 increased over the studied range of the catalyst content from 8 up to about 12–14 mol% (Table 8). Throughout the studied range of the catalyst content, a high value of the inefficient decomposition of hydrogen peroxide was observed (more than 80 % of hydrogen peroxide introduced to the process). At this stage of the studies, the content of the catalyst that amounted to 3 wt% was considered the most favorable.

Table 8 The influence of catalyst content on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in water)

Catalyst content (wt%)	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{1B3O} (mol%)
0	0	0	0	0
0.5	60	20	24	0
1	62	23	36	0
2	55	31	48	33
3	84	38	62	54
4	87	30	56	42
5	87	30	51	35

Catalyst content (wt%)	Efficiency of H ₂ O ₂ (mol%)			
	AA epoxidation	MAA epoxidation	CA epoxidation	1B3O epoxidation
0	0	0	0	0
0.5	73	8	24	0
1	74	9	36	0
2	66	12	49	38
3	100	14	63	63
4	100	11	57	51
5	100	12	52	49


Fig. 9 The influence of reaction time on the course of allylic compounds epoxidation in water: *black diamond* suit glycidol, *Black square* 2-methylglycidol, *Black up-pointing triangle* 2,3-epoxybutane-1-ol, *times symbol* 1,2-epoxybutane-3-ol (temperature 20 °C for AA and 40 °C for MAA, CA and 1B3O, molar ratio allylic compound/hydrogen peroxide 1:1 for all allylic compounds, Ti-SBA-15 catalyst content 3 wt% for all allylic compounds, intensity of stirring 500 rpm)

Studies of the influence of the catalyst content on the course of CA and 1B3O epoxidation have shown that the content of the catalyst that amounted to 3 wt% can be taken as the most favorable (Table 8).

Table 9 The influence of reaction time on the conversion of allylic compounds and the efficiency of H₂O₂ (studies in water)

Reaction time (min)	C _{AA} (mol%)	C _{MAA} (mol%)	C _{CA} (mol%)	C _{IB3O} (mol%)
15	20	0	50	0
30	27	12	60	0
60	44	22	63	33
120	84	37	62	54
180	81	35	61	53

Reaction time (min)	Selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (mol%)		
	AA epoxidation	MAA epoxidation	CA epoxidation
15	26	0	55
30	34	4	65
60	57	7	65
120	100	14	63
180	87	11	61

1B3O epoxidation	
15	0
30	0
60	39
120	63
180	62

Studies of the influence of the reaction time on the course of epoxidation of allylic compounds in an aqueous medium were carried out at temperatures, molar ratios, and catalyst contents considered the most favorable for particular allylic compounds (Fig. 9; Table 9). The intensity of stirring of 500 rpm was also maintained.

Studies on AA epoxidation have shown that the selectivity of glycidol increases from 27 mol% (reaction time: 30 min) up to 73 mol% (reaction time: 120 min), and then remains the same (Fig. 9). For the reaction time of 15 min, the only product is glycerol. In comparison with the studies carried out in acetonitrile, the studies conducted in water had much lower selectivity of the epoxy compound for reaction times up to 60 min. Further selectivity was more or less similar. The AA conversion increased from 20 up to 81 mol% and the efficiency of H₂O₂ from 26 up to 100 mol% (reaction time 120 min) and next decreased to 87 mol% (Table 9). The most favorable time was 120 min.

Studies on MAA epoxidation have shown that the selectivity of 2-methylglycidol is not influenced by reaction times and amounts to 33–34 mol%. No reactions were observed only for the reaction time of 15 min. The MAA conversion increases from 0 up to 37 mol% (reaction time: 120 min) and then it remains practically the same (Table 9). The efficiency of H₂O₂ increases from 4 up to 14 mol% (time: 120 min), and then it also remains practically the same (Table 9). The most favorable time was 120 min.

Studies on the influence of reaction time on CA and 1B3O epoxidation have shown that the most favorable reaction time for CA epoxidation is 1 h and for 1B3O epoxidation is 2 h (Table 9).

Studies on the influence of the mixing speed of the reaction mixture ranged from 450 up to 700 rpm have shown no significant changes in the values of the functions that describe the process in relation to the results obtained at the mixing intensity of 500 rpm.

Conclusions

A comparison of the results obtained during AA epoxidation in an aqueous medium and acetonitrile shows that in the aqueous medium, it is possible to carry out the process in mild conditions. A comparison of the most favorable parameters shows that in an aqueous medium, AA and MAA required other temperatures for conducting the process than in acetonitrile (for AA the temperature was 10 °C lower, and 40 °C lower for MAA). Only for 1B3O, the temperature in the aqueous medium has to be 20 °C higher. In the case of CA, the most favorable reaction temperature was the same for both solvents. The most favorable molar ratio of reactants was identical for both studied solvents. The exception was MAA epoxidation. In the case of this compound in acetonitrile, the most favorable molar ratio of reactants was 5, and 1 in water. Regardless of the solvent used, the most preferred amount of the catalyst for all the studied compounds was 3 wt%. In most cases, the most favorable reaction times were reduced in the aqueous medium: for AA from 3 to 2 h, for CA from 2 to 1 h, and for 1B3O from 3 to 2 h. In the case of

MAA in aqueous medium, the reaction time was extended from 0.5 up to 2 h. The values of the main functions that describe the epoxidation process of AA and CA, as well as 1B3O, are comparable. However, in the case of MAA in an aqueous medium; what was observed was a decrease in the selectivity of the epoxy compound from 100 to 41 mol% with a simultaneous increase in the conversion of MAA from 19 up to 38 mol%, and a decrease in the efficiency of H₂O₂ from 29 to 14 mol%.

To sum up, it can be stated that the aqueous medium is more favorable to carry out epoxidation of allylic compounds over the Ti-SBA-15 catalyst than the use of acetonitrile as a solvent. It provides milder process conditions (reaction temperature) and requires a shorter time. From the point of view of energy used, this is beneficial. The values of the main functions of the process for the research studies carried out in water are similar to those obtained in acetonitrile. Moreover, the phenomenon of hydrolysis of the epoxy ring was not intensified in the aqueous medium. In the case of AA, the etherification reaction did not occur in the aqueous medium. Epoxidation in an aqueous medium seems a preferred alternative to the process carried out in acetonitrile as a solvent, both in terms of raw material consumption and energy. What is more, the use of water does not require solvent recovery and its regeneration after the process (acetonitrile is used in an amount of 40 wt%, and AA—80 wt%), which reduces the cost of the process. Analyzing the environmental aspects of carrying out the process, epoxidation of allylic compounds in water is more beneficial.

The comparison the results presented in this work with our previous results [29] obtained in methanol as solvent for the same 4 allylic compounds shows that the results of the epoxidation obtained in water as the solvent are very close to those obtained in methanol as the solvent but in some cases (AA and MAA), the established the best parameters are more beneficial for the process of the epoxidation in water. For example, the process of AA epoxidation in water needs lower temperature and lower molar ratio of reactants (20 °C and 1:1) than in methanol (40 °C and 2:1) and, moreover, the values of the main functions of the process are higher for the process epoxidation of AA in water (the selectivity of glycidol for the process epoxidation in water amounts to 73 mol% and for the process in methanol 67 mol%, the conversion of AA for the process epoxidation in water amounts to 84 mol% and for the process in methanol 47 mol%).

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