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The utilization of Ti-SBA-15 catalyst in the epoxidation of allylic alcohols

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Abstract Ti-SBA-15, one of the latest titanium silicalite catalysts, has been prepared according to the literature by the direct hydrothermal synthesis using Pluronic 123 as structure-directing agent. The characterization of the catalyst was performed by means of the following methods: XRD, IR, UV–Vis, X-ray microanalysis and SEM. The catalytic properties of the Ti-SBA-15 catalyst have been tested in the epoxidation of allyl alcohol, methallyl alcohol, crotyl alcohol and 1-butene-3-ol with hydrogen peroxide. The process has been described by the following main functions: the selectivity to epoxide compound in relation to allylic compound consumed and the conversion of allylic compound.

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

Mathematics Subject Classification (2000) 32 · 46 · 92

JEL Classification I23 · L65

Introduction

Zeolites with titanium atoms in the structure have wide applications in oxidation processes (especially in epoxidation processes) which are carried out in the presence of hydrogen peroxide (oxidizing agent). To the group of these zeolites belong TS-1 and TS-2 catalysts—the first titanium silicalite catalysts [1, 2]. TS-1 and TS-2 are microporous materials with relatively small pore size (about 0.5 nm), which limits

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their applications to the oxidation processes of organic compounds with a relatively small size of molecules [3]. The next titanium catalysts applied in oxidation processes were mesoporous Ti-MCM-41 and Ti-MCM-48 (pore size 2–3 nm). These catalysts can be used in the oxidation of organic molecules with larger sizes, but their structures are very often sensitive to the conditions under which the reaction is performed [4]. Subsequent investigations led to the discovery of mesoporous Ti-SBA-15 catalyst. Ti-SBA-15 is obtained in an acid medium and in the presence of triblock copolymer of ethylene oxide and propylene oxide—Pluronic 123 as structure-directing agent. This catalyst can have a specific surface from 600 to 1000 m^2/g and the size of pores from 5 to 30 nm. It makes the Ti-SBA-15 catalyst very attractive material for catalytic oxidation processes. There are two main methods of Ti-SBA-15 synthesis: the direct synthesis (during the synthesis of SBA-15 structure titanium is simultaneously incorporated in the structure) and the method by impregnation of titanium on the obtained before the SBA-15 structure [4–6].

Currently, intensive studies are also performed about the utilization of immobilized catalysts in epoxidation processes (the epoxidation of cyclooctene, geraniol, cinamyl alcohol). These catalysts can probably also be used in the epoxidation of allyl alcohol (AA) in the future [7, 8].

Epoxide compounds obtained from AA, methallyl alcohol (MAA), crotyl alcohol (CRA) and 1-butene-3-ol (1B3O) have a lot of applications, especially glycidol. Glycidol is an important monomer and a semi-product in the synthesis of surface-active agents. These agents are the components of cosmetic preparations for skin moisturizing and purifying, hair shampoo, toothpaste, laundering detergents and disinfectants [9]. Surface active agents are also used as food emulgators in the production of margarine, ice-cream, and vegetable butter [10]. Other applications of glycidol include plasticizers, fabric dyes, photochemical compounds, rubbers, varnishes and plastics [11]. Block copolymers swelling in water and methanol are obtained in the reaction with ethylene oxide. It is applicable to the synthesis of many biologically active compounds, primarily obtained from living organisms (algae, fungus). One of the most important applications of glycidol is the synthesis of antiviral and analgesic drugs. An especially important group of antiviral drugs constitute active compounds fighting HIV. With the use of glycidol, active compounds fighting HIV are obtained, equivalents of natural compounds occurring in fungi, as well as new derivatives of nucleotides fighting this and other viruses [11].

By now, in the process of allylic compound epoxidation with hydrogen peroxide, the most commonly used titanium-silicalite catalysts are TS-1, TS-2, Ti-Beta, Ti-MCM-41 and Ti-MCM-48. The utilization of these catalysts is connected with a lot of problems: (1) repeatability the syntheses of titanium silicalite catalysts (Ti content), especially TS-1, TS-2, Ti-Beta, thus these catalysts are not commercially available, (2) leaching of Ti from the structure of the catalyst, and (3) stability of the structure in water solution, especially Ti-MCM-41 and Ti-MCM-48. Our preliminary studies showed that the syntheses of Ti-SBA-15 catalyst are more repeatable, its structure is more stable and that this catalyst can be efficiently used in the process of allylic compounds epoxidation. This article presents the direct

synthesis of the Ti-SBA-15 catalyst (by the method of Berube et al. [12]). The catalytic activity of Ti-SBA-15 material was tested in the epoxidation of AA, MAA, CRA and 1B3O to epoxide compounds by hydrogen peroxide in methanol as a solvent. The obtained results were also compared with our previous results obtained for TS-1 [13], Ti-MCM-41 [14] and Ti-MCM-48 [11] catalysts.

Experimental

The Ti-SBA-15 material was synthesized by the method of Berube et al. [12]. The following raw materials were used in the synthesis: Pluronic P123 (Aldrich, MW = 5800) as structure-directing agent, tetraethylortosilicalite (TEOS 98%, Aldrich) as a silicon source and tetraisopropyl orthotitanate (TiPOT >98%, Merc) as a titanium precursor. 6.0 g of Pluronic P123 was dissolved in 114 g of deionized water and 3.5 g of hydrochloric acid (37%) at 35 °C under magnetic stirring. Then, 13.0 g of TEOH and 0.443 g of TiPOT were premixed and rapidly added to the initial homogeneous solution. The resulting mixture was stirred for 24 h at 35 °C and subsequently hydrothermally treated for an additional 24 h at a given temperature to ensure further framework condensation. The solid product was recovered by filtration and dried in air at 100 °C for 24 h. Finally, the product was calcined at 550 °C for 3 h to remove the template. The characterization of the catalyst was performed with the use of the following conventional techniques: XRD (X'Pert PRO Philips diffractometer, Cu K_α radiation), IR (Shimadzu FTIR-8100 spectrometer, KBr pellet technique), UV–Vis (SPECORD M40 type V-530), X-ray microanalysis (Oxford X-ray analyzer ISIS 300) and SEM (JOEL JSM-6100 instrument).

In the epoxidation of allylic compounds the following raw materials were used: AA (98%, Fluka), MAA (98%, Fluka), CRA (95%, Fluka), 1B3O (97%, Merck), hydrogen peroxide (30 wt% water solution, POCH Gliwice) and methanol (analytical grade, POCH Gliwice). The initial technological parameters were as follows: the molar ratio of allylic compound/H_2O_2 = 1:1, methanol concentration 40 wt%, catalyst concentration 3 wt%, the reaction time 2 h and intensity of stirring 500 rpm. The process was carried out in a glass vial with the capacity of 12 cm^3 equipped with a rubber septum and a capillary. The vials were located in a shaker holder and immersed in a water bath.

In order to calculate the mass balance, the post-reaction mixtures were analyzed in the following way: unreacted hydrogen peroxide was determined by means of the iodometric method [15], glycerol formed in the process was determined by means of the potentiometric method [16]. The remaining products and the unreacted organic substrate were analyzed by means of gas chromatography. The chromatographic analysis was performed on the FOCUS apparatus with a flame-ionization detector (FID) fitted with Quadrex capillary columns filled with methyl-phenyl-siloxanes. The parameters of chromatographic separation were as follows: the pressure of helium 50 kPa, sensitivity 10, the temperature of the sample chamber 150 °C, the detector temperature 250 °C, the temperature of the thermostat was increasing

according to the following program: isothermally at 40 °C for 3 min, an increase to 250 °C at the rate of 10 °C/min, isothermally at 250 °C for 5 min, cooling to 60 °C.

After calculating the mass balance, the main functions describing the process were determined: the selectivity to the epoxide compound in relation to the allylic compound consumed and the conversion of the allylic compound.

Results and discussion

The XRD pattern of Ti-SBA-15 catalyst was the same as in literature [10, 17]. Fig. 1 presents the XRD pattern of the obtained Ti-SBA material.

In the IR and UV–Vis spectra, there were bands confirming the incorporation of titanium into the silica structure (960 cm^{-1} (Fig. 2) and 220 nm).

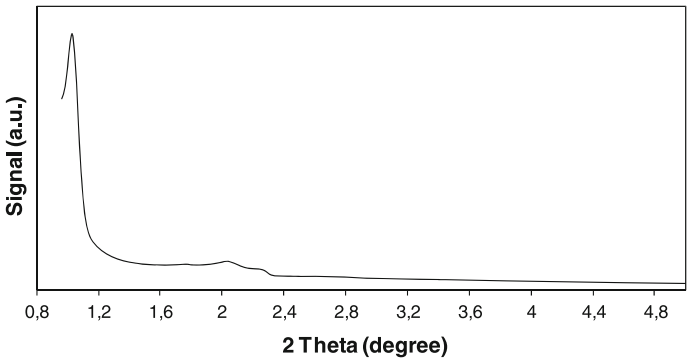


Fig. 1 XRD pattern of the obtained Ti-SBA-15 material

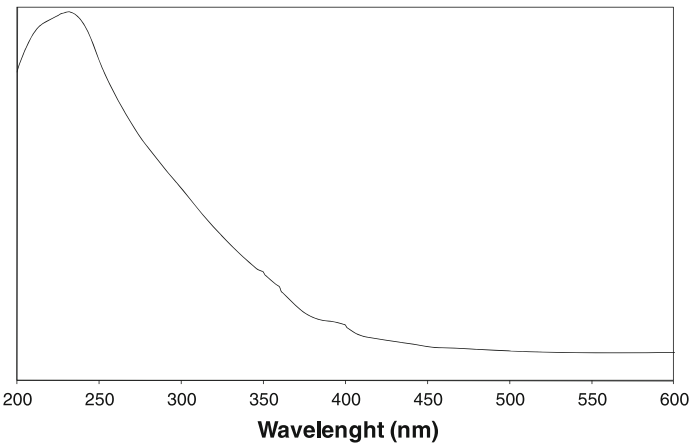


Fig. 2 UV–Vis spectrum of the obtained Ti-SBA-15 material

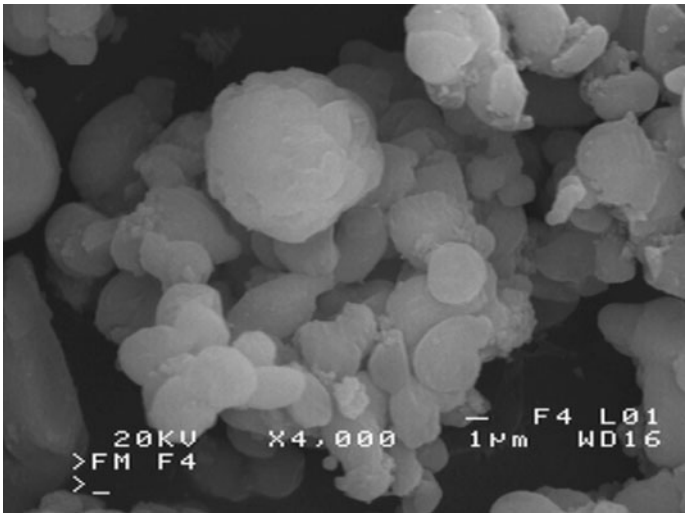


Fig. 3 SEM micrograph of Ti-SBA-15 material

An X-ray microanalysis showed that the amount of Ti in the sample after calcination was 2.46 wt%.

Below (Fig. 3) is presented SEM micrograph of the obtained Ti-SBA-15 material.

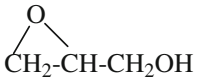
The micrographs show that the material consists of oval and oblong particles with different sizes (from 3–4 to 15°µm).

The main products of the process of allylic compound epoxidation are epoxide compounds. Depending on the conditions, the following compounds are also formed: diols—the products of epoxide ring hydration, ethers, aldehydes and acids. At higher temperatures, polymerization also occurs to a small extent. During the studies, the influence of the following technological parameters was tested: temperature, the molar ratio of allylic compound/hydrogen peroxide, methanol concentration (solvent), catalyst concentration, reaction time and intensity of stirring.

The influence of temperature on the course of allylic compounds epoxidation

The results of the influence of temperature on the process of epoxidation of allylic compounds are shown in Fig. 4.

The main product obtained from epoxidation of AA is glycidol:



glycidol

The research on the influence of temperature in the range between 20 and 60 °C on the process of epoxidation of AA showed that under tested conditions, reaction

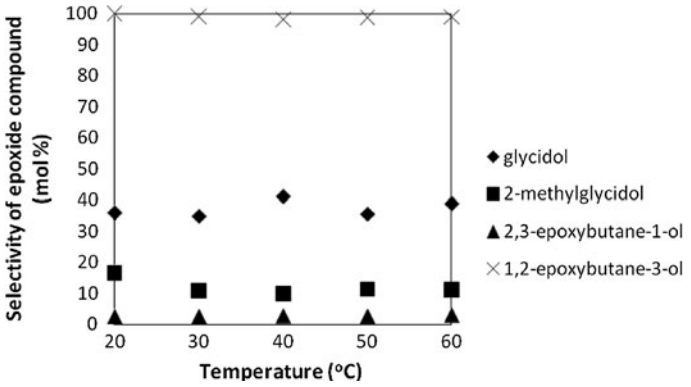
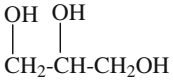


Fig. 4 The influence of temperature on the selectivities of the epoxide compounds. The reaction conditions: the molar ratio of allylic compound/H_2O_2 = 1, methanol concentration 40 wt%, catalyst concentration 3 wt%, reaction time 2 h, intensity of stirring 500 rpm

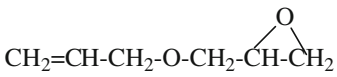
temperature does not significantly affect the selectivity of glycidol (34–41 mol%) and the conversion of AA (68–74 mol%).

The main side product of the process of AA epoxidation is glycerine:

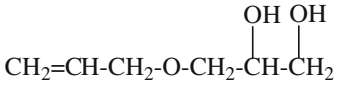


glycerine

As the research revealed, the selectivity of this compound, similarly to the selectivity of glycidol, does not depend on reaction either (36–41 mol%). The next side products of this process are: allyl-glycidyl ether, and 3-allyloxy-1,2-propanediol.

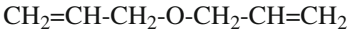


allyl-glycidyl ether



3-allyloxy-1,2-propanediol

These compounds are formed with selectivities of 5 mol% (20 °C)—13 mol% (60 °C). Bis(allyl) ether is formed with the selectivity 3–5 mol%, and acroleine with 1–2 mol%.

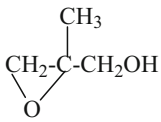


bis(allyl) ether

acroleine

For further research on the process of AA epoxidation, the temperature of 40 °C was chosen as it was the most beneficial.

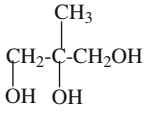
Research on the process of epoxidation of MAA showed that an increase in temperature of the process causes a slight decrease in the selectivity of 2-methylglycidol from 17 mol% (20 °C) to 11 mol% (60 °C).



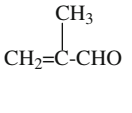
2-methylglycidol

At the same time, in the tested range of temperatures, an increase in MAA conversion from 16 mol% (20 °C) to 34 mol% (30 °C) was observed, whereas a further increase in temperature did not cause any changes in MAA conversion. A comparison of AA and MAA conversions show that under the same conditions, the conversion of AA is 3–4 times higher than that of MAA, which indicates a higher reactivity in comparison with MAA.

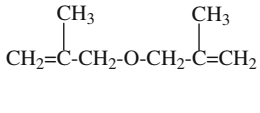
Research carried out for MAA revealed that the following by-products were present in post-reaction mixtures:



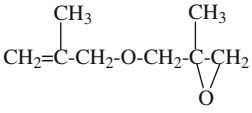
2-methylglycerine



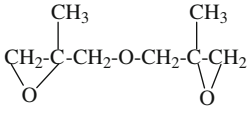
2-methylacroleine



bis(methallyl) ether



methallyl-2-methylglycidol ether



bis(methylglycidol) ether

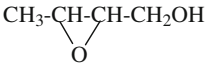
The selectivity of 2-methylglycerine increased together with an increase in temperature of the reaction from 0 mol% (20 °C) to 14 mol% (60 °C), the selectivity of 2-methylacroleine decreased from 67 mol% (20 °C) to 54 mol% (60 °C), the selectivity of bis(methallyl) ether increased from 1 mol% (20 °C) to 7 mol% (60 °C), the selectivity of methallyl-2-methylglycidol ether was virtually constant and it was around 15 mol%, similar to bis(methylglycidol) ether—1 mol%.

For further research on the epoxidation of MAA, the temperature of 20 °C was chosen as the most beneficial.

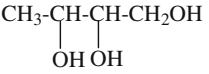
The comparison of the results obtained for AA and MAA epoxidation showed that AA molecules were more reactive than MAA molecules taking into account their conversion. Under the same conditions, the conversion of AA was 3–4 times higher than MAA (respectively: 68–74 and 16–34 mol%). The total selectivity of glycidol and glycerine amounted to 70 mol% (at 20 °C) and 82 mol% (at 60 °C), whereas the total selectivity of 2-methylglycidol and 2-methylglycerine equalled 17 mol% (20 °C) and 25 mol% (60 °C). On the other hand, the selectivity of acroleine was independent of temperature and amounted to 1–2 mol% but the selectivity of 2-methylacroleine reached 67 mol% (20 °C)–54 mol% (60 °C). It shows that in the case of AA, the privileged direction of the reaction is the oxidation

of a double bound, but for the MAA the privileged direction of the reaction is the oxidation of a –OH group. Probably, there are two reasons for this situation: steric hindrance connected with the presence of a $–CH_3$ group in the position 2 in MAA and an electronic displacement from this group in the direction of the double bound which causes that the C atom with the –OH group is more electronegative and therefore more susceptible to oxidation. The studies also presented that the etherification reaction was intensified for AA as well as for MAA at higher temperatures.

Research on the process of CRA epoxidation showed that 2,3-epoxybutane-1-ol formed in the whole range of tested temperatures with a constant selectivity of 3 mol%, at the same time the main side product of the process was 1,2,3-butanetriol, which formed with the constant selectivity of about 65 mol%.

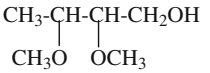


2,3-epoxybutane-1-ol

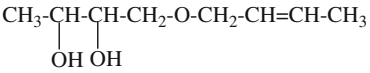


1,2,3-butanetriol

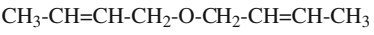
The conversion of CRA was high (slightly higher than of AA) and it was about 82 mol%. Other by-products of the process formed with the following selectivities: 2,3-dimetoxybutane-1-ol (about 4 mol%), 4-(2,3-butenoxy)-butene-2,3-diol (about 2 mol%), bis(2-butene) ether (about 4 mol%), crotyl aldehyde (about 17 mol%) and crotonic acid (2–11 mol%).



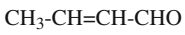
2,3-dimetoxybutane-1-ol



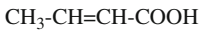
4-(2,3-butenoxy)butene-2,3-diol



bis(2-butene) ether



crotyl aldehyde



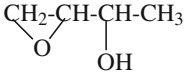
crotonic acid

The research conducted revealed that it is the most beneficial to carry out the process of CRA epoxidation at the temperature of 20 °C.

The comparison the conversions of AA and CRA showed that both alcohols have very close reactivity. It shows that linear molecules (AA and CRA) react easier under the investigated conditions than branched independent of a length of the carbon chain (3 and 4 C atoms). In contrast to the results obtained for AA and MAA, the selectivity of the epoxide compound for CRA epoxidation was very low and amounted to 3 mol%. The total selectivity of 2,3-epoxybutane-1-ol and 1,2,3-butanetriol was about 68 mol% and was close to results for AA. But in the case of CRA, the epoxide compound very easily underwent hydration to 1,2,3-butanetriol. It shows that glycidol was more stable under the investigated conditions than 2,3-

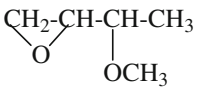
epoxybutane-1-ol. In the post-reaction mixtures obtained for CRA were also present crotyl aldehyde and crotonic acid, the products of –OH group oxidation, with the total selectivity of 28 mol%. The amount of this kind of products was smaller than for MAA, thus, it can be concluded that the C atom with the –OH group in CRA is probably more electronegative than in AA but lower than in MAA. The studies also presented that at higher temperatures, the etherification reaction were not so intensive as for AA and MAA.

Research on the process of 1B3O epoxidation showed that 1,2-epoxy-3-butanol formed in tested conditions with selectivity of about 99 mol%, at the conversion of 1B3O from 20 mol% (20 °C) to 37 mol% (60 °C).

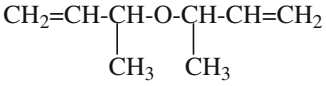


1,2-epoxy-3-butanol

The remaining by-products, such as: 1,2-epoxy-3-methoxybutane and bis(2-methyl-1-propene) ether formed with a very low selectivity of about 1 mol%.



1,2-epoxy-3-methoxybutane



bis(2-methyl-1propene) ether

The most favorable temperature for the process of 1B3O epoxidation was the temperature of 60 °C.

The conversion of 1B3O was comparable with MAA conversion (20–37 mol%), but the selectivity of the epoxide product was considerably higher than for AA, MAA and CRA epoxidation process and amounted closely 100 mol%. It shows that 1B3O as the secondary alcohol is not so reactive as for example AA or CRA, but the location of the $–CH_3$ and –OH groups at the third C atom in 1B3O causes that the epoxide molecule is stable and not susceptible to hydration. Simultaneously, the location of this group prevents the oxidation of –OH group.

The influence of the molar ratio of allylic compound/hydrogen peroxide in the course of allylic compound epoxidation

The results of the influence of the molar ratio allylic compound/hydrogen peroxide on the process of allylic compounds epoxidation are shown in Figs. 5 and 6.

The research on the process of AA epoxidation revealed that an increase in the molar ratio of the reactants caused an increase in the selectivity of glycidol from 41 mol% (the molar ratio AA/H_2O_2 = 1:1) to 72 mol% (the molar ratio AA/H_2O_2 = 5:1). At the same time, in the tested range of molar ratios of the reactants, the conversion of AA decreases from 68 to 20 mol%. Taking results obtained into account, at this stage of the research, the molar ratio of the reactants 2:1 was found to be the most beneficial—working with a higher excess of AA increases the financial costs of carrying out the process due to the necessity of recovery and

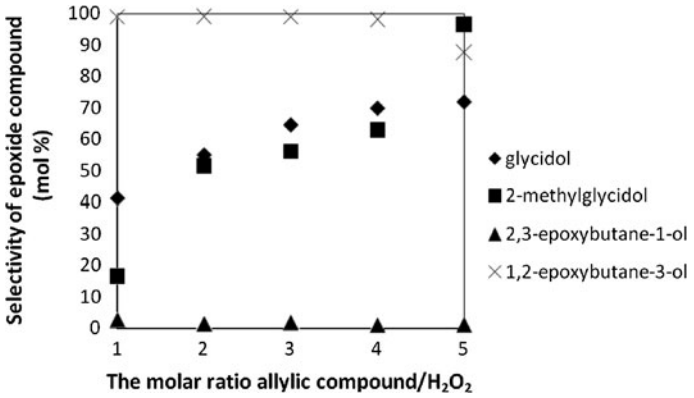


Fig. 5 The influence of the molar ratio of allylic compound/H_2O_2 on the selectivities of the epoxide compounds. The reaction conditions: temperature 20 °C (MAA, CRA), 40 °C (AA), 60 °C (1B3O), methanol concentration 40 wt%, catalyst concentration 3 wt%, reaction time 2 h, intensity of stirring 500 rpm

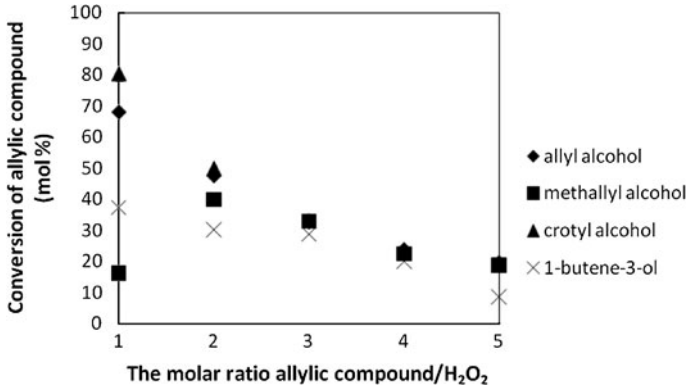


Fig. 6 The influence of the molar ratio of allylic compound/H_2O_2 on the conversions of allylic compounds. The reaction conditions: temperature 20 °C (MAA, CRA), 40 °C (AA), 60 °C (1B3O), methanol concentration 40 wt%, catalyst concentration 3 wt%, reaction time 2 h, intensity of stirring 500 rpm

returning to the process of this raw material. At this molar ratio of the reactants, apart from glycidol (selectivity 55 mol%), the following by-products were present in the post-reaction mixture: glycerine (selectivity 29 mol%), bis(allyl) ether and allyl-glycidyl ether (the selectivity of these compounds amounts to 3 mol%), 3-allyloxy-1,2-propanediol (selectivity 8 mol%) and acroleine (1 mol%).

Research on the epoxidation of MAA showed that, just as in the case of AA epoxidation, here also an increase in the selectivity of the epoxy compound from 17 to 97 mol% can be observed, together with an increase in the molar ratio of reactants. The conversion of MAA for equimolecular ratio of reactants was 16 mol%, amounted to 40 mol% in the case of a 2:1 molar ratio of reactants, and then

decreased to 19 mol%. After analyzing the results, the molar ratio of reagents 2:1 was singled out as the most beneficial at this stage of research. The selectivities of the products of the process at the same molar ratio of regents were the following: 2-methylglycidol 52 mol%, 2-methylacroleine 47 mol%, and bis(methylglycidol) ether 1 mol%.

Research on the process of CRA epoxidation revealed that the selectivity of 2,3-epoxybutane-1-ol did not change together with increasing the molar ratio of reactants, and was about 2 mol%, while the conversion of CRA decreased from 80 to 19 mol%. The equimolar ratio of reactants was considered as the most favorable for the epoxidation of this compound. The selectivities of by-products of the process at this molar ratio were the following: 1,2,3-butanetriol 66 mol%, crotyl aldehyde 17 mol%, 2,3-dimetoxybutane-1-ol and bis(2-butene) ether 5 mol%, crotonic acid 2.4 mol% and 4-(2,3-butenoxy)-butene-2,3-diol 2 mol%.

Research on the epoxidation of 1B3O showed that in the range of molar ratios from 1:1 to 4:1, irrespective of the molar ratio of reactants, the selectivity of the epoxy compound was high and amounted to 99 mol%. For the highest molar ratio of reactants, the selectivity of epoxy compound decreases to 88 mol%, and there appeared an increased amount of bis(2-methyl-1-propene) ether—12 mol%. The conversion of 1B3O decreased together with an increase in the molar ratio of reactants from 37 to 9 mol%. The equimolar ratio of reactants was considered the most beneficial at this stage of research. At this molar ratio of reactants, the selectivity of epoxy compound was 99 mol%, and the selectivity of bis(2-methyl-1-propene) ether 1 mol%.

The comparison of the results obtained at this stage of studies showed that the molar ratio of reactants (allylic compound/hydrogen peroxide) was the most important for the epoxidation of AA and MAA. The selectivity of glycidol and 2–methylglycidol raised with the increase of the allylic compound content in the reaction mixture. This increase in selectivity was probably connected to the phenomenon of surrounding the epoxide compounds molecules by allylic compounds molecules, which caused the stabilization of the epoxide rings and inhibition of the hydration process.

The influence of methanol concentration on the course of allylic compounds epoxidation

The results of the research on the impact of methanol concentration on the process of allylic compound epoxidation are shown in Fig. 7.

The research on AA epoxidation revealed that the selectivity of glycidol increased from 32 to 66 mol% along with increasing the concentration of methanol in the reaction mixture from 10 to 80 wt%. The AA conversion, however, has been almost constant in the range of solvent concentrations tested—about 46 mol%. The methanol concentration of 80 wt% was considered the most beneficial at this stage of research. The following by-products formed at this concentration of solvents: 3-allyloxy-1,2-propanediol 12 mol%, allyl-glycidyl ether 11 mol%, bis(allyl) ether 9 mol% and acroleine 2 mol%.

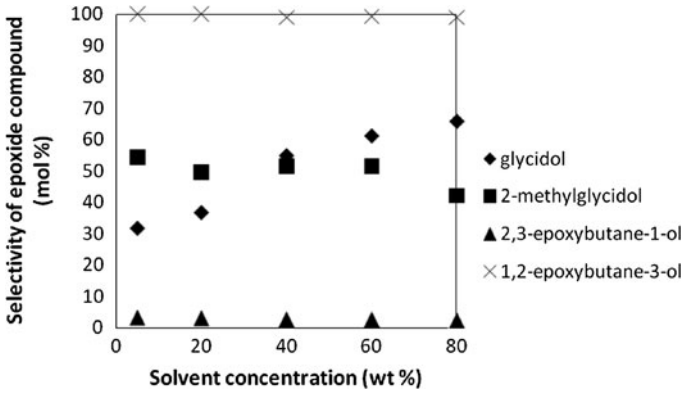


Fig. 7 The influence of solvent concentration (methanol) on the selectivities of the epoxide compounds. The reaction conditions: temperature 20 °C (MAA, CRA), 40 °C (AA), 60 °C (1B3O), the molar ratio of allylic compound/hydrogen peroxide = 1 (CRA, 1B3O) or 2 (AA, MAA), catalyst concentration 3 wt%, reaction time 2 h, intensity of stirring 500 rpm

Research on MAA epoxidation showed that the selectivity of 2-methylglycidol decreased slightly from 54 to 42 mol% in the tested range of solvent concentrations (from 10 to 80 wt%). MAA conversion was practically constant in the tested range of solvent concentrations and was about 39 mol%. The methanol concentration of 10 wt% was found to be the best methanol concentration to carry out the process of AMA epoxidation. At this solvent concentration, the selectivities of other products of the process were as follows: 2-methylacroleine 44 mol%, methallyl-2-methylglycidol ether 1 mol%, and bis(methylglycidol) ether 1 mol%.

The research on CRA epoxidation shows that in the whole range of changes in concentration of the solvent the selectivity of the epoxy compound (2,3-epoxybutane-1-ol) was very low and amounted to 2–3 mol%. The conversion of CRA first increased from 60 to 80 mol% (for methanol concentration to 40 wt%) and then decreased to 51 mol% (methanol concentration 80 wt%). The concentration of methanol equal to 40 wt% was found to be the most beneficial at this stage of research. At this solvent concentration, the selectivities of by-products of the process were as follows: 1,2,3-butanetriol 66 mol%, crotyl aldehyde 17 mol%, 2,3-dimetoxybutane-1-ol 6 mol%, bis 2-butene ether 5 mol%, crotonic acid 2 mol% and 4-(2,3-butenoxy)-butene-2,3-diol 2 mol%.

The research on the influence of solvent concentration on process of 1B3O epoxidation indicates that the change of methanol concentration does not affect the selectivity of the epoxy compound (2-epoxy-3-butanol), which was about 100 mol%. However, 1B3O conversion grew from 20 to 43 mol% at the range of methanol concentration from 10 to 60 wt%, and for the methanol concentration of 80 wt%, it amounted to 43 mol%. The concentration of 60 wt% was found to be the best concentration of solvent at this stage of research. There was only one by-product at this concentration of the solvent: bis(2-methyl-1-propene) ether (selectivity 1 mol%).

The studies showed that the solvent (methanol) concentration is very important parameter for the AA epoxidation (the selectivity of glycidol changed from 32 to

66 mol%). The increase in the amount of methanol molecules in the reaction mixture probably caused that the glycidol molecules were more stable in methanol–water solution. A part of methanol molecules participated in the formation of 5-membered active complexes at active centres (Ti-atoms) and the remaining part of molecules took part in the stabilization of the epoxide molecules. In the case of MAA epoxidation, the selectivity of the epoxide compound slightly decreased (from 54 to 42 mol%). Probably, steric hindrance connected with the presence of $–CH_3$ group decreased the stabilizing effect of the methanol molecules. The methanol concentration was also an important parameter for the conversion of CRA and 1B3O. In the case of CRA conversion, methanol concentrations above 40 wt% were not beneficial, probably methanol molecules in higher concentration hindered the CRA molecules an access to active centres of Ti. It was observed for 1B3O that methanol concentration of 60wt% was the border concentration above of which methanol molecules did not influence the course of epoxidation. Moreover, in the case of 2-epoxy-3-butanol, the stabilizing effect of methanol molecules was not needed.

The influence of the Ti-SBA-15 catalyst concentration on the course of allylic compounds epoxidation

The results of the impact of concentration of the Ti-SBA-15 catalyst on the process of epoxidation of allylic compounds are shown in Fig. 8.

Research on the influence of catalyst concentration on the AA epoxidation process showed that changes in the catalyst concentration had no significant effect on the selectivity of glycidol and conversion of AA, which amounted to 67 and 47 mol% on average. A catalyst concentration equal to 1 wt% was found to be the most beneficial at this stage of research. At this concentration of the catalyst, the AA conversion was slightly higher (47 mol%) than for the catalyst concentration of 0.5

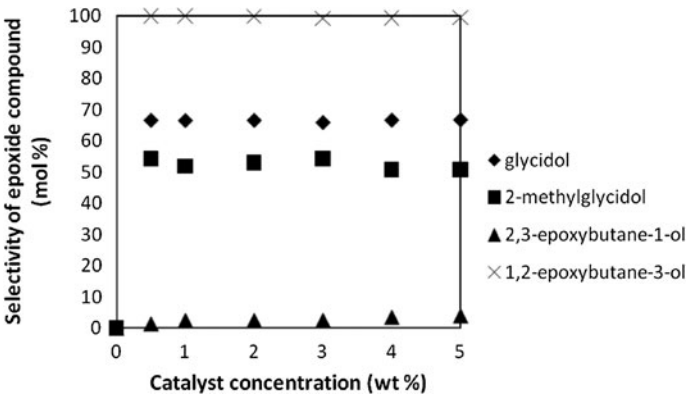


Fig. 8 The influence of the Ti-SBA-15 catalyst concentration on the selectivities of the epoxide compounds. The reaction conditions: temperature 20 °C (MAA, CRA), 40 °C (AA), 60 °C (1B3O), the molar ratio of allylic compound/hydrogen peroxide = 1 (CRA, 1B3O) or 2 (AA, MAA), methanol concentration 80 wt% (AA), 10 wt% (MAA), 40 wt% CRA, 60 wt% 1B3O, reaction time 2 h

wt% (44 mol%), and the by-products formed with the following selectivities: 3-allyloxy-1,2-propanediol 12 mol%, allyl-glycidol ether 11 mol%, bis(allyl) ether 10 mol%, and acroleine 1 mol%. Glycerol, however, was absent in the reaction mixture (the product of the hydration of the epoxide ring).

Research on the influence of catalyst concentration on the selectivity of 2-methylglycidol showed that changing catalyst concentration in the range of 0.5–5 wt% did not cause significant changes in the selectivity of 2-methylglycidol, which amounted to about 52 mol%. MAA conversion, however, was highly dependent on the concentration of the catalyst. As the concentration of Ti-SBA increased from 0.5 to 3 wt%, an increase in MAA conversion was observed (from 21 to 42 mol%), but a further increase in the catalyst concentration did not cause any changes in this function. Having analyzed the results obtained, the concentration of the catalyst equal to 3 wt% was fund to be the most beneficial. The selectivity of by-products of the process at this concentration were as follows: 2-methylglycidol 1 mol%, 2-methylacroleine 44 mol%, methallyl-2-methylglycidol ether 1 mol%, and bis(methylglycidol) ether 1 mol%.

Research on the influence of catalyst concentration on the CRA epoxidation process showed that as the concentration of the catalyst in the reaction mixture grew, the selectivity of 2,3-epoxybutane-1-ol increased slightly from 2 to 4 mol%. The second main function of the process—CRA conversion also increased from 62 mol % (0.5 wt% of Ti-SBA-15) to 80 mol% (3 wt% of Ti-SBA-15), and then decreased to 72 and 67 mol % (concentrations of Ti-SBA-15 equal to 4 and 5 wt%). Taking into account the results obtained, the best catalyst concentration was 3 wt%. The selectivities of by-products at this Ti-SBA-15 concentration were as follows: 1,2,3-butanetriol 66 mol%, crotyl aldehyde 17 mol%, 2,3-dimetoxybutane-1-ol 6 mol%, bis(2-butene) ether 2 mol% and 4-(2,3-butenoxy)butene-2,3-diol 1 mol%.

Research on the influence of the Ti-SBA-15 catalyst concentration on the 1B3O epoxidation showed that changes in catalyst concentration from 0.5 to 5 wt% did not affect the selectivity of the epoxide which amounted to almost 100 mol%, but they did affect the 1B3O conversion, which grew from 8 mol% (0.5 wt% of Ti-SBA-15) to 43 mol% (3 wt% of Ti-SBA-15), and then did not change despite the increase in concentration of Ti-SBA-15 to 5 wt%. A catalyst concentration of 3 wt% was found to be the most beneficial at this stage of research. At this concentration, bis(2-methyl-1-propene) ether with selectivity equal to 1 mol% formed as the only by-product of the process.

The studies on the influence of catalyst concentration presented that the selectivity of all epoxide compounds did not depend on these technological parameters. On the other hand, the conversions of MAA, CRA and 1B3O depended on the amount of the Ti-SBA-15 catalyst. For MAA and 1B3O, the conversion achieved a maximal value at a catalyst concentration 3 wt% (about 43 mol%) and did not change for higher catalyst concentration. In the case of CRA, the conversion first raised from 62 mol% (0.5 wt% of the catalyst) to 80 mol% (3 wt% of the catalyst) and then slightly decreased to 71 mol% (4 wt% of the catalyst) and 67 mol% (5 wt% of the catalyst). This phenomenon could be probably caused by the decomposition of hydrogen peroxide on active centers of Ti.

The influence of the reaction time on the course of allylic compounds epoxidation

The results of the impact of reaction time on the process of epoxidation of allylic compounds are shown in Fig. 9.

Research on the effect of reaction time on the course of AA epoxidation showed that along with increased time of the epoxidation process, the epoxy compound selectivity increased from 6 mol% (15 min) to 64–66 mol% (120–180 min). A similar increase was observed in the case of AA conversion, which amounted to 31 mol% for 15 min of reaction time and 47 mol% for 120 and 180 min. The most favorable time was found to be 120 min taking the obtained results into account. The following products were present in the reaction mixture for this amount of time: 3-allyloxy-1,2-propanediol (selectivity 12 mol%), allyl-glycidyl ether (selectivity 11 mol%), bis(allyl) ether (selectivity 10 mol%) and acroleine (selectivity 1 mol%).

Research on the influence of duration of the reaction on the course of MAA epoxidation show that lengthening the time of the process in tested conditions increases the selectivity of the transformation to 2-metylglycidol from 41 mol% (the reaction time 15 min) to 54–55 mol% (the reaction time 120–180 min). A similar kind of change was observed for the MAA conversion, which for 15 min was equal to 14 mol%, whereas for 180 min amounted to 40 mol%. Analysis of the results led to the conclusion that the time of 2 h is the most advantageous to carry out MAA epoxidation. The following by-products were present in the mixture after the reaction for this reaction time: 2-methylacroleine (selectivity 44 mol%), bis (methylglycidol) ether (selectivity 1 mol%) and methallyl-2-methylglycidol ether (selectivity 1 mol%).

Research on the impact of duration showed that lengthening the CRA epoxidation process has not led to a significant increase in selectivity of 2,3-

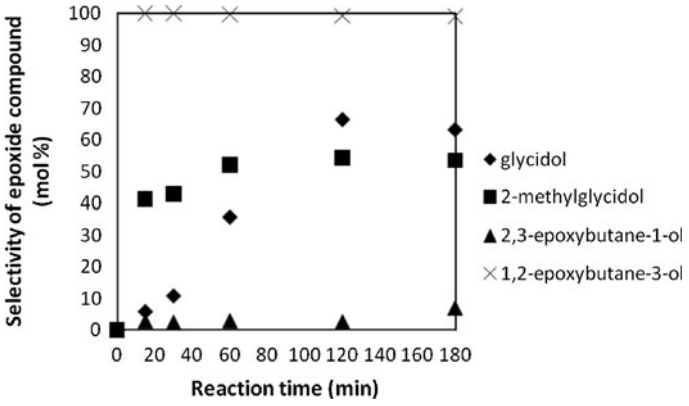


Fig. 9 The influence of the reaction time on the selectivities of the epoxide compounds. The reaction conditions: temperature 20 °C (MAA, CRA), 40 °C (AA), 60 °C (1B3O), the molar ratio of the allylic compound/hydrogen peroxide = 1 (CRA, 1B3O) or 2 (AA, MAA), methanol concentration 10 wt% (MAA), 40 wt% (CRA), 60 wt% (1B3O), 80 wt% (AA), catalyst concentration 1 wt% (AA), 3 wt% (MAA, CRA, 1B3O) and intensity of stirring 500 rpm

epoxybutane-1-ol (15 min—the selectivity of epoxide amounted to 3 mol%, for 180–240 min—the selectivity of epoxide 7 mol%). However, the reaction time exerted a significant effect on CRA conversions (reaction time 15 min—CRA conversion 28 mol%, reaction time: 120–240 min—CRA conversion 80–82 mol%). The most beneficial duration at this stage of research was considered to be 180 min, and the following products were present in the post-reaction mixture for this reaction time: 1,2,3-butanetriol 64 mol%, crotyl aldehyde (selectivity 15 mol%), 2,3-dimetoxybutane-1-ol (selectivity 5 mol%), bis(2-butene) ether (selectivity 5 mol%), crotonic acid (selectivity 4 mol%) and 4-(2,3-butenoxy)-butene-2,3-diol (selectivity 1 mol%).

Research on the influence of duration time on the epoxidation of 1B3O showed that lengthening the process virtually did not affect the selectivity of 1,2-epoxy-3-butanol, which was about 100% mol. Trace amounts of bis(2-methyl-1-propene) ether (selectivity of this compound was less than 1 mol%) were detected in the post-reaction mixture for the longest duration times. The conversion of 1B3O increased along with increasing reaction time from 6 mol% (15 min) to 42 mol% (180 min). Analysis of the results obtained showed that 120 min was the most favorable time.

The studies on the influence of the reaction time showed that for almost all investigated allylic compounds the most beneficial reaction time was 120 min (only for CRA it was 180 min). The selectivity of the epoxide compound for AA, MAA and CRA increased with the prolongation of the reaction time from 15 to 120–180 min. The highest increase in values of this function was observed for AA (10 times—from 6 to 64–66 mol%). The conversions of all allylic compounds also increased with the prolongation of the reaction time. The highest value of the conversion was observed for CRA (80–82 mol%) but this high conversion was connected to the formation a significant amount of by-products during the process.

The influence of intensity of stirring on the course of allylic compounds epoxidation

Studies on the effect of the intensity of stirring on the AA, MAA, CRA and 1B3O epoxidation showed that changes in intensity of stirring from 500 to 700 rpm did not cause any changes in the selectivity of the epoxy compound and in the conversion of allylic compound (the selectivity of glycidol was about 65 mol%, 2-methylglycidol about 53 mol%, 2,3-epoxybutane-1-ol about 5 mol% and 1,2-epoxybutane-3-ol about 100 mol%, the conversion of AA was about 45 mol%, MAA about 40 mol%, CRA about 80 mol% and 1B3O about 45 mol%).

Conclusions

The studies showed that the method of Ti-SBA-15 synthesis presented in the literature makes it possible to obtain an active catalyst for the allylic compounds epoxidation. The following parameters were found to be the most influential on the process of epoxidation: the molar ratio of reagents (mainly for the selectivities of glycidol and 2-methylglycidol), solvent concentration (mainly for the selectivities

of glycidol and 2-methylglycidol and the conversions of CRA and 1B3O), catalyst concentration (conversions of MAA, CRA, 1B3O), and the reaction time (selectivities of glycidol, 2-methylglycidol, CRA and conversions of all allylic compounds).

The results obtained at the end of the studies (under the most beneficial conditions) showed that AA, MAA and CRA molecules had comparable reactivity taking into account their conversion. The conversion of CRA was significantly higher (2 times higher). The total selectivity of the epoxide compound and product of the hydration of the epoxide ring amounted to for AA 65 mol% (the selectivity of glycerine 0 mol%), for MAA 53 mol% (the selectivity of 2-methylglycerine 0 mol%), for CRA 69 mol% (the selectivity of 1,2,3-butanetriol 64 mol%) and for 1B3O 100 mol% (only the epoxide compound was formed). The studies also show that two directions of the oxidation can be possible: the oxidation of the double bound, and the oxidation of –OH group. The structure of the allylic compound, mainly the electronic displacement in the direction of the double bound, and in a consequence the electronegativity the C atom with –OH group were crucial for the direction of the oxidation. In the case of AA, mainly the oxidation of the double bond took place and also the etherification reactions proceeded. For MAA, the oxidation of the double bond proceeded in the same amount as the oxidation of –OH group (the products of etherification were detected in trace amount), for CRA three times more products of the oxidation of the double bond was obtained than the oxidation of –OH group and in the case of 1B3O, only epoxidation took place.

The comparison of the most beneficial parameters and values of the main functions of the process presented in this article with our previous results for TS-1 [11], Ti-MCM-41 [12] and Ti-MCM-48 [9] catalysts (for the most reactive allylic compound—AA) showed that the reactivity of the Ti-SBA-15 catalyst is comparable with TS-1 and Ti-MCM-41 catalysts. Thus, in the future, the Ti-SBA-15 catalyst can also be effectively used in epoxidation processes instead of TS-1 catalyst. Moreover, the synthesis of this catalyst is anvironmentally friendly (the synthesis in the presence of biodegradable polymer as template) what is an additional advantage of the utilization of this catalyst.

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