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Epoxidation of allyl alcohol to glycidol over the microporous TS-1 catalyst

Agnieszka Wróblewska*, Anna Fajdek

Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland

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ABSTRACT

The results of the epoxidation of allyl alcohol with 30% hydrogen peroxide over the TS-1 catalyst have been presented. The studies were carried out under the atmospheric pressure and at the presence of methanol as a solvent. The influence of the following technological parameters on the course of epoxidation was examined: the temperature of 20–60 °C, the molar ratio of AA/H_2O_2 1:1–5:1, the methanol concentration of 5–90 wt%, the catalyst content of 0.1–5.0 wt% and the reaction time 5–300 min. The main functions describing the process were the selectivity to glycidol in relation to allyl alcohol consumed, the conversion of substrates, and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. The parameters at which the functions describing the process reached the highest values were determined.

1. Introduction

New and effective catalysts used in the processes of oxidization have been intensely sought over the last few years. Very active, selective heterogeneous catalysts which allow to conduct chemical processes in harmony with environmental protection requirements are especially significant. Titanium-silicalite catalysts belong to the group of heterogeneous catalysts and are well fitted into the strategy of clean technologies since they catalyze the reaction of oxidation using H_2O_2 which is relatively easy available oxidant forming water as the only by-product of its transformation [1].

The TS-1 catalyst was obtained for the first time by Taramasso in 1983, in Italy. It consists of three-dimensional system of channels which is a combination of linear and zigzag locations (the MFI type structure) [2–4]. It crystallizes in the orthorhombic system, the size of crystallites varies from 0.1 to 1.0 μm. The entrance holes into the channels are limited by 12 edges which dimensions amount to 0.53 nm × 0.56 nm. The templating agent used in the synthesis of the catalyst is tetrapropylammonium hydroxide (TPAOH) [4].

TS-1 is a selective catalyst oxidizing substantial amounts of organic compounds, such as alkanes, olefins, alcohols and phenols, with the use of hydrogen peroxide under the relatively mild conditions [5]. It can be applied to the epoxidation of olefins (ethylene, propylene, 1,2-butylene, allyl chloride, and cyklohexene) [6–11], the monoepoxidation of dienes (allyl ether, acrylate and allyl mathaacrylate, and 1,3-buthadiene) [12], the oxidation of alcohols to aldehydes and ketones [13–15], the oxidation of cyclohexane and other hydrocarbones (hexane, heptane, octane, and nonane), the hydroxylation of phenol and other aromatic compounds (benzene, toluene, chlorobenzene, nitrobenzene, anisole, and acetamide) [7,16–21]. The TS-1 catalyst can also be used in the following type of processes: the hydroxylation of benzene or hexane using oxygen or hydrogen [22], the isomerisation of styrene oxide or its homologues to β-phenylaldehydes [23], the rearrangement of cyclohexanone oxime to ε-aminocaprolactame [24], the ammoximation of cyclohexanone in the gas phase [25], the synthesis of methyl t-butyl ether [26], the oxidation of primary amines [27], the oligomerization of olefins C_2–C_{10} [28–30], and the oxidizing dehydrogenation of ethanol [31].

The epoxidation of allyl alcohol with 30% hydrogen peroxide using the TS-1 titanium-silicalite catalysts and methanol as a solvent is an example of new trends in modern organic technology. Glycidol (2,3-epoxy-1-propanol), which undergoes partial hydration to glycerol in the conditions of a reaction, is the main product of the epoxidation of allyl alcohol. Depending on the conditions of epoxidation small amount of ethers (bis (allyl) ether and allylglycidol ether) is formed in the process. At higher temperature polymerization occurs to a small extent (Scheme 1):

The major product—glycidol is an important monomer and 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 [32]. The surface-active agents are also used as food emulgators in the production of margarine, ice-cream, and vegetable butter [33,34]. Other applications of glycidol

* Corresponding author at: Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland. Tel.: +48 914494875; fax: +48 914494365.
E-mail address: agnieszka.wroblewska@zut.edu.pl (A. Wróblewska).

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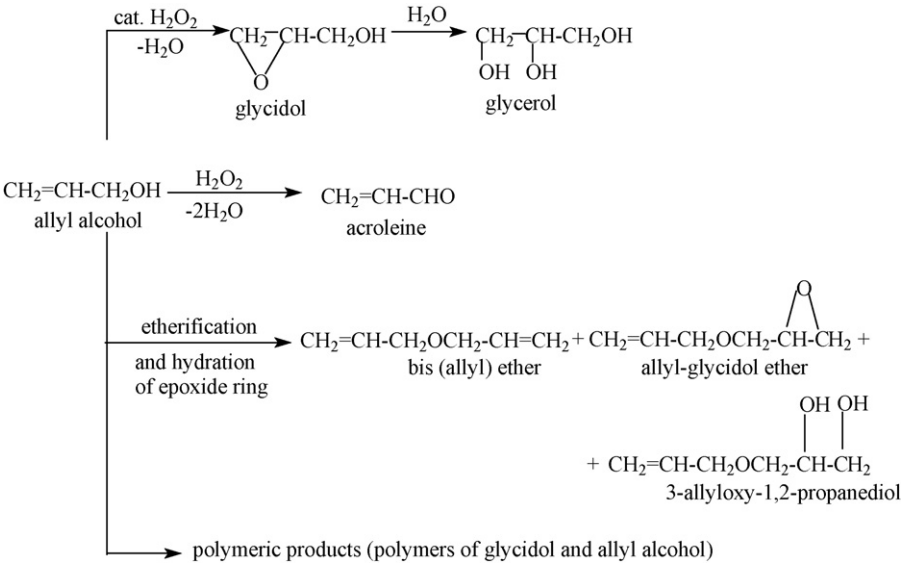


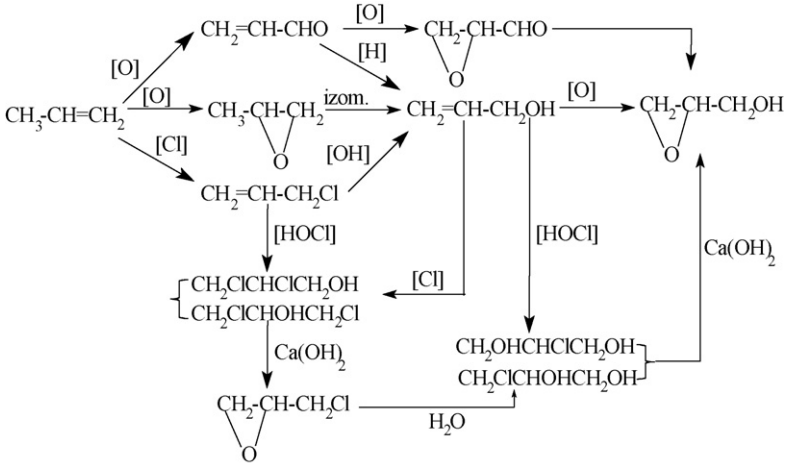
Scheme 1. Major and by-products of the epoxidation of allyl alcohol with 30% hydrogen peroxide over the TS-1 titanium-silicalite catalysts.

include plasticizers, fabric dyes, photochemical compounds, rubbers, varnishes, and plastics [34]. 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 and fungus). One of the most important applications of glycidol is the synthesis of antiviral and analgesic drugs. Especially an important group of antiviral drugs constitute active compounds fighting HIV. With the use of glycidol, active compounds fighting HIV are obtained, the equivalents of natural compounds contained in fungus, as well as new derivatives of nucleotides fighting this and other viruses [34].

Other authors also presented investigations of AA (allyl alcohol) epoxidation over titanium-silicalite catalyst TS-1 [35,36] and the new titanium-silicalite Ti-MWW [37]. The first two articles helped us to choose the best method of TS-1 synthesis and the best solvent for epoxidation of AA. The first article presents the epoxidation of AA over TS-1 catalysts synthesized by the three methods: tetraethyl orthotitanate, fluoride, and tetrabutyl orthotitanate respectively [35]. The epoxidation of AA was carried out in constant conditions (only the reaction time was changed) with help of 70 wt% hydrogen peroxide, at the temperature of 65 °C, in the presence of ethanol as a solvent (the concentration of 82 wt%), as the concentration of catalyst amounted to 1.5 wt%, at the molar ratio $AA/H_2O_2 = 1$. In this study the reaction was carried out even to 24 h (very long in comparison with our investigations). Thus the conversion of AA was from 28 to 55 mol% in dependence of the method of TS-1 catalyst synthesis. The selectivity of transformation to glycidol in the post-reaction mixture was very poor; the main products were products of solvolysis of epoxide ring. On the basis of the article we chose the Thangaraj et al. method as the best for TS-1 synthesis.

The second article [36] presents the investigations over TS-1 catalysts synthesized by four methods, the same as in previous article plus by Qiu et al. The authors carried out the studies at the following temperatures: 20, 50, and 65 °C, at the molar ratio of $AA/H_2O_2 = 1$, the amount of solvent was 45 ml, and the catalyst 0.5 g. The main problem presented in the article was choosing the best solvent for epoxidation of AA. On the basis of these results we chose methanol as the best solvent for our investigations.

Wu and Tatsumi have performed epoxidation of AA [37]. The authors used in the process the new titanium-silicalite catalyst—Ti-MWW. They investigated the influence of the following parameters: Ti content in catalyst, reaction time, reaction temperature, and the kind of the solvent but the authors did not present



Scheme 2. The possible ways of glycidol production.

the full investigations of all parameters of the process, which we made for TS-1. We also synthesized the Ti-MWW catalyst and we are using it in epoxidation of AA. The results are very interesting and promising but the studies are still in the stage of laboratory investigations. Whereas TS-1 and its using in epoxidation of AA is interesting from industry point of view because it is commercially produced and is applied in plants of hydroxylation of phenol and oxidation of propylene to propylene oxide.

The aim of this study was to estimate the most beneficial technological parameters for epoxidation of AA over titanium-silicalite TS-1 catalyst. It would help us to design the process of epoxidation of AA in technical scale and will be good alternative for present glycidol production process. The present process can be divided in two groups: chlorine and chlorine free method [38–40] (Scheme 2).

The first one is chlorohydrine method which generates a lot of chlorine waste, the second used AA, hydrogen peroxide, and for example: V_2O_5, Cr_2O_3, OsO_4, $NaWO_4$, WO_3, and other heavy metal compounds [41,42]. The heavy metal compounds are very harmful for environment. Also peroxyacids are used in chlorine free method and it generates a lot of acid waste [43]. The method presented in this study does not have these drawbacks.

2. Experimental

2.1. Reactants used in the epoxidation of allyl alcohol

In the process of the epoxidation of allyl alcohol the following reactants were used: allyl alcohol—AA (98%, Fluka), the TS-1 titanium-silicalite catalyst (prepared in the Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin), hydrogen peroxide (30% water solution, P.O.Ch. Gliwice), and methanol (cz.d.a., P.O.Ch. Gliwice).

2.2. The synthesis of the TS-1 catalyst

The TS-1 catalyst was prepared according to the method described by Thangaraj et al. [44]. The characterization of catalyst was performed with the use of the following conventional techniques: XRD (X-ray diffraction spectroscopy), XRF (X-ray fluorescence spectroscopy), IR (spectroscopy in infrared), UV–vis (ultraviolet–visible spectroscopy), and SEM (scanning electron microscopy).

2.3. The epoxidation of allyl alcohol

The epoxidation was performed under the atmospheric pressure in a glass reactor (the volume of the reactor was 25 cm^3) fitted with a reflux condenser, thermometer, a magnetic stirrer, and a dropping funnel. The determined amounts of reactants were introduced into the reactor in the following order: the TS-1 titanium-silicalite catalysts, allyl alcohol, and methanol (solvent). Thirty weight percent of hydrogen peroxide was dropped after achieving the reaction temperature. The process was carried out for a specified amount of time. After the process was completed, a post-reaction mixture was weighed and analyzed. The range of changes of the examined technological parameters was as follows: the temperature of 20–60 °C, the molar ratio of AA/H_2O_2 1:1–5:1, the solvent concentration (methanol) of 5–90 wt%, the catalyst content of 0.1–5.0 wt%, and the reaction time 5–300 min.

2.4. Analysis of the composition of post-reaction mixture

In order to calculate the mass balance for the syntheses, post-reaction mixtures were analyzed in the following way: unreacted hydrogen peroxide was determined by means of iodometric method [45], glycerol formed in the process was determined by means of potentiometric method [46]. 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-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. After calculating the mass balance for each of the syntheses, the main functions describing the process were determined: the selectivity to glycidol in relation to allyl alcohol consumed, the conversion of allyl alcohol, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. The magnitudes were calculated in the following way:

$$S_{glc/AA} = \frac{\text{amount of moles of glycidol}}{\text{amount of moles of allyl alcohol consumed}} \times 100\,[\text{mol\%}]$$

$$K_{AA} = \frac{\text{amount of moles of allyl alcohol consumed}}{\text{amount of moles of allyl alcohol nitroduced into reactor}} \times 100\,[\text{mol\%}]$$

$$S_{org./H_2O_2} = \frac{\text{amount of moles of formed organic compounds}}{\text{amount of moles of } H_2O_2 \text{ consumed}} \times 100\,[\text{mol\%}]$$

The selectivity to different by-products was determined the same as glycidol.

3. Results and discussion

3.1. The characteristic of the TS-1 catalyst

The crystalline structure of the TS-1 catalyst was confirmed with the use of X-ray diffraction spectroscopy (XRD) using XPERT PRO diffractometer (Panalytical, Poland). XRD spectrum was recorded within the angle range from 6° to 60° using Cu Kα radiation—Fig. 1. Obtained spectrum was consistent with the literature data [44].

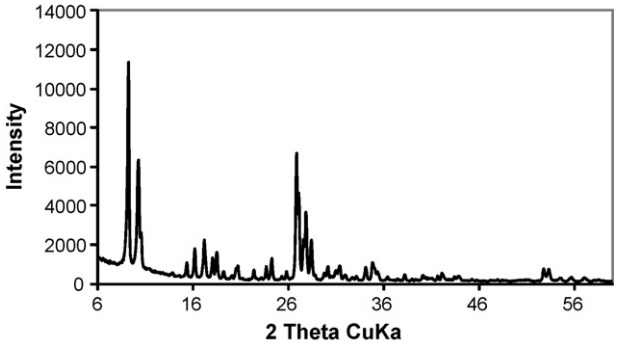


Fig. 1. XRD spectra of the obtained TS-1 catalyst.

The titanium content was determined with the use of XRF method, and was established as 1.7 wt% of TiO_2. The research was conducted using VRA 30 spectrometer.

IR spectrum of the TS-1 catalyst was recorded with the use of JASCO FT/IR spectrometer using the potassium bromide (KBr) pellet technique. An absorption band 960 cm^{-1} appeared in IR spectrum of the obtained catalyst—Fig. 2.

UV–vis spectra were recorded on SPECORD M40 spectrometer. 220 nm band appeared in the spectra, which confirms the incor-

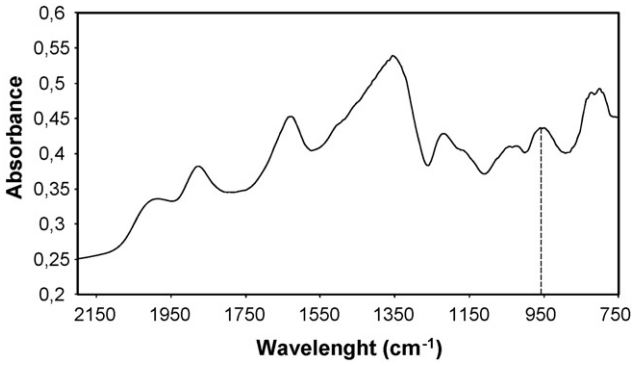


Fig. 2. IR spectra of the obtained TS-1 catalyst.

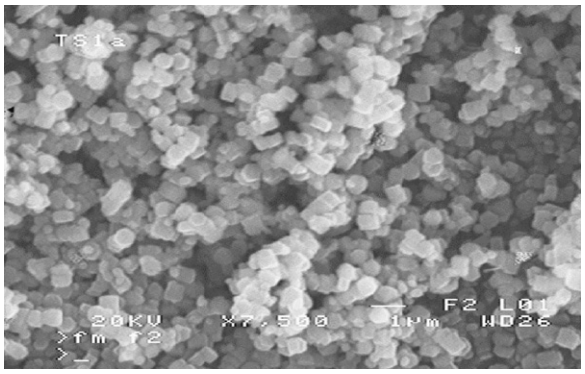


Fig. 3. SEM photography of the obtained TS-1 catalyst.

poration of Ti^{4+} into the crystal structure of silica whereas lack of 300 nm band confirms that titanium was not present in anatase.

The morphology of crystallites of the TS-1 catalyst was determined on the basis of SEM photograph taken with the use of Joel JSM-6100 scanning electron microscope. On the basis of SEM photograph it can be concluded that the TS-1 catalyst consists of homogeneous crystallites whose size amounts to about 0.5 μm—Fig. 3.

3.2. The influence of the temperature

Fig. 4 presents the selectivity to glycidol in relation to allyl alcohol consumed, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, and the conversion of allyl alcohol at the temperature of conducting the

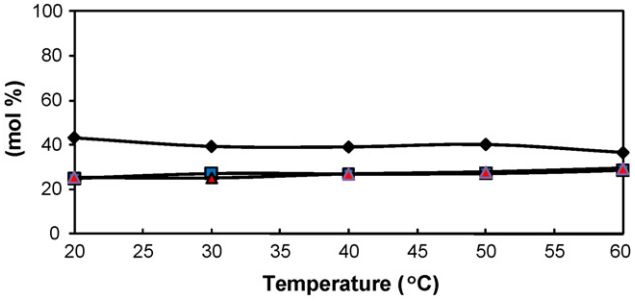


Fig. 4. The influence of the temperature on epoxidation over the TS-1 catalyst (♦—the selectivity to glycidol in relation to allyl alcohol consumed, ■—the conversion of allyl alcohol, and ▲—the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). The reaction conditions: the molar ratio of AA/H_2O_2 = 1:1, the solvent concentration (methanol) of 40 wt%, the catalyst concentration of 1 wt%, and the reaction time 3 h.

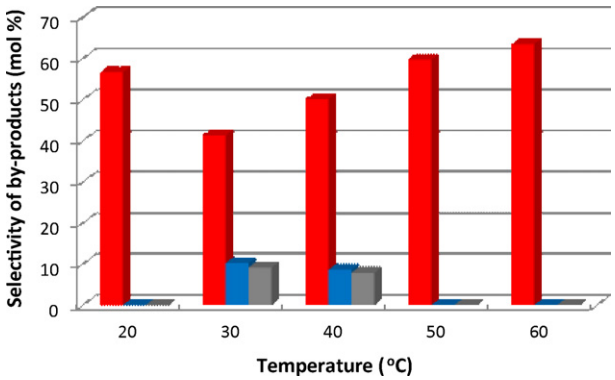


Fig. 5. The distribution of the by-products of the epoxidation of allyl alcohol depending on the temperature (■—the selectivity of glycerol, ■—the selectivity of 3-allyloxy-1,2-propanediol, and ■—the selectivity of allyl-glycidol ether). The reaction conditions: the molar ratio of AA/H_2O_2 = 1:1, the solvent concentration (methanol) of 40 wt%, the catalyst concentration of 1 wt%, and the reaction time 3 h.

process. The starting conditions of epoxidation were as follows: the molar ratio of AA/H_2O_2 = 1:1, the solvent concentration (methanol) of 40 wt%, the catalyst concentration of 1 wt%, and the reaction time 3 h.

It follows from the research that the temperature does not have a significant impact on the selectivity to glycidol in relation to allyl alcohol consumed. The values of this function change marginally in the examined range of temperatures. Such course of the process is caused by the rate of the epoxidation of allyl alcohol to glycidol along with slower progression of the hydration of glycidol to glycerol. Its average value amounts to about 40 mol%. The conversion of allyl alcohol virtually does not change in the examined range of temperatures and amounts to 25–28 mol%. The function of the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed has a similar course and amounts to about 27 mol%.

The selectivity to glycerol increases with the increase of the temperature and reaches its maximal value (60 mol%) at the temperature of 60 °C—Fig. 5. Within the range from 30 to 40 °C another by-products were formed i.e. allyl-glycidol ether and 3-allyloxy-1,2-propanediol with selectivities amounting to about 8–10 mol%. The research indicates that the temperature does not have a significant impact on the course of the epoxidation of allyl alcohol. Presumably, a change of solvent for the one boiling in lower temperature and the extension of examined range of the temperature would result in bigger changes of the values of the main functions of a process. On the basis of the obtained results the temperature of 20 °C was established as optimal.

3.3. The influence of molar ratio of AA/H_2O_2

The influence of the molar ratio of AA/H_2O_2 on the course of epoxidation was examined in the range from 1:1 to 5:1 and at the temperature of 20 °C. The other starting parameters were not changed. The results from this investigation are presented in Fig. 6.

On the basis of Fig. 6 it can be concluded that the increasing molar ratio of AA/H_2O_2 affects the selectivity to glycidol in relation to allyl alcohol. For the lower molar ratios (1:1) the value of this function amounts to about 43 mol%. As the molar ratio of AA/H_2O_2 increases within the range of 2:1–4:1 the selectivity to glycidol establishes at the level of 71 mol%. Further increase to 80 mol% occurs at the molar ratio 5:1. The conversion of allyl alcohol decreases with the increase of the molar ratio of AA/H_2O_2 from 25 mol% (the molar ratio of AA/H_2O_2 = 1:1) to 8 mol% (the molar ratio of AA/H_2O_2 = 5:1). Such course of the changes is the result of the excess of allyl alcohol in relation to hydrogen peroxide. At

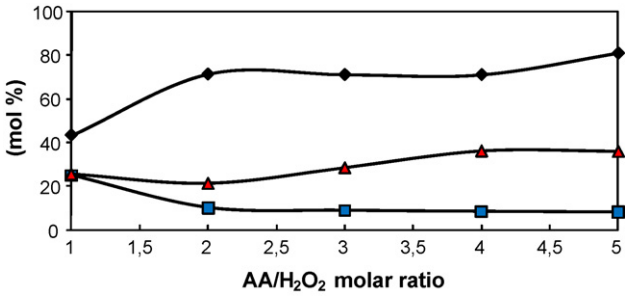


Fig. 6. The influence of molar ratio of AA/H_2O_2 on the epoxidation of allyl alcohol over the TS-1 catalyst (♦—the selectivity to glycidol in relation to allyl alcohol consumed, ■—the conversion of allyl alcohol, and ▲—the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). The reaction conditions: temperature 20 °C, the solvent concentration (methanol) of 40 wt%, the catalyst concentration of 1 wt%, and the reaction time 3 h.

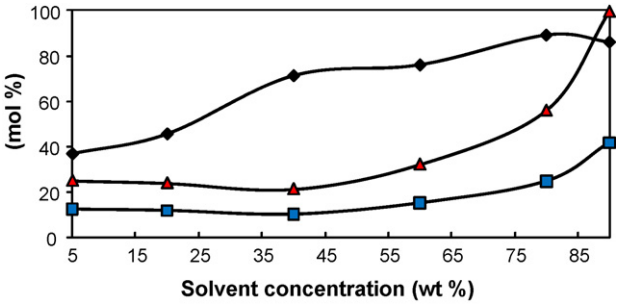


Fig. 8. The influence of the solvent concentration (methanol) on the course of the epoxidation of allyl alcohol over the TS-1 catalyst (♦—the selectivity to glycidol in relation to allyl alcohol consumed, ■—the conversion of allyl alcohol, and ▲—the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the catalyst concentration of 1 wt%, and the reaction time 3 h.

the most interesting molar ratio of AA/H_2O_2 = 2:1 a half of introduced alcohol is consumed. The selectivity of the transformation to organic compounds in relation to hydrogen peroxide consumed increases from about 26 to 36 mol%.

The only by-product forming at this stage of the investigations is glycerol. Its selectivity decreases with the increase of the molar ratio of AA/H_2O_2 from 14 to 2 mol%—Fig. 7. Thus, the molar ratio of AA/H_2O_2 = 2:1 is the most optimal in the process of epoxidation with regard to high selectivity of the transformation to glycidol. The experiments at the molar ratios of AA/H_2O_2 < 1 have not been conducted, since it follows from the literature data [47] that the excess of H_2O_2 in post-reaction mixture leached titanium from the structure of the catalyst, which changes the conditions of the process and decreases the selectivity of transformation. The second unwanted phenomenon is the ineffective decomposition of H_2O_2.

3.4. The influence of the solvent concentration

Fig. 8 presents the influence of the solvent concentration on the epoxidation of allyl alcohol, at the temperature of 20 °C and at the molar ratio of AA/H_2O_2 = 2:1. Other starting parameters were not changed.

Analyzing the influence of the solvent concentration—methanol on the selectivity to glycidol it was concluded that the value of this function increases with the increase of the methanol concentration. The function reaches the highest value for the methanol concentration of 80 wt% (86 mol%). After the methanol concentration increases to 90 wt% the value of this function changes to a small extent. The biggest increase of the conversion of allyl alcohol occurs in the range of the methanol concentration of 40–90 wt%. At the lowest methanol concentration (5 wt%) the conversion of allyl alcohol amounts to 12 mol%. The selectivity of the transformation to organic compounds increases with the increase of the methanol concentration and rises to 99 mol% (90 wt% of solvent).

The selectivity of glycerol, as the only by-product formed during epoxidation process, decreases significantly with the increase of the solvent concentration from 63 mol% (5 wt% of solvent) to 14 mol% (90 wt% of solvent)—Fig. 9. Therefore, the most optimal methanol concentration amounts to 90 wt%. The advantages of using high methanol concentration can be the result of the hydrophilic character of the catalyst. In accordance with the mechanism of reaction, methanol plays a key role in the formation of the 5-membered active adducts at the positions bound with titanium in-built into the structure of the catalyst—Fig. 10. The high methanol concentration accelerates the rate of epoxidation and limits the formation of by-products. The results confirm that the mechanism of epoxidation proposed in the literature [48] is correct.

Allyl alcohol has hydroxyl group in α position to a double bond, therefore it is a difficult substrate for epoxidation. The mechanism of the epoxidation of allyl alcohol over the titanium-silicalite catalysts can be explained in the following way: by adding hydrogen peroxide solution and methanol to the catalyst (structure I) cyclic 5-membered active adduct is formed (structure II). It is formed by substituting siloxane group (Si–O) with H_2O_2 molecule. Formed hydrogen peroxide bond is bound with allyl alcohol molecule which forms coordination bond to the active site (Ti atom) through a hydrogen bond. Methanol is in this case a suitable solvent, since

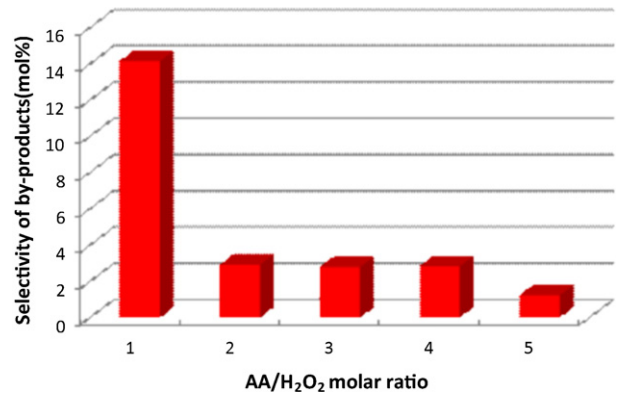


Fig. 7. The distribution of by-products of the epoxidation of allyl alcohol depending on the molar ratio of AA/H_2O_2 (■—the selectivity of glycerol). The reaction conditions: temperature 20 °C, the solvent concentration (methanol) of 40 wt%, the catalyst concentration of 1 wt%, and the reaction time 3 h.

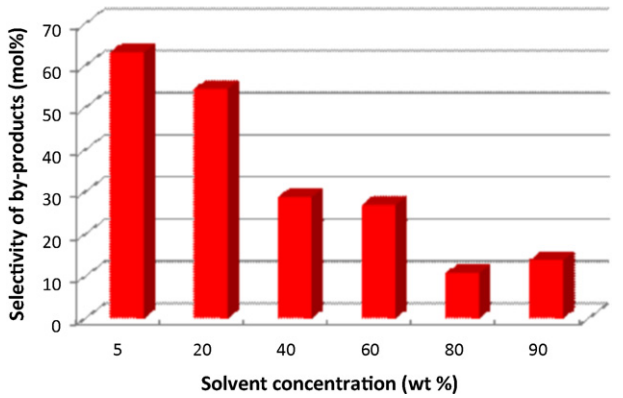


Fig. 9. The distribution of by-products of the epoxidation of allyl alcohol depending on the solvent concentration (methanol) (■—the selectivity of glycerol). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the catalyst concentration of 1 wt%, and the reaction time 3 h.

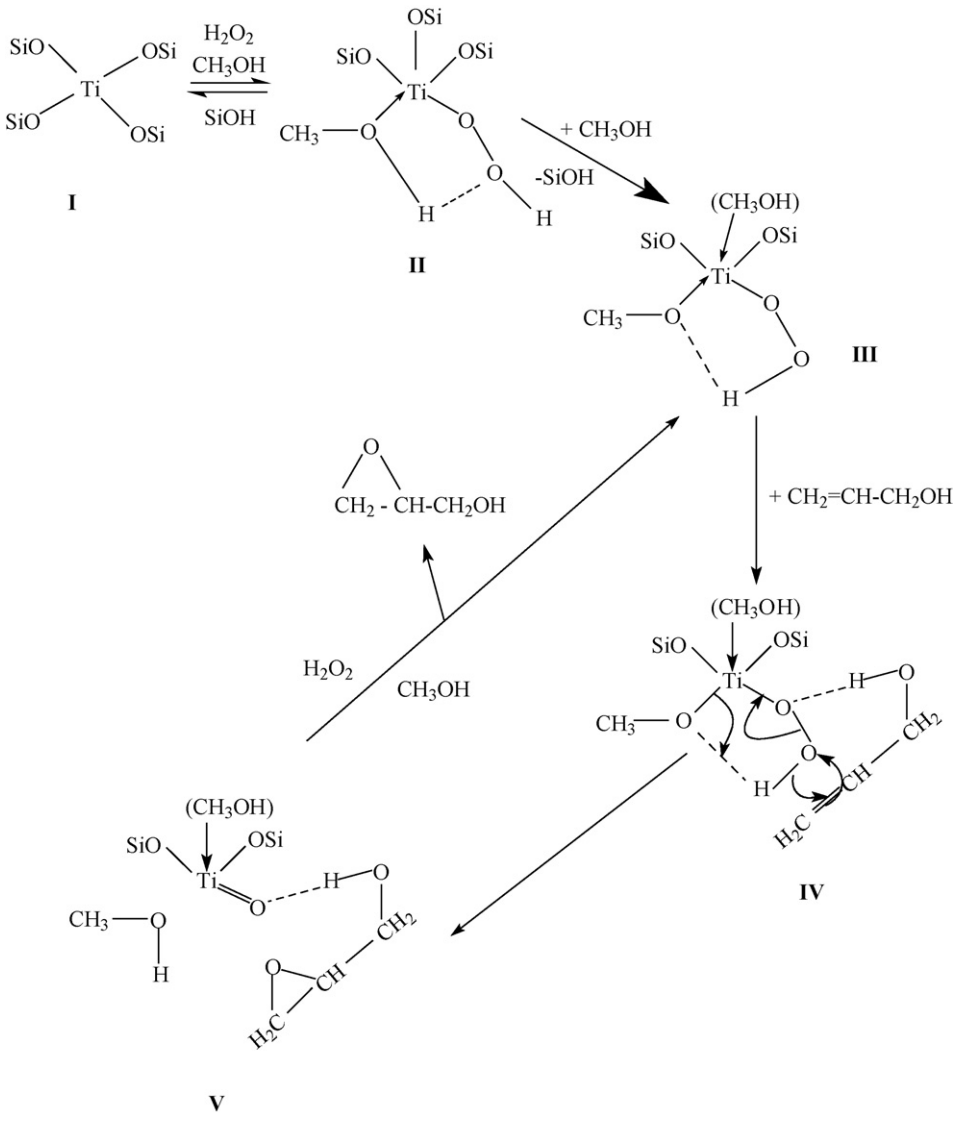


Fig. 10. The mechanism of epoxidation process.

it does not pose spatial obstacles and it does not hinder the oxygen transfer to organic substrate. Active bond II exists only in low-pH conditions. After an increase in pH level a structure which is neutral in the reaction with olefins is formed.

After adding consecutive water or methanol molecules, structure III is formed. In this structure water or methanol molecules form a direct bond with Ti, not a coordinate one. Structure IV is formed when allyl alcohol is added. In this structure allyl alcohol is bound with active bond III through a hydrogen bond formed between the –OH group of allyl alcohol and oxygen located closer to Ti atom in active bond III. A hydrogen bond stabilizes the system and prevents the oxidation of –OH group.

3.5. The influence of the catalyst concentration

The influence of the catalyst concentration was examined in the range of 0.1–5.0 wt%, at the temperature of 20 °C, at the molar ratio of AA/H_2O_2 = 2:1, at the solvent concentration of 90 wt%, and over the reaction time 3 h.

In the range of low catalyst concentration i.e. 0.1–0.5 wt% the selectivity to glycidol amounts to 48 mol%—Fig. 11. The function reaches the maximal value of 86 mol% (1 wt% of the TS-1 catalyst) and subsequently decreases for the catalyst concentration exceeding 1 wt% and reaches the value of 47 mol% (5 wt% of the catalyst concentration). The conversion of the allyl alcohol increases with the increase in the catalyst concentration from 40 to 63 mol%. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed amounts to 100 mol%.

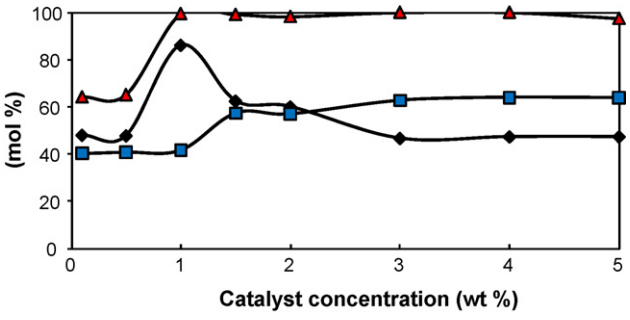


Fig. 11. The influence of the catalyst concentration on the epoxidation of allyl alcohol over the TS-1 catalyst (♦—the selectivity to glycidol in relation to allyl alcohol consumed, ■—the conversion of allyl alcohol, and ▲—the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the methanol concentration of 90 wt%, and the reaction time 3 h.

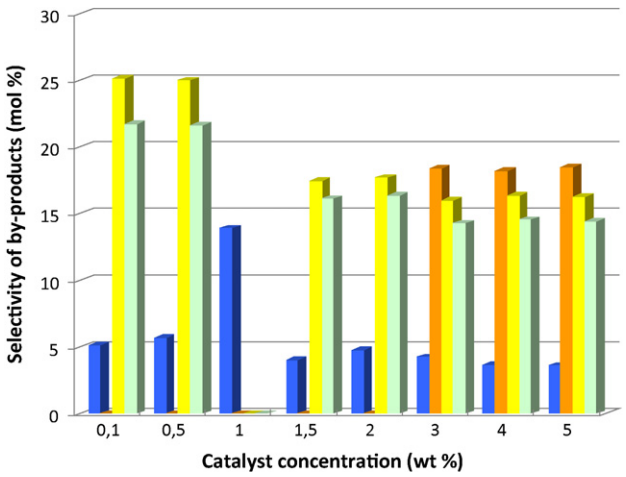


Fig. 12. The distribution of by-products of the epoxidation of allyl alcohol depending on the catalyst concentration (■—the selectivity of glcerol, ■—the selectivity of bis(allyl) ether, ■—the selectivity of allyl-glycidol ether, and ■—the selectivity of 3-allyloxy-1,2-propanediol). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the methanol concentration of 90 wt%, and the reaction time 3 h.

Along with the increase of the TS-1 catalyst concentration more by-products are formed (bis(allyl) ether, allyl-glycidol ether) whose selectivity decreases with the increase of the catalyst concentration—Fig. 12. Likewise, the selectivity of glycerol decreases with the increase of the catalyst concentration and reaches the lowest value of 4 mol% (5 wt% of the catalyst concentration). The optimal parameter at this stage of the process is the catalyst concentration of 1 wt%.

3.6. The influence of the reaction time

The influence of the reaction time on the course of epoxidation was examined in the range from 5 to 300 min (Fig. 13). Other parameters corresponded to the values previously established as optimal.

The analysis of the curve of the selectivity of the main product indicates that the function reaches the highest value 100 mol% in the range from 5 to 120 min. The prolongation of the reaction time causes a decrease in the value of the selectivity to glycidol to about 62 mol% (300 min). The conversion of allyl alcohol rises from 20 to about 40 mol% for the reaction time in the range of 5–30 min and next in the range of the reaction time 30–180 min is practically constant and amounts about 40 mol%. In the range of reaction time 180–300 min the conversion of allyl alcohol again rises and it

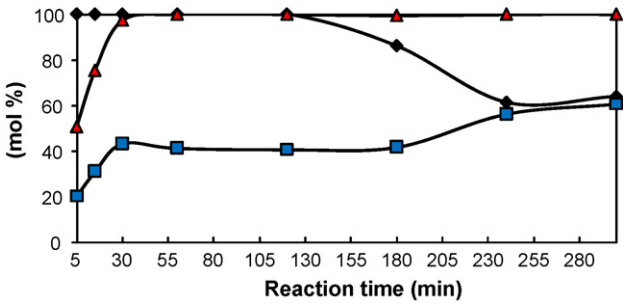


Fig. 13. The influence of the reaction time on the epoxidation of allyl alcohol over the TS-1 catalyst (♦—the selectivity to glycidol in relation to allyl alcohol consumed, ■—the conversion of allyl alcohol, and ▲—the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the methanol concentration of 90 wt%, and the catalyst concentration of 1 wt%.

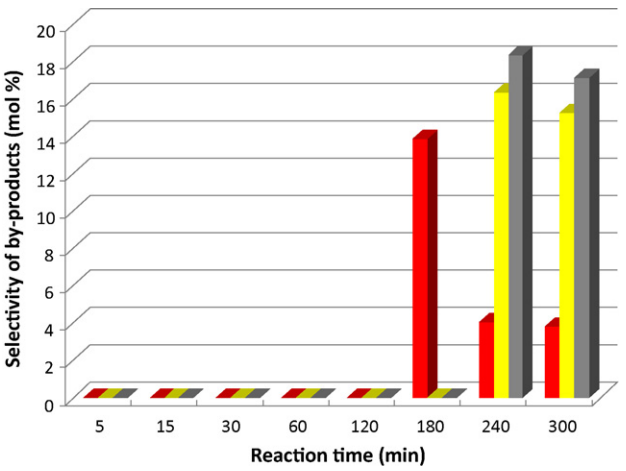


Fig. 14. The distribution of by-products of the epoxidation of allyl alcohol depending on the reaction time (■—the selectivity of glycerol, ■—the selectivity of allyl-glycidol ether, and ■—the selectivity of bis(allyl) ether). The reaction conditions: temperature 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the methanol concentration of 90 wt%, and the catalyst concentration of 1 wt%.

reaches the maximal value of 61 mol% after 300 min. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is close to 100 mol% in the whole range of the reaction time.

Glycerol can be observed in post-reaction mixture in the range from 180 to 300 min but its selectivity decreases with the prolongation of the reaction time—Fig. 14. The phenomenon that glycerol comes out in reaction at 180 min, and before 180 min it is not detected is probably connected with the value of glycidol concentration in reaction mixture. When the concentration exceeds the certain value of glycidol concentration, this compound starts to reacts to glycerol. The prolongation of the reaction time causes formation of other by-products, such as allyl-glycidol ether and bis (allyl) ether (in the range from 240 to 300 min). Their selectivities decrease with the prolongation of the reaction time. The reaction time 30 min was established as optimal at this stage of the research.

4. Conclusions

The results from this study give the optimal parameters of epoxidation of allyl alcohol to glycidol over the microporous TS-1 catalyst to be the temperature of 20 °C, the molar ratio of AA/H_2O_2 = 2:1, the methanol concentration of 90 wt%, the catalyst concentration of 1 wt%, and the reaction time 30 min. Under these conditions the selectivity to glycidol in relation to allyl alcohol consumed amounts to 100 mol%, the conversion of allyl alcohol to 43 mol%, and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed to 97 mol%.

The comparison of our previous papers [49,50] which also presented the epoxidation AA over TS-1 catalyst (and TS-2, too) shows that the method epoxidation at atmospheric pressure gives similar but generally better results to the epoxidation method at autogenic pressure in autoclave. The most beneficial technological parameters for autogenic pressure method [49] were as follows: temperature 20 °C, the molar ratio of AA/H_2O_2 = 5:1, methanol concentration 80 wt%, TS-1 catalyst concentration 1 wt%, and reaction time 60 min (the selectivity to glycidol in relation to AA consumed amounts to 94 mol%, and conversion of AA 69 mol%). For TS-2 catalyst the most beneficial parameters were similar, only conversion of AA was higher and amounts to 98 mol%. The optimal technological parameters for autogenic pressure method (established by help of mathematical method of process design) [50] were as follows: temperature 60 °C, the molar ratio of AA/H_2O_2 = 1:1, methanol con-

centration 90 wt%, TS-1 catalyst concentration 1 wt% and reaction time 120 min (the selectivity of transformation to glycidol in relation to AA consumed amounts to 61 mol%, and conversion of AA 60 mol%). These investigations showed a usefulness of mathematical functions to approximate describing the course of epoxidation process. The technological parameters for atmospheric pressure method presented in this paper are close to presented above, but these parameters allow to achieve 100 mol% the selectivity of transformation to glycidol in relation to AA consumed. This is important from the point of view of separation of the products and the by-products utilization, even at lower conversion of AA, because it can be easily separated by distillation and turn back to the process. But the most important is the cost of pressure system for epoxidation in comparison with equipment for the epoxidation at atmospheric pressure. In addition the presented method of epoxidation fulfills the requirements of "green chemistry". It is an environmentally friendly method using "a green oxidant"—hydrogen peroxide as an oxidizing agent. It is worth emphasizing that water is the only product of the transformation of hydrogen peroxide. In addition, the technology of H_2O_2 production is well developed and thus it is currently an easily available oxidizing agent.

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