Selective liquid-phase oxidation of allyl alcohol to glycidol over MWW type titanosilicalite

Anna Fajdek · Agnieszka Wróblewska ·
Eugeniusz Milchert

Received: 4 February 2011 / Accepted: 23 March 2011 / Published online: 7 April 2011
© The Author(s) 2011. This article is published with open access at Springerlink.com

Abstract The results of the epoxidation of allyl alcohol with 30% hydrogen peroxide over the Ti-MWW catalyst have been presented. The studies were carried out under atmospheric pressure and in the presence of methanol as a solvent. The influence of the following technological parameters on the course of epoxidation was examined: temperature (20–60 °C), the molar ratio of AA/H₂O₂ (1:1–5:1), methanol concentration (5–90 wt%), catalyst content (0–5.0 wt%), reaction time (5–300 min) and intensity of stirring (0–500 rpm).

Keywords Glycidol · Ti-MWW catalyst · Liquid-phase epoxidation · Hydrogen peroxide

Introduction

Zeolites are crystalline aluminosilicates with 133 known frameworks. Their pores are highly monodisperse and have a fixed directionality within the crystal. The pores in these systems often have a character of cages and connection tubes. The uniformity of the channels in the zeolitic system means that they are extremely selective adsorbents for small molecules of particular geometries and sizes and so make highly selective catalytic supports and adsorbents. Due to the pore sizes comparable to the molecular dimensions, zeolites are also called molecular sieves [1].

MWW (MCM-22) is a molecular sieve which crystallizes as thin sheets or plates and has a unique and unusual crystal structure. The thin crystals exhibit a hexagonal morphology, with the unit cell *c*-axis perpendicular to the plate surface. The

A. Fajdek · A. Wróblewska (✉) · E. Milchert
Institute of Organic Chemical Technology, West Pomeranian University of Technology Szczecin,
Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: agnieszka.wroblewska@zut.edu.pl

framework topology is composed of two independent pore systems. One of these pore systems is defined by two-dimensional sinusoidal channels, which maintain an effective 10-ring diameter throughout the entire structure. The other system is composed of large supercages whose inner free diameter 7.1 Å, is defined by 12-rings and whose inner height is 18.2 Å [1].

Ti-MWW is not only more active than TS-1 and Ti-Beta in the liquid-phase epoxidation of small, linear alkenes with hydrogen peroxide, but is also highly selective for the formation of epoxides [2]. In addition, this material also exhibits a unique feature of selective epoxidation of the trans isomer in the oxidation of *cis*- and *trans*-2-hexenes [3, 4]. Actually, a potential advantage of the MWW structure is expected from its interlayer supercages and side pockets, which could be very useful for catalyzing the reactions involving bulky molecules (for this reactions now are also effectively used mesoporous titanium silicalite catalysts, for example Ti-MCM-41, Ti-MCM-48 or Ti-SBA-15). The retention of lamellar-like structure with expanded layer spacing after calcinations would be an alternative way to create the open reaction space in the disproportionation of toluene and in the alkylation of benzene [5]. Ti-MWW catalyzes the epoxidation of bis(allyl) ether (BAE) to allyl-glycidyl ether (AGE) and bis(glycidyl) ether (BGE) with aqueous hydrogen peroxide [6]. Ti-MWW is capable of catalyzing the liquid-phase ammoxidation of cyclohexanone to oxime at a conversion and selectivity >99% in the presence of water under the optimum conditions, and proves to be a promising catalyst for oxime synthesis [7].

The epoxides belong to a group of ethers; however, their properties are different from those of the typical ethers, due to the internal strain in the heterocyclic ring [8]. The major product of liquid-phase oxidation of allyl alcohol-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 [9]. The surface-active agents are also used as the food emulsifiers in the production of margarine, ice-cream, and vegetable butter [10, 11]. Other applications of glycidol include plasticizers, fabric dyes, photochemical compounds, rubbers, varnishes and plastics. One of the most important applications of glycidol is the synthesis of antiviral and analgesic drugs. The active compounds fighting HIV constitute especially component group of antiviral drugs. With the use of glycidol, the active compounds fighting HIV are obtained, which comprise the equivalents of natural compounds contained in fungus, as well as new derivatives of nucleotides fighting HIV and other viruses [11].

Experimental

Preparation of Ti-MWW catalyst and its characteristics

The Ti-MWW catalyst was prepared according to the method described by Wu et al. [12]. The detailed characteristic of the catalyst was presented in our previous work [13].

Epoxidation of allyl alcohol

In the process of allyl alcohol epoxidation, the following reactants were used: allyl alcohol (AA, 98 wt%, Fluka), the Ti-MWW titanium silicalite catalyst (prepared in the Institute of Organic Chemical Technology, West Pomeranian University of Technology, Szczecin), hydrogen peroxide (30 wt% water solution) and methanol (analytical grade both were from P.O.Ch. Gliwice, Poland).

The epoxidation was performed under atmospheric pressure in a glass reactor with a magnetic stirrer. The determined amounts of reactants were introduced into the reactor in the following sequence: the Ti-MWW catalyst, allyl alcohol, methanol (solvent) and a 30 wt% hydrogen peroxide was added at the reaction temperature. The process was carried out for a specified period 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/H₂O₂ 1:1–5:1, solvent concentration (methanol) of 5–90 wt%, catalyst content of 0–5.0 wt%, reaction time of 5–300 min and the intensity of stirring 0–500 rpm.

In order to calculate the mass balance for the syntheses performed, the post-reaction mixtures were analyzed in the following way: unreacted hydrogen peroxide was determined by means of the iodometric method, glycerol formed in the process was determined by means of potentiometric method. The remaining products and the unreacted organic substrate were analyzed by gas chromatography. The chromatographic analysis was performed on the FOCUS apparatus with a flame-ionization detector (FID) fitted with Quadrex capillary columns (30 m × 250 μm × 0.25 μm) 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 increased according to the following program: isothermally at 50 °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 the calculation of mass balance for each of the syntheses, the main functions describing the process were determined: the selectivity of the transformation to glycidol and by-products (glycerol, bis(allyl) ether, allyl-glycidyl ether, acrolein, 2-allyloxy-1,2-propanediol) in relation to the 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:

$$S_{AA}^{glc} = \frac{\text{amount of moles of glycidol (or by-product)}}{\text{amount of moles of allyl alcohol consumed}} \times 100 \text{ [mol\%]}$$

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

$$S_{H_2O_2}^{org} = \frac{\text{amount of moles of formed organic compounds}}{\text{amount of moles of H}_2\text{O}_2 \text{ consumed}} \times 100 \text{ [mol\%]}$$

Glycidol, which undergoes a partial hydration to glycerol under the reaction conditions, is the main product of the epoxidation of allyl alcohol. Depending on the conditions of epoxidation, a small amount of ethers (bis(allyl) and allyl-glycidyl)

Fig. 1 Major and by-products of the epoxidation of allyl alcohol with 30% hydrogen peroxide over the Ti-MWW titanium silicalite catalyst

are formed in the process. In higher temperature the polymerization occurs to a small extent (Fig. 1):

Results and discussion

The influence of temperature

The influence of the temperature in the range of 20–60 °C during the course of allyl alcohol epoxidation over Ti-MWW catalyst was studied (Fig. 2). The initial parameters of the epoxidation in the stage were as follows: the molar ratio $\text{AA}/\text{H}_2\text{O}_2 = 1:1$, methanol concentration (solvent) 40 wt%, Ti-MWW concentration 2 wt%, the reaction time 3 h and the intensity of stirring 500 rpm.

As the results show, an increase in the temperature from 20 to 60 °C does not have a significant impact on the selectivity of transformation to glycidol in relation to allyl alcohol consumed. The values of this function are at the level of about 20 mol%. The analysis of the composition indicates a slight increase in the part of glycerol, which is a consequence of hydrolysis of the epoxy ring in glycidol. The etherification products do not change, for example: allyl-glycidyl and bis(allyl) ether (Table 1).

At the time of the reaction, the first part of the hydrogen peroxide transforms into organic compounds and the second part of it decomposes ineffectively to oxygen and water. For safety reasons, hydrogen peroxide should be decomposed before the stage of product separation by fractional distillation. Owing to this, the possibility of violent decomposition of H_2O_2 and explosion is avoided. It is beneficial that the conversion of allyl alcohol should be the highest possible with simultaneously high selectivity of transformation to organic compounds in relation to hydrogen peroxide

Fig. 2 The influence of temperature on the allyl alcohol epoxidation over Ti-MWW catalyst; AA/H₂O₂ = 1:1 molar ratio, methanol concentration 40 wt%, Ti-MWW concentration 2 wt%, reaction time 3 h, intensity of stirring 500 rpm

Table 1 The influence of temperature on the selectivity of transformation to by-products in the epoxidation of allyl alcohol over Ti-MWW catalyst

Selectivity of transformation to by-products in the epoxidation of allyl alcohol $S_{\text{by-product/AA}}$ (mol%)					
Temperature (°C)	Glycerol (GLYC) $S_{\text{Glyc/AA}}$ (mol%)	Bis(allyl) ether (EBA) $S_{\text{EBA/AA}}$ (mol%)	Allyl-glycidyl ether (EAG) $S_{\text{EAG/AA}}$ (mol%)	Acrolein (ACR) $S_{\text{ACR/AA}}$ (mol%)	3-Allyloxy-1,2-propanediol (3A2PD) $S_{\text{3A12PD/AA}}$ (mol%)
20	62	6	5	0	5
30	65	4	5	0	5
40	67	4	5	0	5
50	68	4	5	0	4
60	67	4	5	1	4

consumed. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed changes insignificantly in the temperature range studied from 52 mol% at 20 °C to 58 mol% at 60 °C. It is the result of the lower rate of the amount of organic compounds.

The conversion of hydrogen peroxide presented in this study is the sum of effective conversion of hydrogen peroxide (to organic compounds) and ineffective conversion of hydrogen peroxide which is connected with decomposition of hydrogen peroxide. With the increase of the temperature from 20 to 60 °C, the increase of conversion of hydrogen peroxide is slow. It is possible that unreacted hydrogen peroxide is retained in the zeolite pores. This hydrogen peroxide is not determined by iodometric titration as unreacted hydrogen peroxide but is taken into consideration in the calculation of the total conversion of hydrogen peroxide, which remains very high. In the range of 20–40 °C, the allyl alcohol conversion slightly increases from 48 to 56 mol%. The latter observation shows that the allyl alcohol conversion is practically constants with the increase of temperature.

Hence, the optimum temperature of epoxidation is 20 °C at which the selectivity of the transformation to glycidol in relation to allyl alcohol consumed at this temperature and the H_2O_2 conversion are high. However, it should be noted that the conversion of allyl alcohol and the selectivity of transformation to organic compounds in relation to H_2O_2 consumed are lower.

The influence of molar ratio

The influence of the molar ratio of $\text{AA}/\text{H}_2\text{O}_2$ on the course of epoxidation was examined in the range from 1:1 to 5:1 and at the temperature of 20 °C, while the other starting parameters were unchanged. The results from this investigation are presented in Fig. 3 and Table 2.

On the basis of Fig. 3, it can be concluded that the increasing molar ratio of $\text{AA}/\text{H}_2\text{O}_2$ affects the selectivity to glycidol in relation to allyl alcohol. With the lower molar ratios (1:1) the value of this function amounts to about 22 mol%. As the molar ratio of $\text{AA}/\text{H}_2\text{O}_2$ increases within the range of 2:1–5:1 the selectivity to glycidol takes values at the level of 41 mol%.

As a result of appropriately high and increasing concentration of allyl alcohol in the reaction mixture, the access of water molecule to the glycidol molecule becomes more difficult and the hydrolysis of the epoxy ring proceeds more slowly. The hydrolysis has the main role in lowering the selectivity of transformation of allyl alcohol to glycidol because of high rate of reaction. However, conducting of the operation with such high excess of organic raw material ($\text{AA}/\text{H}_2\text{O}_2 = 5:1$) is not beneficial due to expenditure of energy associated with the subsequent recovery and recycling of unreacted of allyl alcohol to the process. The conversion of allyl alcohol decreases with the increase of the molar ratio of $\text{AA}/\text{H}_2\text{O}_2$ from 47 mol% (the molar ratio of $\text{AA}/\text{H}_2\text{O}_2 = 1:1$) to 13 mol% (the molar ratio of $\text{AA}/\text{H}_2\text{O}_2 = 5:1$). It confirms that the side reactions associated with the conversion of allyl alcohol, etherification type do not proceed more intensively. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed increases from about 52–76 mol%.

Fig. 3 The influence of the $\text{AA}/\text{H}_2\text{O}_2$ molar ratio on the allyl alcohol epoxidation over Ti-MWW catalyst; temperature 20 °C, methanol concentration 40 wt%, Ti-MWW concentration 2 wt%, reaction time 3 h, intensity of stirring 500 rpm

Table 2 The influence of the AA/H₂O₂ molar ratio on the selectivity of transformation to by-products in the epoxidation of allyl alcohol over Ti-MWW catalyst

Selectivity of transformation to by-products in the epoxidation of allyl alcohol $S_{\text{by-product/AA}}$ (mol%)					
Molar ratio AA/H ₂ O ₂	Glycerol (GLYC) $S_{\text{GLYC/AA}}$ (mol%)	Bis(allyl) ether (EBA) $S_{\text{EBA/AA}}$ (mol%)	Allyl-glycidyl ether (EAG) $S_{\text{EAG/AA}}$ (mol%)	Acrolein (ACR) $S_{\text{ACR/AA}}$ (mol%)	3-Allyloxy-1,2- propanediol (3A2PD) $S_{\text{3A12PD/AA}}$ (mol%)
1:1	62	5	5	0	6
2:1	62	5	6	0	6
3:1	51	6	7	0	8
4:1	41	7	8	0	10
5:1	31	8	9	0	11

Thus, the molar ratio of AA/H₂O₂ = 1:1 is the optimal in the process of epoxidation. At this molar ratio, the selectivity of transformation to glycidol in relation to allyl alcohol amounts to 22 mol%, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed equals 52 mol%, the conversion of allyl alcohol is 47 mol% and the conversion of hydrogen peroxide is 94 mol%. The experiments at the molar ratios of AA/H₂O₂ < 1 were not conducted, because according to the literature data [14], the excess of H₂O₂ in the post-reaction solution leached titanium from the structure of the catalyst, which changes the conditions of the process and decreases the selectivity of transformation. The second undesired phenomenon is an ineffective decomposition of H₂O₂.

The influence of solvent concentration

The effect of methanol concentration on the course of the epoxidation reaction was studied in the range of 5–90 wt%, at the temperature of 20 °C and at the molar ratio of AA/H₂O₂ = 1:1 (Fig. 4 and Table 3). Other starting parameters were unchanged.

Analyzing the influence of the solvent concentration—methanol on the selectivity of transformation 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—68 mol% for the methanol concentration of 90 wt%.

The largest increase of the conversion of allyl alcohol occurs in the range of the methanol concentration of 50–90 wt%. At the lowest methanol concentration (5 wt%) the conversion of allyl alcohol is equal to 65 mol% and at the highest methanol concentration (90 wt%) it achieves 85 mol%. The selectivity of transformation to organic compounds increases with the increase of the methanol concentration and rises to 77 mol% (80 wt% of solvent). With this solvent concentration, the selectivity of transformation to glycidol in relation to allyl alcohol consumed reaches to 42 mol%, the conversion of allyl alcohol reaches to 81 mol%, the conversion of hydrogen peroxide is 97 mol%.

The advantages of using high methanol concentration can be the result of the hydrophilic character of the catalyst. In accordance with the reaction mechanism, methanol plays a key role in the formation of the five-membered active adducts at

Fig. 4 The influence of solvent concentration (methanol) on the allyl alcohol epoxidation over Ti-MWW catalyst; temperature 20 °C, AA/H₂O₂ = 1:1 molar ratio, Ti-MWW concentration 2 wt%, reaction time 3 h, intensity of stirring 500 rpm

Table 3 The influence of solvent concentration on the selectivity of transformation to by-products in the epoxidation of allyl alcohol over Ti-MWW catalyst

Selectivity of transformation to by-products in the epoxidation of allyl alcohol $S_{\text{by-product/AA}}$ (mol%)					
Methanol concentration (wt%)	Glycerol (GLYC) $S_{\text{Glyc/AA}}$ (mol%)	Bis(allyl) ether (EBA) $S_{\text{EBA/AA}}$ (mol%)	Allyl-glycidyl ether (EAG) $S_{\text{EAG/AA}}$ (mol%)	Acrolein (ACR) $S_{\text{ACR/AA}}$ (mol%)	3-Allyloxy-1,2-propanediol (3A2PD) $S_{\text{3A12PD/AA}}$ (mol%)
5	81	2	2	1	3
10	78	3	3	0	4
20	75	3	3	0	4
30	70	4	4	0	5
40	62	5	5	0	6
60	54	6	6	0	7
80	28	9	10	0	11
90	23	5	4	0	0

the positions bound with titanium built into the structure of the catalyst. 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 [15] is correct.

The influence of catalyst concentration

The influence of catalyst concentration in the epoxidation of allyl alcohol over Ti-MWW catalyst was presented in our previous work [13]. The optimal catalyst concentration at this stage of the process is 2 wt%.

The influence of reaction time

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

The studies showed (Fig. 5) that time has a very significant effect on the way of changing values of the functions describing the process only in range of 5 min to 20 min. After 20 min or longer time of the reaction, they maintain a constant value or they undergo little changes. The selectivity of transformation to glycidol after 20 min reaches 47 mol% and practically does not undergo any changes to 300 min. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed reaches the highest value (98 mol%) after 180 min and does not undergo any changes during longer time of reaction. The conversion of H_2O_2 as a function of time exhibits similar changes. A slight increase of the conversion of allyl alcohol marks from 10 min to 180 min (from about 71 mol% to 82 mol%) and for longer reaction this function does not change. The main quantity of glycidol is formed after 180 min, but the maximum amount is received after 180 min. The selectivity of transformation to by-products, over a time period of 15–300 min are on a similar level, and the selectivities of by-products amount to: glycerol 20–29 mol%, bis(allyl) ether 8–10 mol%, allyl-glycidyl ether 8–11 mol%, 3-allyl-oxy-1,2-propanediol 8–10 mol% (Table 4).

Therefore 60 min time of reaction is the most beneficial to carry out the epoxydation of allyl alcohol over Ti-MWW catalyst taking into consideration the values of remaining parameters.

The influence of intensity of stirring

The influence of stirring speed was investigated in the range from 0 to 500 rpm and the course of functions of conversion and selectivity is presented in Fig. 6 and

Fig. 5 The influence of the reaction time on the allyl alcohol epoxidation over Ti-MWW catalyst; temperature 20 °C, AA/ H_2O_2 = 1:1 molar ratio, methanol concentration 80 wt%, Ti-MWW concentration 2 wt%, intensity of stirring 500 rpm

Table 4 The influence of reaction time on the selectivity of transformation to by-products in the epoxidation of allyl alcohol over Ti-MWW catalyst

Reaction time (min)	Glycerol (GLYC) $S_{\text{Glyc/AA}}$ (mol%)	Bis(allyl) ether (EBA) $S_{\text{EBA/AA}}$ (mol%)	Allyl-glycidyl ether (EAG) $S_{\text{EAG/AA}}$ (mol%)	Acrolein (ACR) $S_{\text{ACR/AA}}$ (mol%)	3-Allyloxy-1,2-propanediol (3A2PD) $S_{\text{3A12PD/AA}}$ (mol%)
5	0	0	0	0	0
10	26	9	10	0	12
15	21	10	11	0	11
30	21	10	11	0	12
60	21	10	11	0	12
120	24	10	11	0	12
180	27	9	10	0	11
240	27	9	10	0	11
300	27	9	10	0	11

Fig. 6 The influence of stirring intensity on the allyl alcohol epoxidation over Ti-MWW catalyst; temperature 20 °C, AA/H₂O₂ = 1:1 molar ratio, methanol concentration 90 wt%, Ti-MWW concentration 2 wt%, reaction time 60 min

Table 5. The constant parameters in this series studies were as follows: temperature 20 °C, AA/H₂O₂ = 1:1 molar ratio, methanol concentration 80 wt%, catalyst concentration 2 wt% and time 60 min.

The reaction does not proceed when the intensity of stirring is in the range 0–50 rpm. The value of function of the selectivity of transformation to glycidol increases to 54 mol% at a stirring intensity of 100–300 rpm. In the range of 350–500 rpm, a small decrease of value is observed. It results from more intense hydration of glycidol to glycerol in the consecutive reaction. The conversion of AA and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed exhibit similar tendencies changes. In the range 350–500 rpm, the conversion of AA is constant and achieves the maximum value 73 mol%. At this

Table 5 The influence of stirring intensity on the selectivity of transformation to by-products in the epoxidation of allyl alcohol over Ti-MWW catalyst

Intensity of stirring (RPM)	Glycerol (GLYC) $S_{\text{Glyc/AA}}$ (mol%)	Bis(allyl) ether (EBA) S_{EBAAA} (mol%)	Allyl-glycidyl ether (EAG) $S_{\text{EAG/AA}}$ (mol%)	Acrolein (ACR) $S_{\text{ACR/AA}}$ (mol%)	3-Allilox-1,2-propanediol (3A2PD) $S_{\text{3A12PD/AA}}$ (mol%)
100	8	12	12	0	14
200	8	12	12	0	14
300	10	11	12	0	14
350	19	10	11	0	12
400	21	10	11	0	11
450	21	10	11	0	11
500	21	10	11	0	11

stirring speed, the selectivity of transformation to organic compounds also achieves the maximum value equal to 80 mol%. The increase in stirring speed causes an increase of the selectivity of transformation to organic compounds in relation to H_2O_2 consumed, especially in the range 50–100 rpm. At constant conversion of H_2O_2 , this means the growth of the total amount of organic compounds. At the highest value of stirring speed the value of conversion of AA is 73% mol. The increase of stirring speed causes increase the conversion of AA and the selectivity of transformation to organic compounds. At constant conversion of H_2O_2 that means increase of overall amount of forming organic compounds.

Initially, during a low intensity of stirring (50–100 rpm) the reaction proceeds in a dynamic range. The slowest stage, which limits the rate of epoxidation, is the transport of H_2O_2 and the AA to active centre of catalyst. In the range of stirring intensity 100–300 rpm, only 16% of the obtained glycidol undergoes hydration to glycerol (selectivity of glycidol about 54 mol%, selectivity of glycerol about 8–10 mol%). In the range of stirring intensity 300–350 rpm, the selectivity of glycerol increases to 19–20 mol%, and the selectivity of glycidol decreases to 48 mol%–28%, glycidol undergoes hydration to glycerol. Simultaneously, the increase in values of conversion of AA and selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is observed. Above the stirring intensity of 350 rpm, the main functions describing the process do not change. The stirring speed, with steady remaining parameters unchanged, should be at least 350 rpm.

Conclusions

The process of allyl alcohol (AA) epoxidation over the titanium silicalite catalyst Ti-MWW, under atmospheric pressure has been found to be the most effective when is conducted at temperature of 20 °C, the molar ratio of $\text{AA}/\text{H}_2\text{O}_2 = 1:1$, methanol concentration of 80 wt%, the catalyst concentration of 2 wt%, in the time of 60 min

and with the stirring intensity over 500 rpm. Under these conditions, the selectivity of transformation to glycidol in relation to AA consumed is 47 mol%, the AA conversion reaches 73 mol% and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is 81 mol%. The studies also showed that the temperature and catalyst concentration [13] do not have a significant impact on the selectivity of transformation to glycidol. On the other hand, the rest of the technological parameters changed significantly values this main function of the process: the molar ratio of AA/H₂O₂ in the range of 1:1–5:1 (from 20 to 41 mol%), methanol concentration in the range of 5–90 wt% (from 10 to 60 mol%), the reaction time in the range of 5–20 min (from 0 to 47 mol%) and intensity of stirring in the range of 100–300 rpm (from 0 to 54 mol%).

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. Baerlocher Ch, Meier W, Olson D (2001) Atlas of zeolite framework types. 5th revised edition. Elsevier, Amsterdam
2. Fan W, Wu P, Namba S, Tatsumi T (2006) Synthesis and catalytic properties of a new titanasilicate molecular sieve with the structure analogous to MWW-type lamellar precursor. *J Catal* 243:183–191
3. Wu P, Tatsumi T, Komatsu T, Yashima T (2002) A novel Titanasilicate with MWW structure: II catalytic properties in the selective oxidation of alkenes. *J Catal* 202:245–255
4. Wu P, Tatsumi T (2002) Preparation of B-free Ti-MWW through reversible structural conversion. *Chem Commun* 1026–1027
5. Degnan T (2003) The implications of the fundamentals of shape selectivity for the development of catalysts for the petroleum and petrochemical industries. *J Catal* 216:32–46
6. Wu P, Liu Y, He M, Tatsumi T (2004) A novel Titanasilicate with MWW structure: catalytic properties in selective epoxidation of Diallyl ether with hydrogen peroxide. *J Catal* 228:183–191
7. Song F, Liu Y, Wu H, He M (2006) A novel Titanasilicate with MWW structure: highly effective liquid-phase ammoxidation of cyclohexanone. *J Catal* 237:359–367
8. Wróblewska A, Rzepkowska M, Milchert E (2005) Optimization of technological parameters of epoxidation of allyl alcohol by hydrogen peroxide over Ti-Beta catalyst. *Appl Catal A Gen* 294:244–255
9. Kłopotek A, Kłopotek B (1990) 2,3-Epoksypropanol-1-ol jako substrat środków powierzchniowo-czynnych. *Przem Chem* 69:248–251
10. Von Wolfgang M, Klemann A, Schreyer G (1975) Glycid—Herstellung and Eigenschaften. *Chemiker-Zeitung* 1:19–26
11. Wróblewska A, Milchert E (2003) Bezodpadowe epoksywanie alkoholu alilowego w obecności katalizatorów tytanowo-silikatowych. *Przem Chem* 82:1063–1065
12. Wu P, Tatsumi T, Komatsu T, Yashima T (2001) A novel titanasilicate with MWW structure. I. Hydrothermal synthesis, elimination of extraframework titanium, and characterizations. *J Phys Chem B* 105:2897–2905
13. Wróblewska A, Fajdek A, Milchert E, Grzmil B (2010) The Ti-MWW catalyst—its characteristic and catalytic properties in the epoxidation of allyl alcohol by hydrogen peroxide. *Pol J Chem Technol* 12:29–34
14. Davies L, McMorn P, Bethell D, Bulman P, King F, Hancock F, Hutchings G (2000) By-product formation causes leaching of Ti from the redox molecular sieve TS-1. *Chem Commun* 1807–1808
15. Adam W, Corma A, Reddy T, Renz M (1997) Diastereoselective catalytic epoxidation of chiral allylic alcohols by the TS-1 and Ti-Beta zeolites: evidence for hydrogen-bonded, peroxy-type loaded complex as oxidizing species. *J Org Chem* 62:3631–3637