

Epoxidation of allyl alcohol over mesoporous Ti-MCM-41 catalyst

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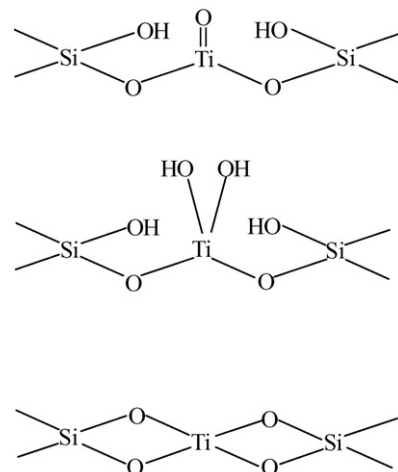
ABSTRACT

Epoxidation of allyl alcohol with 30 wt% hydrogen peroxide over Ti-MCM-41 catalyst under atmospheric pressure and in the presence of methanol as a solvent has been studied. The influence of the following parameters: temperature (20–60 °C), the molar ratio of AA/H₂O₂ (0.5–5), methanol concentration (5–90 wt%), catalyst concentration (0.1–5.0 wt%) and reaction time (5–180 min) has been investigated. The process has been described by the following functions: the selectivity of transformation to glycidol in relation to allyl alcohol consumed, conversions of the substrates and selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. The technological parameters, at which the functions describing the process take the optimum values, have been established.

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1. Introduction

One of the main challenges in contemporary chemical technology is development of new alternative technologies exerting lower pressure on the natural environment, i.e. cleaner, safer and environmentally friendly. New processes should be more efficient, use less energy, raw products and have a minimum effect on the natural environment. Much helpful in realization of these goals proved to be heterogeneous catalysts, e.g. molecular sieves of the redox type, e.g. zeolites, in which oxygen is bonded with metal in an inorganic matrix (TS-1 [1–3], TS-2 [4–6], Ti-Beta [7–9], Ti-MCM-41 [10,11] and Ti-MCM-48 [12]). The structure of titanium-silicalite catalysts is presented below [1–3]:



Development of such catalysts belongs to the area of nanotechnologies currently of great interest.

The titanium-silicalite catalysts such as TS-1, TS-2, Ti-Beta, Ti-MCM-41 and Ti-MCM-48 have been applied in the processes of hydroxylation of aromatic compounds, epoxidation of unsaturated compounds by hydrogen peroxide, oxidation of alkenes, alcohols and ketones [13]. They have been tested in the processes of epoxidation by hydrogen peroxide because they show high selectivity (including stereoselectivity) and permit performing the processes in mild temperatures and under atmospheric pressure. Moreover, very often the reactions lead to high conversion of hydrogen peroxide and the unsaturated compound [14]. Because of their beneficial

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properties they have been tested in new – satisfying the green chemistry demands – technologies of production of the known or new chemical compounds. The mesoporous sieves can act as a catalyst or a support. They have been successfully used in production of fine chemicals and pharmaceutical products, in petrochemical industry and in oxidation of organic compounds in the liquid phase [15,16].

The Ti-MCM-41 catalyst has a hexagonal structure with regularly arranged groups of mesopores. The mesopores are distributed in the form of long, unbranched and one-dimensional channels of the same diameters. The average MCM-41 pore diameter is 4.9 nm × 7.6 nm, the surface area of this catalyst is 1200 m²/g and the thickness of the pore walls varies in the range of 0.8–1.2 nm. Because of larger size of pores in Ti-MCM-41 relative to those in TS-1, TS-2, Ti-Beta, during the organic compound oxidation can have easier access to the active sites of titanium [17]. The MCM-41 catalyst has been used in the following processes: hydrodesulfurization, hydrocarbon cracking, polyethylene conversion, naphthalene and anthracene alkylation by alcohols, naphthalene hydrogenation, polymerisation of propene, styrene and aniline, dimerization of ethylene, decomposition of cumene into phenol and acetone [17]. Moreover, the Ti-MCM-41 catalyst has been used in the processes of oxidation and epoxidation of various organic compounds, e.g. oxidation of D-glucose, propylamine, propylene, epoxidation of crotyl alcohol, α-terpineol and terpinen-4-ol [17]. In these processes this catalyst shows high selectivity. From among the other catalysts of this type, TS-1, TS-2, Ti-Beta, the Ti-MCM-41 catalyst is distinguished by having channels of greater diameter, showing smaller diffusion effects of the reagents and products, and offering the possibility of oxidation of large volume molecules of organic compounds. The best catalytic performance of this catalyst was observed in the oxidation of branched and cyclic alcohols. An interesting catalyst was obtained by introducing Ti-MCM-41 into polydimethylsiloxane polymer. The spaces between the polymer and the catalyst particles formed an additional channels system.

2. Experimental

2.1. Raw materials used in the epoxidation of allyl alcohol

In the epoxidation of allyl alcohol (AA) the following materials were used: allyl alcohol (98 wt%, Fluka), titanium-silicalite catalyst Ti-MCM-41 (prepared at the Institute of Organic Chemical Technology, Szczecin University of Technology), hydrogen peroxide (30 wt% water solution, P.O.Ch. Gliwice, Poland), methanol (analytical grade, P.O.Ch. Gliwice, Poland).

2.2. Preparation of Ti-MCM-41 catalyst and its characteristics

Ti-MCM-41 catalyst was prepared by the method described by Schumacher et al. [18]. A glass reactor was charged with hexadecyltrimethylammonium bromide, deionised water, ammonia solution (33 wt%) and ethanol. The content of the reactor was vigorously stirred for 15 min and subsequently tetrabutyl o-titanate and tetraethyl o-silicate were dropped very slowly. The mixture was stirred for 2 h before being heated at 70 °C for 4 h. The solid product was washed with deionised water and methanol, and next dried at 60 °C for 5 h. The product was calcined in air at 550 °C for 5 h.

The catalyst was characterised by the techniques: XRD (the X-ray diffraction spectroscopy), XRF (the X-ray fluorescence spectroscopy), IR (the spectroscopy in infrared radiation), UV–vis (the spectroscopy in ultra-violet and blank space visible) and SEM (the scanning electron microscopy). The X-ray diffractions pattern of the obtained Ti-MCM-41 catalyst (Fig. 1) was the same as in literature [18,19].

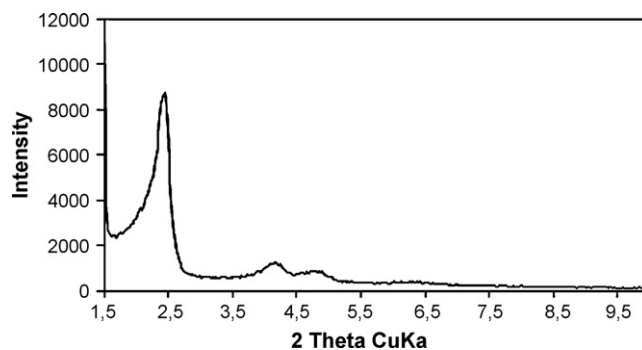


Fig. 1. XRD pattern of the obtained Ti-MCM-41 catalyst.

The SEM micrograph of the Ti-MCM-41 is typical of MCM-41 mesoporous metallosilicalites and is shown in Fig. 2.

The FT-IR spectra of Ti-MCM-41 catalyst revealed a band at around 960 cm⁻¹ and the UV–vis spectrum shows a band at 210 nm. The bands confirm that titanium is incorporated in silica structure (presence of titanium species with tetrahedral oxygen coordination).

2.3. Epoxidation procedure, apparatus and analytical methods

The process of allyl alcohol epoxidation was carried out under atmospheric pressure in a glass reactor equipped with a reflux condenser, thermometer, mechanical stirrer and a dropping funnel. The substrates, in proper amounts, were introduced into the reactor in the following sequence: titanium-silicalite catalyst Ti-MCM-41, allyl alcohol and methanol as a solvent. When temperature reached a target value 30 wt% water solution of hydrogen peroxide was dropped in. The process was performed for a certain time, then the reactor content was weighted and the product was subjected to analyses.

In order to make mass balances of the syntheses performed, the following analyses were made: unreacted hydrogen peroxide was iodometrically determined [19], glycerine formed in the process was potentiometrically determined [20], the other products and the unreacted allyl alcohol were determined by a gas chromatography. The chromatographic analyses were performed on a FOCUS GC instrument (Thermo, Poland) equipped with a flame-ionization detector (FID), using a capillary column Quadrex 30 m × 250 μm × 0.25 μm packed with methylsiloxane modified with phenyl groups. The parameters of chromatographic separation were as follows: helium pressure 50 kPa, sensitivity 10, sample chamber temperature 150 °C, detector temperature 250 °C. The thermostat temperature was programmed in the following way: isothermally 40 °C for 3 min, followed by an increase at the rate

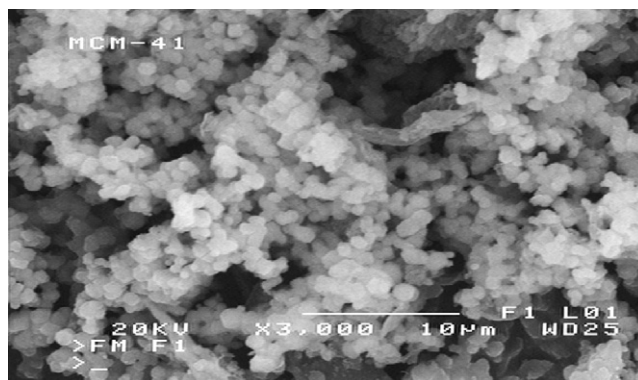


Fig. 2. SEM micrograph of Ti-MCM-41 catalyst obtained.

10 °C/min to 250 °C, isothermally 250 °C for 5 min, cooling to 60 °C. After the mass balance calculation for each synthesis, the main functions describing the process were determined, i.e. selectivity of transformation to glycidol in relation to allyl alcohol consumed, allyl alcohol conversion, selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. These functions were calculated according to the following formula.

Selectivity of transformation to glycidol in relation to allyl alcohol consumed ($S_{\text{glyc/AA}}$):

$$S_{\text{glyc/AA}} = \frac{\text{amount of glycidol obtained (mol)}}{\text{amount of allyl alcohol consumed (mol)}} \times 100\%$$

Conversion of allyl alcohol (C_{AA}):

$$C_{\text{AA}} = \frac{\text{amount of allyl alcohol consumed (mol)}}{\text{initial amount of allyl alcohol (mol)}} \times 100\%$$

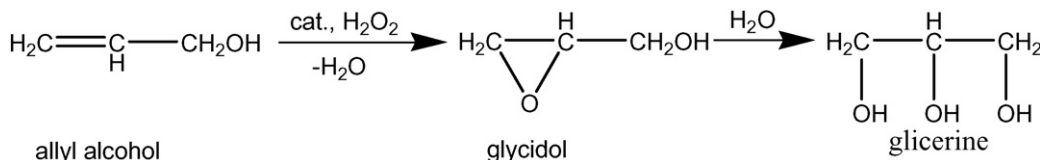
Selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed ($S_{\text{org/H}_2\text{O}_2}$):

$$S_{\text{org/H}_2\text{O}_2} = \frac{\text{amount of organic comp. obtained (mol)}}{\text{amount of H}_2\text{O}_2 \text{ consumed (mol)}} \times 100\%$$

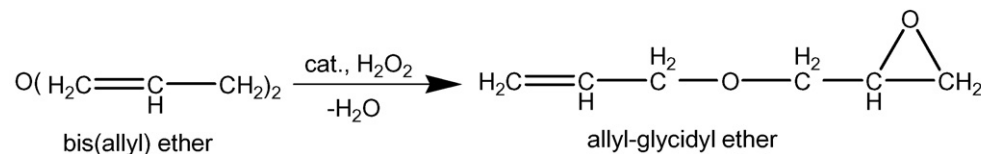
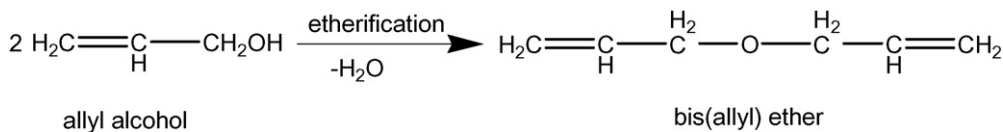
The conversion of hydrogen peroxide was calculated in a similar way as the conversion of allyl alcohol. Selectivity of transformations to by-products: glycerine, bis(allyl) ether and allyl-glycidyl ether were calculated in a similar way as the selectivity of transformation to glycidol.

3. Results and discussion

Epoxidation of allyl alcohol over titanium-silicalite catalyst by a 30 wt% water solution of hydrogen peroxide in methanol as a solvent leads to glycidol (2,3-epoxy-1-propanol) as the main product, which in the reaction conditions is partly hydrated to glycerine.



Depending on the conditions of epoxidation, also small amounts of ethers (bis(allyl) ether and allyl-glycidyl ether) are formed.



At higher temperatures some polymerisation processes also can take place.

The ranges of variation of the technological parameters studied were: temperature 20–60 °C, AA/H₂O₂ molar ratio 0.5–5, solvent concentration (methanol) 5–90 wt%, catalyst concentration 0.1–5.0 wt% and reaction time 5–180 min.

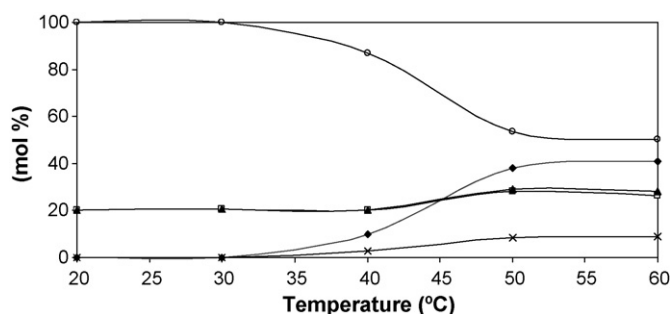


Fig. 3. The influence of temperature on the allyl alcohol epoxidation over Ti-MCM-41 catalyst: (♦) selectivity of transformation to glycidol in relation to allyl alcohol consumed, (□) conversion of allyl alcohol, (▲) selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, (○) selectivity of transformation to glycerine in relation to allyl alcohol consumed, (×) selectivity of transformation to bis(allyl) ether in relation to allyl alcohol consumed; AA/H₂O₂ = 1:1 molar ratio, methanol concentration 40 wt%, catalyst concentration 5 wt%, reaction time 3 h.

3.1. The influence of temperature

The initial conditions of the epoxidation process were as follows: the molar ratio of AA/H₂O₂ = 1:1, methanol concentration 40 wt%, catalyst concentration 5 wt% and the reaction time 3 h.

Fig. 3 presents the temperature dependencies of the selectivity of transformation to glycidol, glycerine and bis(allyl) ether in relation to allyl alcohol consumed, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed and conversion of allyl alcohol.

As follows from the results, the selectivity of transformation to glycidol in relation to allyl alcohol consumed increases with temperature increasing from 30 to 60 °C. The lack of glycidol and a low selectivity of transformation in the range of 20–30 °C, is a result of the lower rate of allyl alcohol epoxidation relative to that of glycidol hydration to glycerine. With temperature increasing to 50 °C, the epoxidation rate increases and greater amount of glycidol is found in the reaction products.

In the range of 40–50 °C, the allyl alcohol conversion slightly increases similarly as the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, whereas the selectivity of transformation to glycidol in relation to allyl alcohol consumed increases significantly. The latter observation means

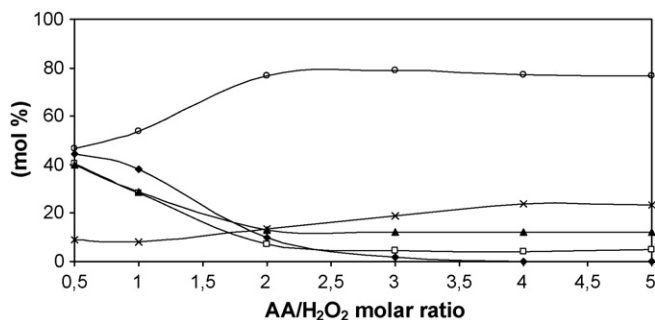


Fig. 4. The influence of the AA/H₂O₂ molar ratio on the allyl alcohol epoxidation over Ti-MCM-41 catalyst: (◆) selectivity of transformation to glycidol in relation to allyl alcohol consumed, (□) conversion of allyl alcohol, (▲) selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, (○) selectivity of transformation to glycerine in relation to allyl alcohol consumed, (×) selectivity of transformation to bis(allyl) ether in relation to allyl alcohol consumed; temperature 50 °C, methanol concentration 40 wt%, catalyst concentration 5 wt%, reaction time 3 h.

that the allyl alcohol epoxidation rate has significantly increased. At 50 °C, the selectivity of transformation to glycidol is 38 mol% and at 60 °C it increases to 40 mol%. The products of the reaction conducted in the range of 40–60 °C contain bis(allyl) ether. The bis(allyl) ether concentration at 60 °C reaches 9 mol%. These observations mean that the process of etherification of allyl alcohol has been intensified. In the same range of temperatures (20–60 °C), the efficiency of hydrogen peroxide used in the process of allyl alcohol epoxidation to glycidol is similar; however, the ineffective decomposition of hydrogen peroxide to oxygen and water takes place. The concentration of hydrogen peroxide in the reaction products is on average 0.7 wt%, at the hydrogen peroxide conversion of 97 mol%. For the safety reasons, hydrogen peroxide should be decomposed before the stage of products separation by fractional distillation. In the system studied, the most beneficial temperature of epoxidation is 50 °C; the main factor for this choice was the high selectivity of transformation to glycidol in relation to the allyl alcohol consumed.

3.2. The influence of the molar ratio of AA/H₂O₂

The influence of the molar ratio of AA/H₂O₂ on the course of epoxidation was studied at the temperature of 50 °C, in the range of its variation from 0.5 to 5, while the other parameters were unchanged. The results are shown in Fig. 4.

The analysis of the dependencies presented in Fig. 4 implies that the process should be performed at the molar ratios of AA/H₂O₂ < 2:1. The functions reach high values for the AA/H₂O₂ ratios of 0.5–1.0. In this range the selectivity of transformation to glycidol in relation to allyl alcohol consumed decreases from 44 mol% at AA/H₂O₂ = 0.5:1 to 39 mol% at AA/H₂O₂ = 1.0:1. The conversion of hydrogen peroxide and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed decrease a little more. At the molar ratios AA/H₂O₂ > 3, the selectivity of transformation to glycidol takes values below 1 mol%. With increasing excess of allyl alcohol, the selectivity of transformation to bis(allyl) ether increases and at AA/H₂O₂ = 5:1 it reaches 24 mol%. A significant decrease in the allyl alcohol conversion from 40 mol% at AA/H₂O₂ = 0.5 to 4 mol% at AA/H₂O₂ = 5 is mainly a consequence of an increasing excess of AA with respect to H₂O₂ and the method of the calculation. For the AA/H₂O₂ ratios higher than 2, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is constant and equals 12 mol%. At a constant conversion of hydrogen peroxide, this implies formation of the same total amount of organic compounds. The reaction product contains glycerine and bis(allyl) ether, besides glycidol and unreacted allyl alcohol. At the above technological param-

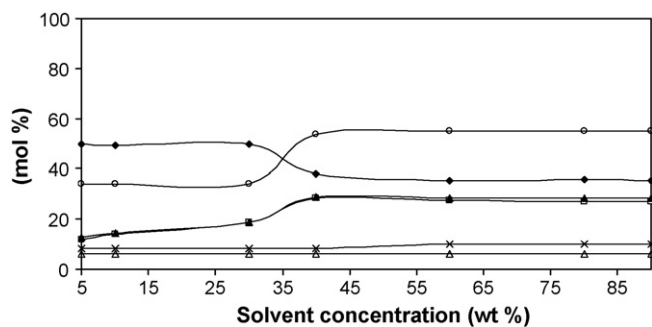


Fig. 5. The influence of solvent concentration (methanol) on the allyl alcohol epoxidation over Ti-MCM-41 catalyst: (◆) selectivity of transformation to glycidol in relation to allyl alcohol consumed, (□) conversion of allyl alcohol, (▲) selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, (○) selectivity of transformation to glycerine in relation to allyl alcohol consumed, (×) selectivity of transformation to bis(allyl) ether in relation to allyl alcohol consumed, (Δ) selectivity of transformation to allyl-glycidyl ether in relation to allyl alcohol consumed; temperature 50 °C, AA/H₂O₂ = 1:1 molar ratio, catalyst concentration 5 wt%, reaction time 3 h.

ters, the hydrogen peroxide conversion decreases from 99 mol% at AA/H₂O₂ = 0.5 to 86 mol% at AA/H₂O₂ = 5. At this stage of the investigation the equimolecular molar ratio of AA/H₂O₂ was considered as the most beneficial.

3.3. The influence of solvent concentration

The influence of the solvent concentration (methanol) on the allyl alcohol epoxidation was studied at 50 °C, at the molar ratio of AA/H₂O₂ = 1 and at the other parameters of the process unchanged.

According to the results presented in Fig. 5, the selectivity of allyl alcohol transformation to glycidol decreases in the methanol concentration range of 30–40 wt%, and for higher concentrations it remains unchanged. The dependence reaches the highest value of about 50 mol% for the methanol concentrations of 5–30 wt%. In this range of concentrations bis(allyl) ether is formed with the selectivity of about 10 mol% and allyl-glycidyl ether is formed with a selectivity of about 6 mol%. The conversion of allyl alcohol and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed change with increasing methanol concentration in a similar way. These functions reach the highest values for the methanol concentration from the range 30–40 wt%. At the lowest methanol concentration of 5 wt%, the conversion of allyl alcohol and the selectivity of transformation to organic com-

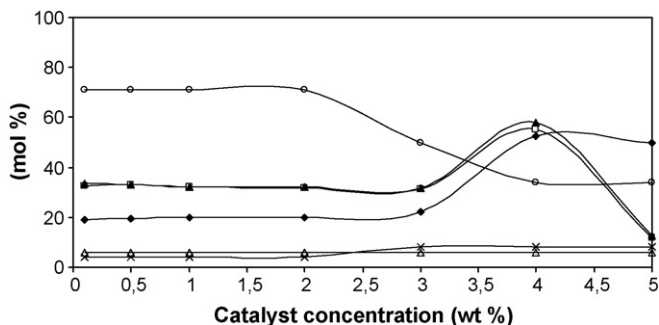
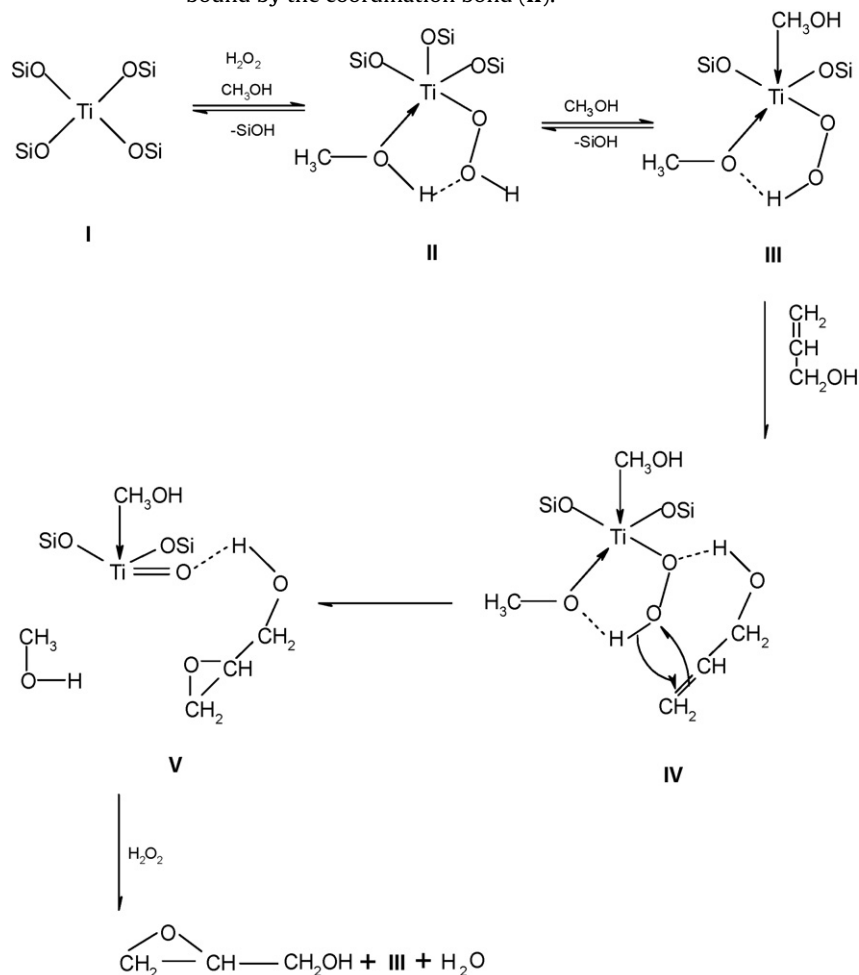


Fig. 6. The influence of catalyst concentration on the allyl alcohol epoxidation over Ti-MCM-41 catalyst: (◆) selectivity of transformation to glycidol in relation to allyl alcohol consumed, (□) conversion of allyl alcohol, (▲) selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, (○) selectivity of transformation to glycerine in relation to allyl alcohol consumed, (×) selectivity of transformation to bis(allyl) ether in relation to allyl alcohol consumed, (Δ) selectivity of transformation to allyl-glycidyl ether in relation to allyl alcohol consumed; temperature 50 °C, AA/H₂O₂ = 1:1, solvent concentration 5 wt%, reaction time 3 h.

pounds in relation to hydrogen peroxide consumed, is 14 mol%. A significant increase the allyl alcohol conversion and the selectivity of transformation to organic compounds for the methanol concentration range of 30–40 wt% is a consequence of the use of allyl alcohol for formation of bis(allyl) ether, which in a low degree is transformed into allyl-glycidol ether. Therefore, the most beneficial concentration of methanol is 5–30 wt%.

decrease in this selectivity. The increase in the selectivity of transformation to glycidol has been explained in terms of the mechanism of epoxidation proposed by Adam et al. [21,22]. According to this mechanism, the essential role in the process is played by the active centre related with the presence of titanium built in the silica structure and the polar solvent. At a certain concentration of methanol (the solvent) and the catalyst, the five-membered active complex (III) is formed, at this stage an additional methanol molecule is bound by the coordination bond (II).



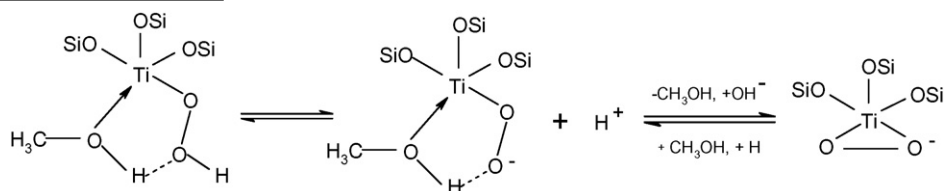
3.4. The influence of catalyst concentration

The influence of the Ti-MCM-41 catalyst concentration was tested in the range of its variation from 0.1 to 5 wt%, at 50°C , at the molar ratio of $\text{AA}/\text{H}_2\text{O}_2 = 1:1$, at methanol concentration of 5 wt%, and for the reaction time of 3 h.

In the range of low concentrations of the catalyst, 0.1–2 wt%, the selectivity of transformation to glycidol is constant and equals to 18 mol% (Fig. 6). With the catalyst concentration increased to 4 wt%, this selectivity increases to about 52 mol%. A further increase in the catalyst concentration, to above 4 wt%, is accompanied by a small

In the structure of (IV) the allyl alcohol molecule is connected by hydrogen bond with the active compound (III). This hydrogen bond is made by hydrogen atom from the allyl alcohol molecule and the oxygen atom closer to the Ti atom in the active compound (III). The hydrogen bond stabilises the system. After the reaction, the glycidol molecule is abstracted and the active compound (III) is regenerated. The process involves methanol – as a polar solvent – and hydrogen peroxide. The regeneration of the active compound (III) is the condition for the continuation of the reaction.

The active compound (II) exists only at low pH. On increasing pH the structure neutral in reaction with allyl alcohol is formed. This may be explained by the following equilibria:



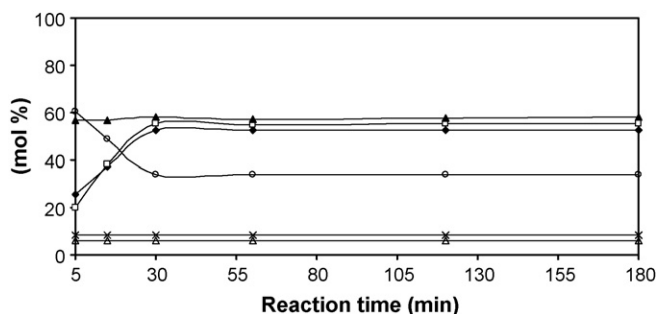


Fig. 7. The influence of the reaction time on the allyl alcohol epoxidation over Ti-MCM-41 catalyst: (◆) selectivity of transformation to glycidol in relation to allyl alcohol consumed, (□) conversion of allyl alcohol, (▲) selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, (○) selectivity of transformation to glycerine in relation to allyl alcohol consumed, (×) selectivity of transformation to bis(allyl) ether in relation to allyl alcohol consumed, (△) selectivity of transformation to allyl-glycidol ether in relation to allyl alcohol consumed; temperature 50 °C, AA/H₂O₂ = 1:1 molar ratio, methanol concentration 5 wt%, catalyst concentration 4 wt%.

In the reaction conditions glycidol relatively easily undergoes hydration to glycerine. The selectivity of transformation to glycerine decreases from 70 mol% at the catalyst concentration of 0.1–2 wt% to 34 mol% at the Ti-MCM-41 catalyst concentration of 4 wt% and above. Increased amount of the catalysts has no substantial effect on the rate of the process. In the whole range of the catalyst concentrations studied, allyl-glycidol ether is formed with a selectivity of about 6 mol%, while the selectivity of bis(allyl) ether formation varies from 4 mol% (0.1 wt%) to 9 mol% (5 wt%). The dependencies of the allyl alcohol conversion and selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed on the catalysts concentration have similar shapes and up to about 3 wt% of the catalyst their values are unchanged. For the catalyst concentrations higher than 3 wt% these dependencies increase reaching maxima of about 56 mol% at 4 wt% of the Ti-MCM-41 catalyst. In the Ti-MCM-41 concentration range of 4–5 wt%, the selectivity of transformation to organic compounds rapidly decreases, which is related to hydrogen peroxide decomposition to oxygen and water. For the catalyst concentration above 4 wt%, the conversion of allyl alcohol also decreases, which probably is also related to decomposition of hydrogen peroxide. In the catalyst and methanol (the solvent) concentration ranges studied, the conversion of hydrogen peroxide is constant and equal to 97 mol%. The above analysis has shown that the most beneficial concentration of the Ti-MCM-41 catalyst is 4 wt%. It is the lowest concentration of catalyst at which the highest selectivity of allyl alcohol transformation to glycidol is obtained.

3.5. The influence of the reaction time

The influence of the reaction time was investigated in the range of 5–180 min. The other parameters were as follows: the temperature of 50 °C, the molar ratio of AA/H₂O₂ = 1:1, the methanol concentration 5 wt%, the catalyst concentration 4 wt%.

In the time from 5 to 30 min the selectivity of transformation to glycidol in relation to allyl alcohol consumed increases to about 52 mol% and then its value remains at this constant level (Fig. 7). Allyl alcohol is consumed also in the processes of glycerine, bis(allyl) ether and allyl-glycidol ether formation. In the time period studied, bis(allyl) ether is formed with a selectivity of about 8 mol% in relation to allyl alcohol consumed, while allyl-glycidol ether is formed with a selectivity of 6 mol%. The amount of allyl alcohol transformed to glycerine is constant starting from 50 min after the reaction initiation. The selectivity of the transformation to glycerine is then 34 mol%. The selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is constant

throughout the time period studied. At the optimum parameters of the reaction the conversion of hydrogen peroxide is always greater than 97 mol%. The time 60 min has been taken as the most beneficial among the investigated reaction times.

4. Conclusions

As follows from the above-discussed results, the epoxidation of allyl alcohol to glycidol over mesoporous Ti-MCM-41 catalyst is effective at 50 °C, at the equimolecular AA/H₂O₂ molar ratio, at the methanol (the solvent) concentration of 5 wt%, at the catalyst concentration of 4 wt% and for the reaction time of 1 h.

In the most beneficial conditions established in this study the selectivity of transformation to glycidol in relation to allyl alcohol consumed is 52 mol%. The conversion of allyl alcohol and the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed are at the same level of 56 mol%, while the conversion of hydrogen peroxide reaches 97 mol%. The selectivity of transformation to glycidol is similar to that of glycerine and that of allyl-glycidol ether, the functions amount (1–3 mol%). At the most beneficial selected parameters bis(allyl) ether is not formed. The products contain small amounts of hydrogen peroxide, but its concentration does not exceed 1 wt%.

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