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Synthesis of allyl-glycidyl ether by the epoxidation of diallyl ether with t-butyl hydroperoxide over the Ti-MWW catalyst

Agnieszka Wróblewska[a*], Marika Walasek[a] and Beata Michalkiewicz[b]

[a]*West Pomeranian University of Technology, Szczecin, Institute of Organic Chemical Technology, Pulaskiego 10, 70-322 Szczecin, Poland*
[b]*West Pomeranian University of Technology, Szczecin, Institute of Inorganic Chemical Technology and Environment Engineering, Pulaskiego 10, 70-322 Szczecin, Poland*

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A B S T R A C T

In this paper, modified hydrothermal method for Ti-MWW catalyst preparation has been shown. Instrumental analysis of the zeolite material Ti-MWW has been performed by means of UV-vis spectrometry, infrared spectrometry (IR), scanning electron microscope (SEM), X-ray diffraction (XRD), and X-ray microanalysis. Moreover, the results of the epoxidation of diallyl ether (DAE) over the titanium silicate catalyst Ti-MWW and in the presence of methanol have been presented. t-Butyl hydroperoxide have been applied for the first time as an oxidant for this process. The influence of temperature (20-130°C), DAE/TBHP molar ratio (1:1-3:1), methanol concentration (10-80 wt%), amount of catalyst (1-7 wt%) and reaction time (60-1440 min.) was studied. The main functions describing the process were determined on the basis of the results obtained from the gas chromatography method.

1. Introduction

Allyl-glycidyl ether (allyl-2,3-epoxypropyl ether/AGE) is a valuable compound used as a modifier for elastomers, adhesives and fibers, and also as a reactive diluent for epoxy resins.[1] It is used in a production of poly(vinylcaprolactam), which is a polymer, that acts as a nonionic film-forming agent and fixative for hair care products like aerosol sprays, pump sprays and lotions (known under the trade mark Luviskol® Plus, supplied by BASF company).[2] Moreover, it is a component of novel coatings,[3] hydrogels,[4] detergents,[5] and many others.[6]

Allyl-glycidyl ether is primarily obtained in a process of allyl alcohol and epichlorohydrin condensation. Most of the processes described in literature requires multi-stage procedures. Moreover, the reaction occurs in homogeneous medium, using acidic catalysts such as boron trifluoride (BF_3), which is corrosive. The main disadvantage of this process is obtaining chlorine as one of the by-products. Referring to the latest reports, total chlorine amount can be reduced even up to 1 wt% in the

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* Corresponding author.
E-mail address: agnieszka.wroblewska@zut.edu.pl (A. Wróblewska)

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post-reaction mixtures. However, a necessity of removal chlorine and its utilization still can be a problem in producing of allyl-glycidyl ether on the global scale.[7-11]

A great alternative for condensation of allyl alcohol and epichlorohydrin can be epoxidation of diallyl ether (DAE). According to the literature data, in this process titanium silicate materials have been used as highly active catalysts, and as an oxidant - aqueous solution of hydrogen peroxide has been applied so far. Unfortunately, these methods are not completely elaborated. Another studies shown, that when the titanium silicate material is exposed to the water introduced into the reaction medium, this may lead to the change of coordination of titanium ions bounded in the silica structure, from Ti^{4+} to Ti^{6+}. That, in turn can contribute to a rapid deactivation of the catalyst.[12]

It can be stated, that the process of diallyl ether epoxidation is difficult, because of the low stability of the epoxide compounds in the reaction mixture and side reactions occur competitively. Additionally, use of hydrogen peroxide aqueous solution can contribute to the preparation of more by-products, than in the case of anhydrous oxidants. Possible reaction pathways in the epoxidation of diallyl ether are shown in the Fig. 1.

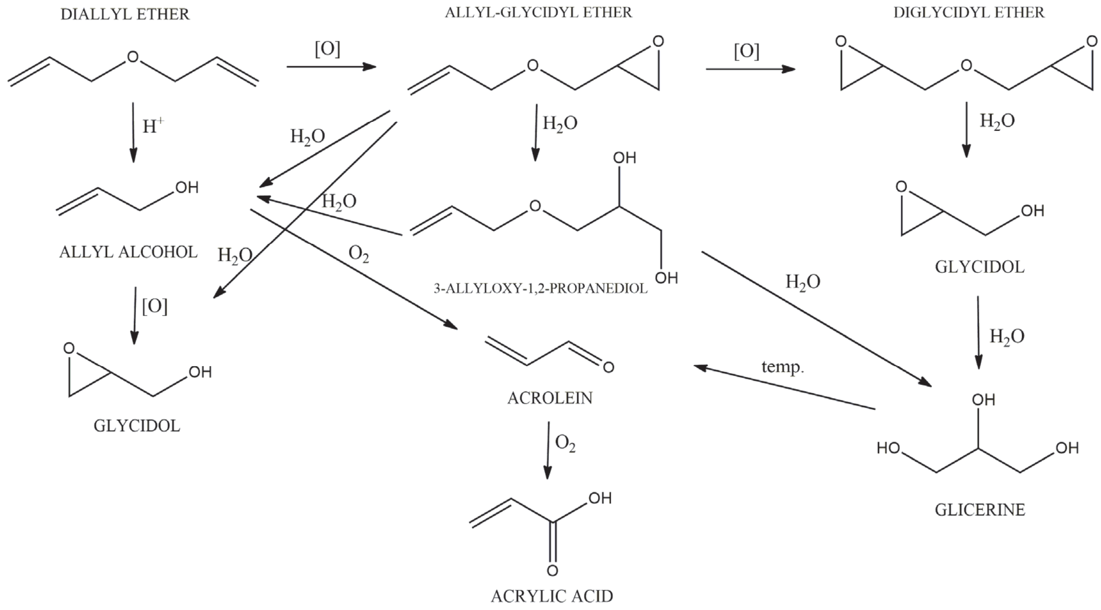

Fig.1. Possible reaction paths occurring during the epoxidation of DAE

Therefore, the values of the functions describing the process are not high enough to compete with existing methods of allyl-glycidyl ether preparation. Nowadays, the subject of investigation in this area of science is the selection of reactants and technological parameters for the DAE epoxidation, which could increase the selectivity of epoxy compounds with decreasing the products of DAE decomposition.[13-16]

The main aim of this work was to synthesize Ti-MWW catalyst using modified hydrothermal method. The activity of the catalyst was tested in the epoxidation of diallyl ether (DAE). Moreover, the results of studies on the influence of technological parameters on the epoxidation of diallyl ether is shown. In this process, anhydrous oxidant - t-butyl hydroperoxide has been applied for the first time. As a solvent – methanol has been chosen.

2. Results and Discussion

2.1. Characteristics of the Ti-MWW catalyst

The selection of instrumental methods to characterize the catalyst proved to be sufficient and very similar with previous literature reports.[18] UV-Vis spectroscopy results are shown in the Figure 2. UV-vis spectrum showed a characteristic absorption band at 260 nm wavelength, which is ascribed to octahedral bounded titanium.[14] Octahedral Ti is present in the Ti-O-Ti bound and it is a proof of the inclusion of titanium in the crystalline silica structure. The characteristic absorption band for anatase phase is present in the wavelength range 330 nm.[19]

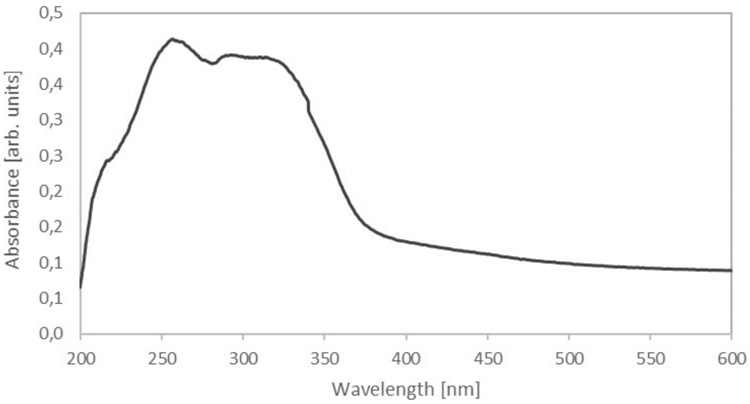

Fig. 2. UV-Vis spectra of the obtained Ti-MWW catalyst

Another instrumental method, that was used to confirm the incorporation of titanium in the structure of silica was IR spectroscopy. The absorption band characteristic for the tetrahedral titanium occurs at a wavenumber - 960 cm^{-1}.[17] The presence of this band was confirmed in the analysed samples of Ti-MWW material. Furthermore, the band of 3450 cm^{-1} wavenumber indicates the presence of hydroxyl group, whereas band at 930 cm^{-1} wavenumber is associated with the presence of boron in the silica structure.[17] The most intense band in the range 1100 cm^{-1} is caused by Si-O-Si vibrations,[20] and less intense in the range of 1400 cm^{-1} is attributed to the presence of Si-O-B group.[17] Bands in the range of 400-900 cm^{-1} are characteristic for both MFI and MWW structure.[21]

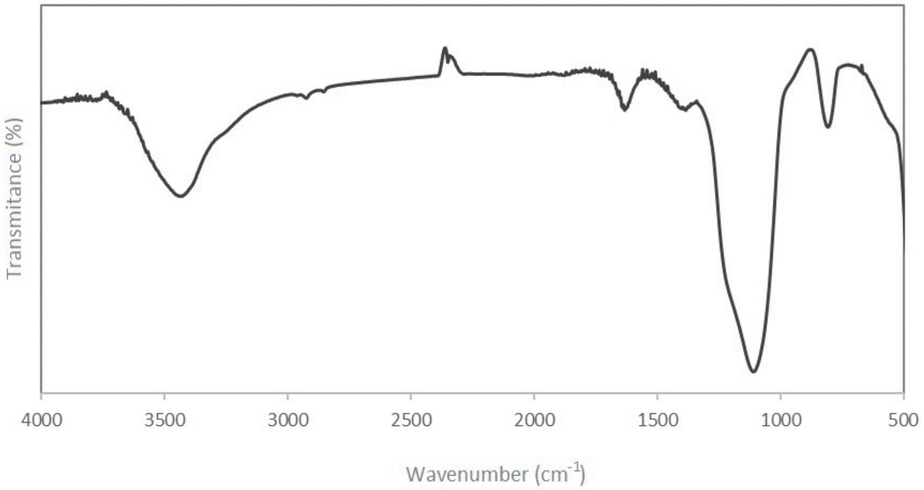

Fig. 3. IR spectra of the obtained Ti-MWW catalyst

X-ray diffraction was used in order to confirm a crystalline structure of the obtained catalyst. The patterns were consistent with the Ti-MWW XRD patterns presented in the literature.[17] Analysing the spectrum shown in Fig. 4. it can be said that the peaks at 2θ = 5-7° (P1 - P2) are characteristic of a lamellar structure along *c*-direction, while other peaks (P3-P7) are related with the crystalline sheets parallel to the *ab*-planes.[18]

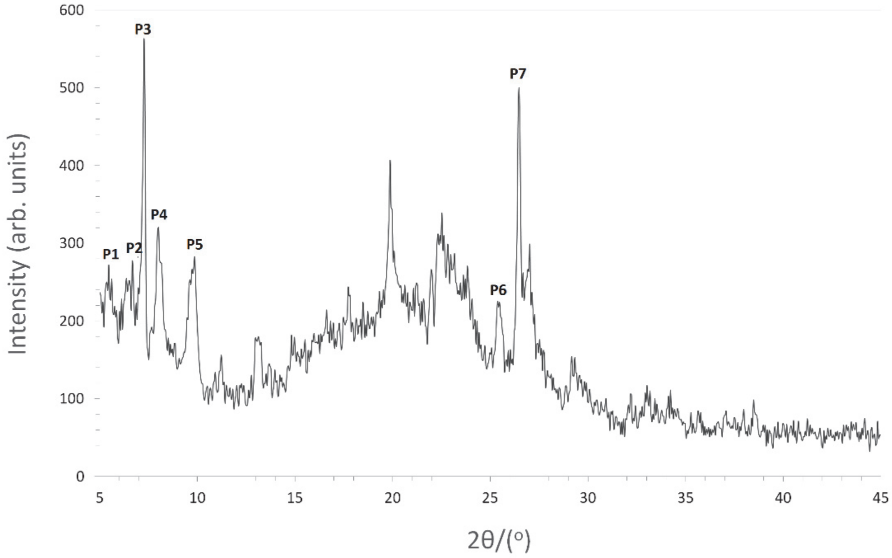

Fig. 4. XRD pattern of the Ti-MWW catalyst

Morphology of the catalyst crystals was determined on the basis on the SEM micrographs, that are shown in Fig. 5. It can be concluded from them, that crystals of the catalyst have irregular shape, size about 0.2 nm and form bigger aggregates.

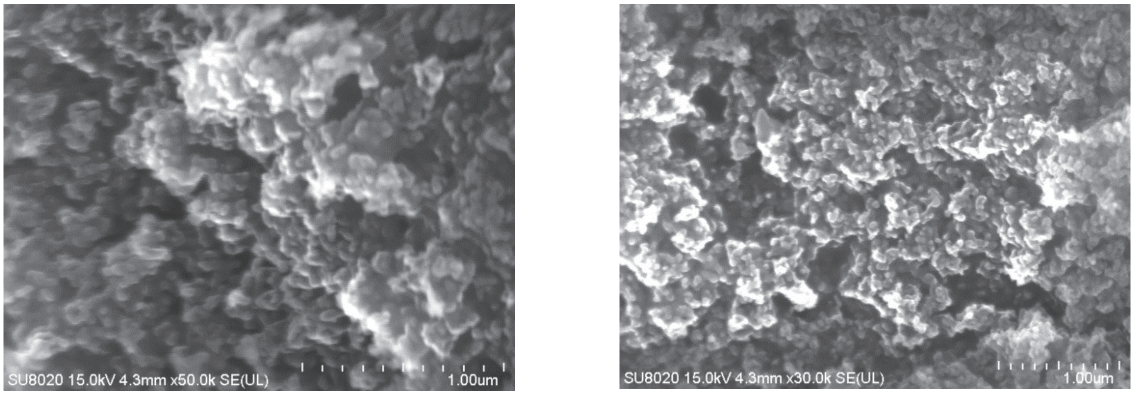

Fig. 5. SEM micrographs of the Ti-MWW catalyst

The investigations by X-ray microanalysis shown, that the content of Ti on the surface of the sample of Ti-MWW material was equal to 1.0(1)wt%.

2.2. Epoxidation of DAE

On the basis of the results of chromatographic analyses, we have established several compounds in the post-reaction mixtures, such as: allyl-glycidyl ether, diglycidyl ether, glycidol and allyl alcohol. The influence of following technological parameters was studied: temperature (20-130 °C), DAE/TBHP molar ratio (1:1-3:1), methanol concentration (10-80 wt%), Ti-MWW catalyst amount (1-7 wt%) and reaction time (60 – 1440 min.).

2.3. The influence of technological parameters on the course of DAE epoxidation

In order to investigate the temperature effect on the epoxidation of diallyl ether several syntheses were carried out. The temperature varied in the range of 20-130°C, while other technological parameters remained unchanged and amounted respectively: DAE/TBHP molar ratio = 1:1, methanol concentration 80 wt%, Ti-MWW content 3 wt% and reaction time 180 min. The obtained results are shown in Fig. 6. The conversion of DAE reached a maximum at 120°C, whereas other functions, such as selectivity and yield of allyl-glycidyl ether reached maximum value at 130°C. Unfortunately, we noticed the pressure increase in the reaction medium at 100°C, and constantly increasing up to 130°C, which can be dangerous. Because of the danger of explosion, it was decided that the temperature selected for the next stage of research will be 90°C. The synthesized Ti-MWW catalyst was the most active at a temperature above 20°C. In the obtained mixtures we have determined three products of this process, such as allyl-glycidyl ether, glycidol and allyl alcohol.

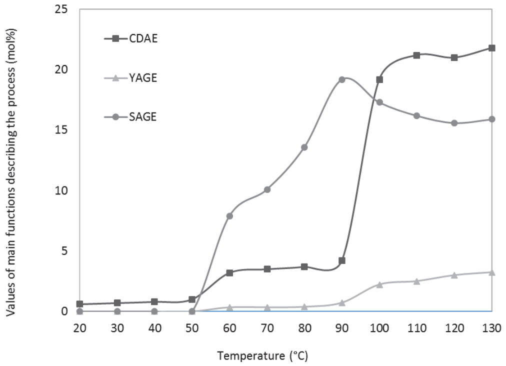

Fig. 6. Values of main functions describing the process for different temperatures (CDAE – diallyl ether conversion, YAGE – allyl-glycidyl ether yield, SAGE – allyl-glycidyl ether selectivity)

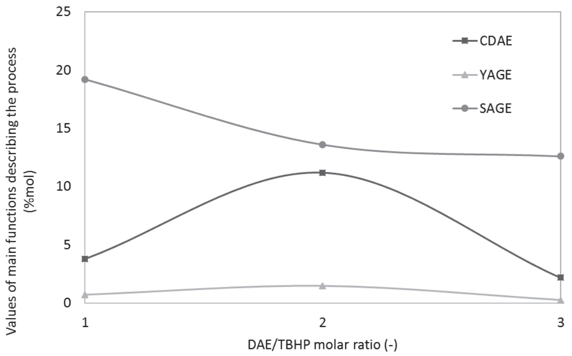

Fig. 7. Values of main functions describing the process for different DAE/TBHP molar ratios (CDAE – diallyl ether conversion, YAGE – allyl-glycidyl ether yield, SAGE – allyl-glycidyl ether selectivity)

The research on the DAE/TBHP molar ratio effect showed, that the most preferred ratio is 2:1. This decision has been taken based mainly on the highest values of the product yield and diallyl ether conversion (Fig. 7). A series of reaction mixtures have been prepared and the influence of methanol concentration has been examined (Fig. 8.). It has been shown, that the most beneficial concentration of solvent is 70 wt% - all of the studied functions reached the highest values at this concentration.

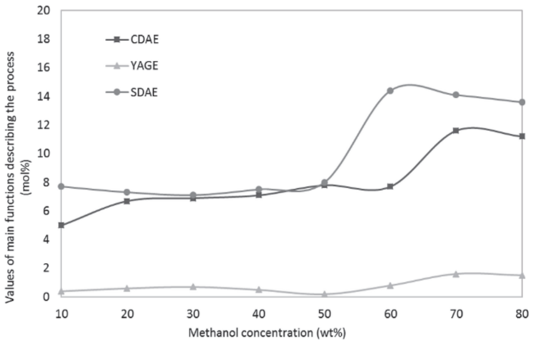

Fig. 8. Values of main functions describing the process for different solvent concentrations (CDAE – diallyl ether conversion, YAGE – allyl-glycidyl ether yield, SAGE – allyl-glycidyl ether selectivity)

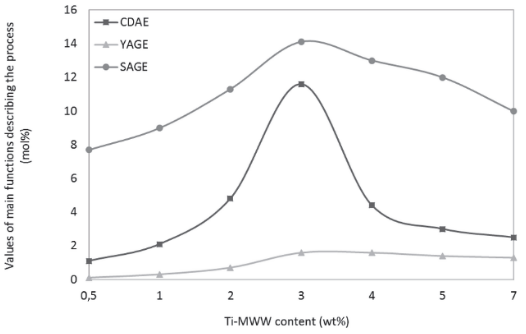

Fig. 9. Values of main functions describing the process for different catalyst amounts (CDAE – diallyl ether conversion, YAGE – allyl-glycidyl ether yield, SAGE – allyl-glycidyl ether selectivity)

In further studies it has been shown, that the content of the Ti-MWW catalyst has the strongest influence on the process in an amount of 3 wt%. The values of the main functions increase with the amount of catalyst, but only up to the amount of 3 wt%. The larger Ti-MWW content is not beneficial for the epoxidation process (Fig. 9.).

The last stage of the establishing the most beneficial technological parameters for DAE epoxidation was selection of the most preferred time. The result of the research is the choice 180 minutes as the most beneficial time for this process (Fig. 10.). The main decisive functions in the selection of this parameter were AGE yield and DAE conversion.

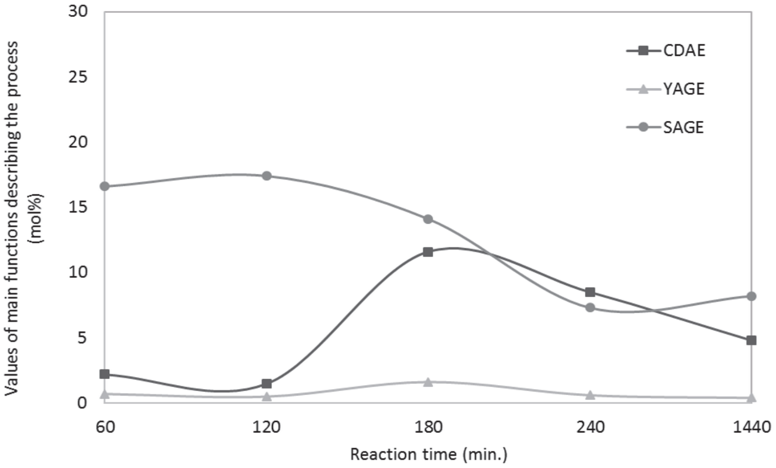

Fig. 10. Values of main functions describing the process for different reaction times (CDAE – diallyl ether conversion, YAGE – allyl-glycidyl ether yield, SAGE – allyl-glycidyl ether selectivity)

3. Conclusions

We have successfully synthesized using the modified hydrothermal method titanium containing zeolite material, described in the literature as the Ti-MWW material. The obtained material was highly active catalyst in the process of diallyl ether epoxidation.

Moreover, we have conducted the studies on the influence of technological parameters on the epoxidation of DAE using t-butyl hydroperoxide as the oxidant. The novelty was the use of this oxidant in describing process. In this way we managed to decrease the quantity of side products, formed in the presence of water, when hydrogen peroxide was used as an oxidant. As a result, we have determined only three products: allyl-glycidyl ether, allyl alcohol and glycidol.

As the most favourable parameters, the following have been chosen: temperature 90 °C, DAE/TBHP molar ratio = 2:1, methanol concentration 70 wt%, Ti-MWW catalyst amount 3 wt%, and the reaction time - 180 minutes. In these conditions, main functions describing the process reached the follow values: CDAE – 12 mol%, YAGE – 2 mol%, SAGE – 14 mol%.

4. Experimental

4.1. Preparation of the Ti-MWW catalyst

The Ti-MWW material was synthesized by the modified method of Wu et al.[17] For the synthesis of Ti-MWW catalyst the following raw materials were applied: tetrabutyl o-titanate (TBOT, $Ti(OBu)_4$, 95%, Fluka) as a source of titanium, hexamethyleneimine (HMI, >98%, Merck) as a template, boric acid (H_3BO_3, 99.5%, Chempur), and fumed silica (Cab-o-sil M5, Biesterfeld) as a silica source.

Synthesis of this material consisted of several steps. The first one was to prepare two solutions with deionized water and hexamethyleneimine. To the first solution, tetrabutyl o-titanate was added dropwise, and to the second – boric acid. Fumed silica was added as a last ingredient of both of the mixtures and agitated at room temperature until the gel was substantially homogeneous. The next step was crystallization of the resulting gel in the autoclave with PTFE insert (500 cm^3). The crystallization was performed for 14-16 days at the temperature of 175 °C, and with intensity of stirring: 300 rpm. The obtained material was filtered off, washed with 1000 cm^3 deionized water and then dried at 55 °C for 4 days. In order to remove boron atoms from silica structure the material was treated by 2 M nitric acid at higher temperature (90-100°C) for two days. Resultant material was then dried again at 55 °C for 4 days and calcinated at 550 °C for 16 hours.

Confirmation of the inclusion of titanium in the structure of the silica was made possible by UV–visible spectroscopy on a SPECORD M40 type V-530 and the IR investigation, which was made on Shimadzu FTIR-8100 spectrometer using the KBr pellet technique. The crystalline structure was confirmed with XRD diffraction using X'Pert PRO Philips diffractometer (CuKα radiation). Scanning electron micrographs were made on JOEL JSM-6100 instrument and helped defining the shape and size of crystals. The investigations by X-ray microanalysis was made by the Energy Dispersive Spectroscopy system (EDS) connected with Ultra-High Resolution Field Emission Scanning Electron Microscope UHR FE-SEM Hitachi SU8020.

4.2. Studies on the epoxidation of DAE

In a studies on epoxidation of diallyl ether, the following raw material were used: diallyl ether (98%, Sigma-Aldrich), methanol (analytical grade, Chempur), and t-butyl hydroperoxide solution (~5.5M in decane, Sigma-Aldrich).

The epoxidation of diallyl ether (DAE) with t-butyl hydroperoxide (TBHP) was carried out under vigorous stirring (300 rpm) in a 100-mL Berghof autoclave. In a regular run, the raw materials were introduced to the autoclave in following order: Ti-MWW catalyst, diallyl ether, methanol and t-butyl hydroperoxide. After the reaction, the catalyst was separated from the mixture using a centrifuge. The resultant mixture was then analyzed on a gas chromatograph (Focus GC, Thermo) using a Quadrex 007-5 capillary column filled with methyl-phenyl-siloxanes (30 m x 250 μm x 0,25 μm) and a FID detector. All of the products were verified using chemicals commercially available and using the external standard method on GC.

The influence of following technological parameters was studied: temperature, DAE/TBHP molar ratio, methanol concentration, catalyst amount and reaction time. Mass balances were calculated on the basis of the results of chromatographic analyses and the selection of the most beneficial parameter was based on three main functions describing the process, such as conversion of diallyl ether (CDAE), selectivity of allyl-glycidyl ether (SAGE) and allyl-glycidyl ether yield (YAGE).

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