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APPLICATION OF Ti-MCM-48 CATALYST IN 1-BUTENE- -3-OL EPOXIDATION

ZASTOSOWANIE KATALIZATORA Ti-MCM-48 W EPOKSYDACJI 1-BUTEN-3-OLU

Abstract

The influence of technological parameters on 1-butene-3-ol (1B3O) epoxidation over Ti-MCM-48 catalyst has been presented. A 30 wt% H₂O₂ was used as an oxidizing agent in the presence of solvent (methanol). The epoxidation was carried out at autogenic pressure. The major product of epoxidation was 1,2-epoxybutane-3-ol (1,2EB3), an epoxide compound with a lot of applications.

Keywords: Ti-MCM-48 catalyst, zeolites, liquid-phase epoxidation: 1,2-epoxybutane-3-ol

Streszczenie

W artykule przedstawiono wpływ parametrów technologicznych na epoksydację 1-buten-3-olu (1B3O) na katalizatorze Ti-MCM-48. Jako utleniacz zastosowano 30% nadtlenek wodoru w obecności metanolu jako rozpuszczalnika. Epoksydację prowadzono pod ciśnieniem autogenicznym. Głównym produktem epoksydacji był 1,2-epoksybutan-3-ol (1,2EB3), związek epoksydowy o licznych zastosowaniach.

Słowa kluczowe: katalizator Ti-MCM-48, zeolity, epoksydacja w fazie ciekłej, 1,2-epoksybutan-3-ol

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1. Introduction

A new family of mesoporous molecular sieves was invented by Mobil R&D Corporation at the beginning of the 1990s [1]. The most widely researched members of the M41S family are MCM-41 and MCM-48 materials. MCM-41 consists of a hexagonal array and has a unidirectional pore structure. MCM-48 consists of a cubic array with a three-dimensional pore network [2]. Mesoporous materials are used in processes of synthesis of fine chemicals. Zeolites with Ti catalyze selective oxidation of alkenes, aromatics and epoxidation olefins [3].

In the work the results of 1B3O epoxidation under autogenic pressure were presented. The process was described by the following functions: selectivity of transformation to 1,2-epoxybutane-3-ol (1,2EB3) in relation to 1B3O consumed, selectivity of transformation to organic compounds in relation to H_2O_2 consumed and conversion of 1B3O and hydrogen peroxide.

The objective of these studies was to determine the optimal conditions of preparation of 1,2EB3 with high selectivity in relation to 1B3O consumed, at high conversion of 1B3O and H_2O_2 and high selectivity of transformation to organic compounds in relation to H_2O_2 consumed.

2. Experimental

2.1. Raw materials

In the epoxidation process the following raw materials were used: 1-butene-3-ol (1B3O) (pure 98%, Fluka), hydrogen peroxide (30 wt.%, POCh, Gliwice), methanol (analytical grade, POCh, Gliwice) and Ti-MCM-48 catalyst prepared at the Institute of Organic Chemical Technology (Szczecin University of Technology, Poland).

2.2. Synthesis of Ti-MCM-48 catalyst

Ti-MCM-48 catalyst was prepared by a method described by K. Schumacher et al. [4]. The catalyst was characterized using the following methods of instrumental analyses: XRD (X-ray diffraction spectroscopy), XRF (X-ray fluorescence spectroscopy), IR (infrared spectroscopy), UV-VIS (ultraviolet visible spectroscopy) and SEM (scanning electron microscopy).

The crystalline structure of Ti-MCM-48 catalyst was confirmed by XRD method using an XPERT PRO diffractometer with a copper lamp as the source of irradiation at 0.179 nm (Fig. 1).

By XRF measurement the content of titanium in this catalyst expressed in TiO_2 was 0.41 wt.%. The IR spectrum of the catalyst showed an intense absorption band at 960 cm^{-1} . The UV-VIS spectrum showed a band at 220 nm and no band at 300 nm, which means that Ti^{4+} ions had been incorporated into the crystalline structure of silica and no TiO_2 in the form of anatase was detected.

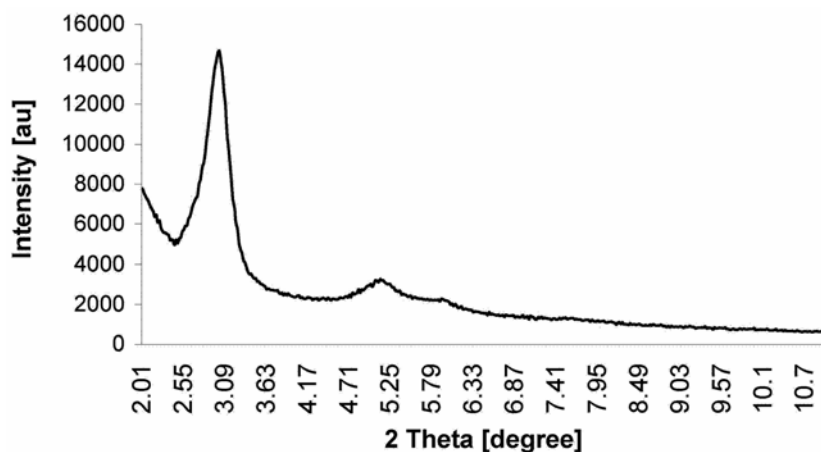


Fig. 1. XRD pattern of Ti-MCM-48 catalyst obtained

Rys. 1. Widmo XRD otrzymanego katalizatora Ti-MCM-48

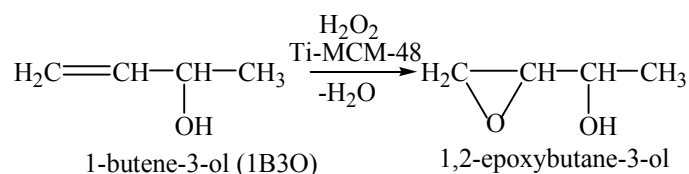
2.3. Epoxidation procedure

1B3O epoxidation was carried out under autogenic pressure. A stainless steel autoclave equipped with a PTFE insert of 7 cm³ capacity was used in this method. The autoclave was charged with reagents in the following order: the catalyst, 1B3O, methanol and hydrogen peroxide. The autoclave was located in a shaker holder and immersed in the oil bath. The bath temperature was controlled by a thermostat. The influence of the following technological parameters: temperature 20–120°C, molar ratio of 1B3O/H₂O₂ 1:1–5:1, methanol concentration 5–90 wt.%, Ti-MCM-48 concentration 0.1–5.0 wt.% and reaction time 0.5–5.0 h were investigated. The initial parameters of epoxidation were as follows: molar ratio of 1B3O/H₂O₂ = 1:1, methanol concentration (solvent) 40 wt.%, Ti-MCM-48 concentration 3 wt.% and reaction time 3 h.

The products were analyzed quantitatively using a gas chromatograph. The concentration of unreacted hydrogen peroxide was determined iodometrically [2]. After performing the mass balance for each of the syntheses, the main functions characterizing the process such as selectivity of transformation to 1,2EB3 in relation to 1B3O consumed, conversion of 1B3O and hydrogen peroxide, and selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed were determined.

3. Results and discussion

1B3O epoxidation over Ti-MCM-48 catalyst with 30 wt.% hydrogen peroxide in the presence of methanol as a solvent leads to formation of 1,2EB3 as a major product.



Depending on the epoxidation conditions other compounds were also formed in this process such as: 1,2,3-butanetriol, 1,2,3-methoxybutanetriol and ethers such as: bis(3-methyl-1-propene), 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane, bis(3-methyl-1,2-epoxypropane), 4-(1-methyl-2-propene)-butane-2,3-diol, bis(2,3-dihydroxybutane) and 3-(2,3-dihydroxybutane)-3-methyl-1,2-epoxypropane.

3.1. The influence of temperature

The influence of temperature on 1B3O epoxidation was studied in the range of 20–120°C. The following initial parameters were assumed: molar ratio of 1B3O/H₂O₂ = 1:1, solvent concentration (methanol) 40 wt.%, Ti-MCM-48 catalyst concentration 3 wt.% and reaction time 3 h. The syntheses were carried out under autogenic pressure.

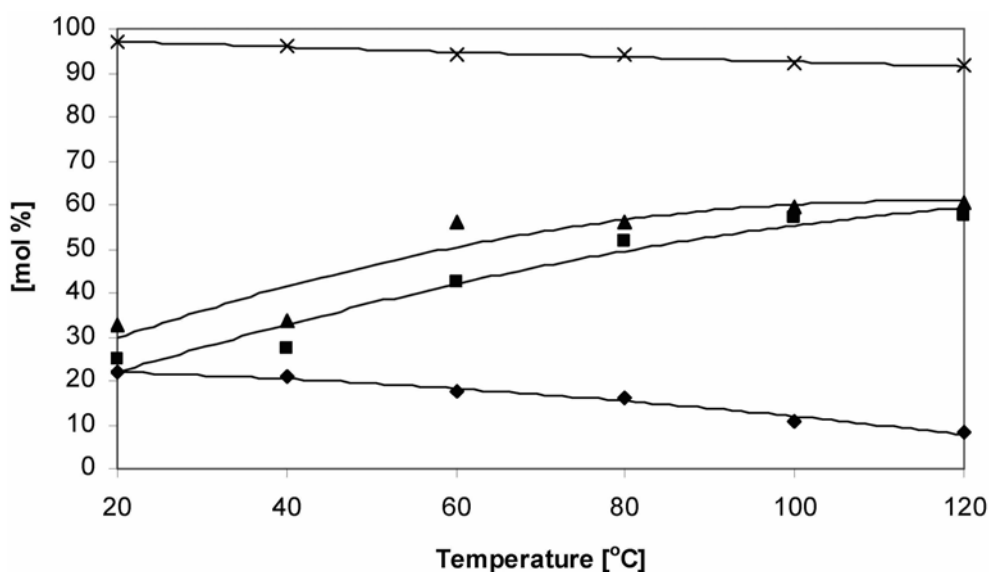


Fig. 2. Effect of temperature on 1B3O epoxidation under autogenic pressure: selectivity of transformation to 1,2EB3 in relation to 1B3O consumed (◆), selectivity of transformation to organic compounds in relation to H₂O₂ consumed (■), 1B3O conversion (▲), H₂O₂ conversion (x)

Rys. 2. Wpływ temperatury na epoksydację 1B3O pod ciśnieniem autogenicznym: selektywność przemiany do 1,2EB3 w odniesieniu do przereagowanego 1B3O (◆), selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H₂O₂ (■), konwersja 1B3O (▲), konwersja H₂O₂ (x)

It results from Fig. 2 that the selectivity of transformation to 1,2EB3 in relation to 1B3O consumed significantly decreases from 21.7 mol % to 8.1 mol % along with elevation of the process temperature from 20°C to 120°C. This results from the fact that at temperatures (20–60°C) the ethers such as: bis(3-methyl-1-propene) are formed more readily. Moreover, hydrolysis and methanolysis of the epoxy group in 1,2EB3 also proceeds, whereas at the highest temperatures (100–120°C) the following ethers: 4-(1-methyl-2-propene)-butane-2,3-diol are formed. The selectivity of transformation to organic compounds in relation to H₂O₂ consumed and 1B3O conversion have almost an identical course and they increase along with elevation of the process temperature. Selectivity increases from 24.8 to 57.7 mol %, whereas conversion from 32.6 to 60.6 mol %. H₂O₂ conversion in the studied range of temperatures is practically constant and amounts to about 95 mol %. 20°C was taken as the optimum temperature, taking into account, primarily, high selectivity of transformation to 1,2EB3 in relation to 1B3O consumed. However, 1B3O conversion and selectivity of transformation to organic compounds in relation to H₂O₂ consumed were lower at this temperature.

3.2. The influence of molar ratio 1B3O/H₂O₂

The influence of 1B3O/H₂O₂ molar ratio was studied in the range of 1:1–5:1 at temperature 20°C. The other initial parameters remained unchanged.

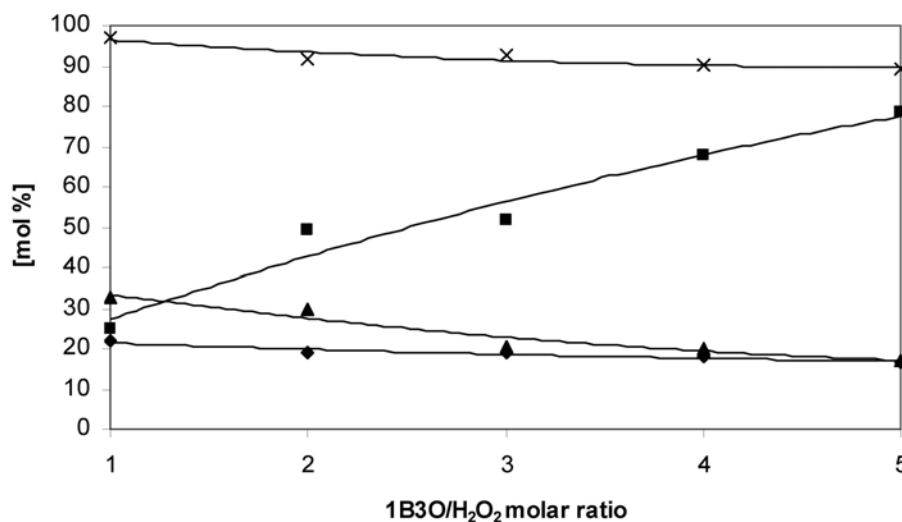


Fig. 3. Influence of 1B3O/H₂O₂ molar ratio on 1B3O epoxidation under autogenic pressure: selectivity of transformation to 1,2EB3 in relation to 1B3O consumed (◆), selectivity of transformation to organic compounds in relation to H₂O₂ consumed (■), 1B3O conversion (▲) and H₂O₂ conversion (x)

Rys. 3. Wpływ stosunku molowego 1B3O/H₂O₂ na epoksydację 1B3O pod ciśnieniem autogenicznym: selektywność przemiany do 1,2EB3 w odniesieniu do przereagowanego 1B3O (◆), selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H₂O₂ (■), konwersja 1B3O (▲), konwersja H₂O₂ (x)

Selectivity of transformation to 1,2EB3 in relation to 1B3O consumed is practically constant and amounts to about 21.7–16.6 mol % (Fig. 3). Selectivity of transformation to organic compounds in relation to H_2O_2 consumed increases along with the increase of the reagents molar ratio from 13.2 mol % at molar ratio of 1:1 to 78.4 mol % when the molar ratio is 5:1. 1B3O conversion decreases from 32.6 mol % at the ratio of $1\text{B3O}/\text{H}_2\text{O}_2 = 1:1$ to 17.2 mol % for the ratio of $1\text{B3O}/\text{H}_2\text{O}_2 = 5:1$. H_2O_2 conversion is decreases from 95.7 mol % to 89.5 mol %. Hence, in the process, the molar ratio of $1\text{B3O}/\text{H}_2\text{O}_2 = 1:1$ is the most advantageous with regard to high selectivity of 1,2EB3 and high conversion of both 1B3O and H_2O_2 .

3.3. The influence of solvent concentration

The influence of solvent (methanol) concentration was studied in the concentration range of 5–90 wt.%, at temperature 20°C and at molar ratio of $1\text{B3O}/\text{H}_2\text{O}_2 = 1:1$.

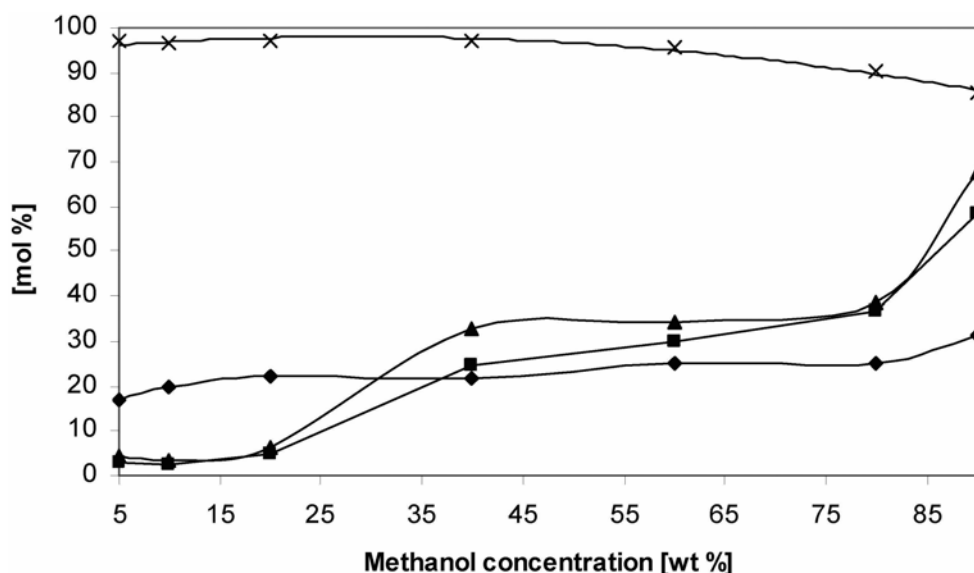


Fig. 4. Effect of methanol concentration on 1B3O epoxidation under autogenic pressure: selectivity of transformation to 1,2EB3 in relation to 1B3O consumed (◆), selectivity of transformation to organic compounds in relation to H_2O_2 consumed (■), 1B3O conversion (▲) and H_2O_2 conversion (x)

Rys. 4. Wpływ stężenia metanolu na epoksydację 1B3O pod ciśnieniem autogenicznym: selektywność przemiany do 1,2EB3 w odniesieniu do przereagowanego 1B3O (◆), selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2 (■), konwersja 1B3O (▲), konwersja H_2O_2 (x)

The influence of methanol concentration on 1B3O epoxidation under autogenic pressure was presented in Fig. 4. Selectivity of transformation to 1,2EB3 increases from 16.6 mol %

to 31,2 mol % during the elevation of methanol concentration from 5 to 90 wt.% (Fig. 4). Selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed and 1B3O conversion also achieves the highest value at methanol concentration of 90 mol %. This confirms a significant role of polar solvent (methanol) in the studied process. H_2O_2 conversion is decreases from 95.7 mol % to 89.5 mol %. Hence, the most advantageous concentration of methanol is 90 wt.%.

3.4. The influence of catalyst concentration

The influence of Ti-MCM-48 catalyst concentration was studied at temperature 20°C, at molar ratio of $1\text{B}3\text{O}/\text{H}_2\text{O}_2 = 1:1$, at methanol concentration of 90 wt.%, and after 3 h.

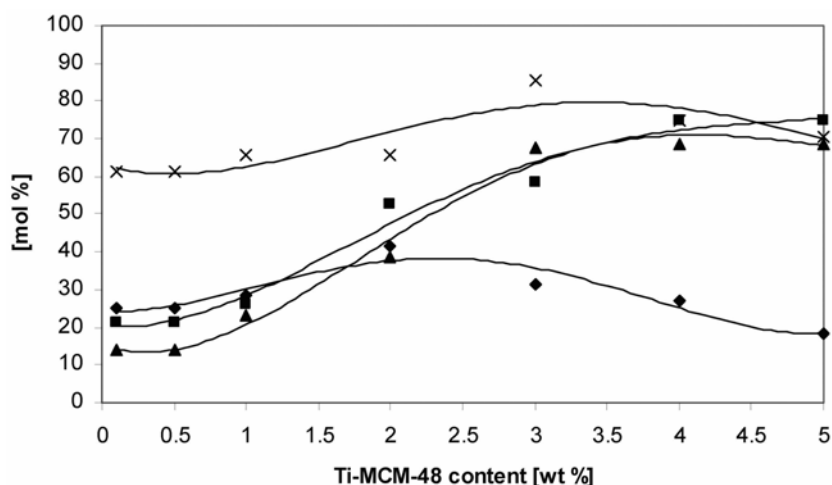


Fig. 5. Influence of Ti-MCM-48 catalyst concentration on 1B3O epoxidation under autogenic pressure: selectivity of transformation to 1,2EB3 in relation to 1B3O consumed (♦), selectivity of transformation to organic compounds in relation to H_2O_2 consumed (■), 1B3O conversion (▲) and H_2O_2 conversion (x)

Rys. 5. Wpływ stężenia katalizatora Ti-MCM-48 na epoksydację 1B3O pod ciśnieniem autogenicznym: selektywność przemiany do 1,2EB3 w odniesieniu do przereagowanego 1B3O (♦), selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2 (■), konwersja 1B3O (▲), konwersja H_2O_2 (x)

In the epoxidation process the selectivity of transformation to 1,2EB3 increases from 25 mol % to 41.7 mol % during the elevation catalyst concentration from 0.1 to 2 wt.% (Fig. 5). A further increase of catalyst concentration from 2 to 5 wt.% causes a decrease of values of this function.

Selectivity of transformation to organic compounds in relation to H_2O_2 consumed achieves the highest value (75 mol %) at Ti-MCM-48 catalyst concentration of 5.0 wt.%. 1B3O conversion increases along with an increase in the catalyst concentration from 13.8 to 68.8 mol %. 2 wt.% was taken as the optimum catalyst concentration, taking into account, primarily, high selectivity of transformation to 1,2EB3 in relation to 1B3O consumed.

3.5. The influence of reaction time

The influence of reaction time was studied after establishing the parameters previously recognized as the optimal ones.

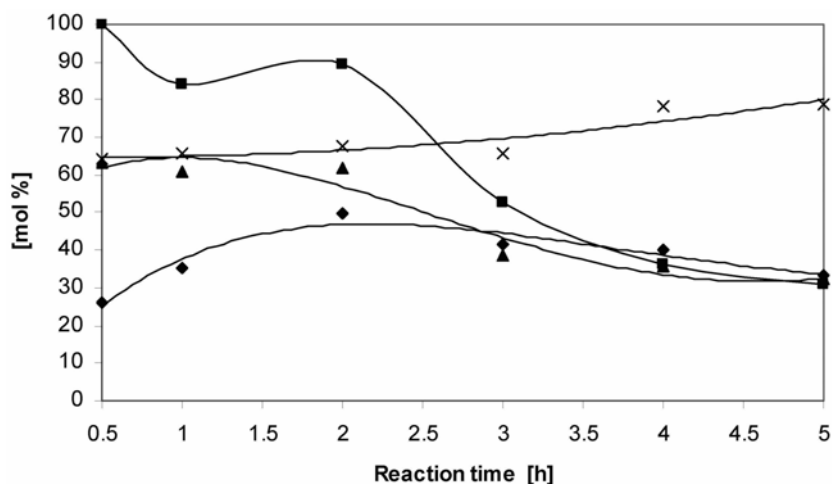


Fig. 6. Influence of reaction time on 1B3O epoxidation in the autoclave: selectivity of transformation to 1,2EB3 in relation to 1B3O consumed (◆), selectivity of transformation to organic compounds in relation to H₂O₂ consumed (■), 1B3O conversion (▲) and H₂O₂ conversion (x)

Rys. 6. Wpływ czasu reakcji na epoksydację 1B3O pod ciśnieniem autogenicznym: selektywność przemiany do 1,2EB3 w odniesieniu do przereagowanego 1B3O (◆), selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H₂O₂ (■), konwersja 1B3O (▲), konwersja H₂O₂ (x)

The selectivity of transformation to 1,2EB3 increases from 25 mol % to 41.7 mol % during the reaction time increase from 0.5 to 2 h. Further prolongation of the reaction time causes a decrease of values of this function to 33.3 mol % (5 h). The selectivity of transformation to organic compounds in relation to H₂O₂ consumed decreases during prolongation of the time of process performing from 100 mol % (0.5 h) to 30.7 mol % (5 h) (Fig. 6). Such dependence can be accounted for by decomposition of H₂O₂, which prevents it from participation in the epoxidation process. The course of curve of 1B3O conversions takes a constant value of about 83 mol % in the range from 0.5 to 3 h. The studies of 1B3O epoxidation demonstrated, that the time of 2 h is the most advantageous in the case of process proceeding under autogenic pressure.

4. Conclusions

Epoxidation of 1-butene-3-ol (1B3O) with 30 wt.% hydrogen peroxide over Ti-MCM-48 catalyst in the presence of methanol as a solvent is an example of new trends in modern technologies. This is a low-tonnage technology, fulfilling the requirements of green

chemistry. Titanium silicalite catalyst Ti-MCM-48 is an efficient heterogeneous catalyst for epoxidation process in the presence of hydrogen peroxide. It is easily separated from the post-reaction mixture and can be recycled. Hydrogen peroxide is considered to be the most ecological oxidizing agent. It is cheap, readily available and gives water as the only by-product [5]. Protic solvent (methanol) can be recovered by distillation and recycled to the process. The optimal parameters and corresponding to them the values of functions describing the process are presented in Table 1.

Table 1

Optimal parameters of 1B3O epoxidation over Ti-MCM-48 catalyst

Optimal conditions	
Temperature	20
Molar ratio of 1B3O/H ₂ O ₂	1:1
Methanol concentration [wt.%]	90
Ti-MCM-48 content [wt.%]	2.0
Reaction time [h]	2.0
S _{1,2EB3/1B3O} [mol %]	50.0
C _{1B3O} [mol %]	62.1
C _{H₂O₂} [mol %]	67.9
S _{org. comp./H₂O₂} [mol %]	89.5

S_{1,2EB3/1B3O} – selectivity of transformation to 1,2-epoxybutane-3-ol (1,2EB3) in relation to 1B3O consumed

C_{1B3O} – conversion of 1-butene-3-ol

C_{H₂O₂} – conversion of H₂O₂

S_{org. comp./H₂O₂} – selectivity of transformation to organic compounds in relation to H₂O₂ consumed

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