Epoxidation of Methallyl Chloride with a 30 % H_2O_2 over the TS-1 Catalyst

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The process of epoxidation of methallyl chloride to β-methylepichlorohydrin was carried out with a 30 % hydrogen peroxide in the presence of the titanium silicalite catalyst TS-1. The process was carried out in an autoclave or in a glass reactor at atmospheric pressure. The optimum technological parameters (temperature 20 °C, mole ratio $n(\text{MAC})/n(\text{H}_2\text{O}_2)$ 1:1, methanol content 40 mass %, TS-1 content 1.0—2.0 mass %, reaction time 120 min) were determined so that the applied epoxidation system allowed obtaining β-methylepichlorohydrin with a good selectivity (93—94 mole %) and high conversion of hydrogen peroxide (95—99 mole %).

In the recent years more and more attention has been paid to the development of waste-free and low-polluting technologies. This can be achieved, among others, through the management of waste by-products, elimination or reduction of solvent consumption or the application of more selective catalyst.

A chemical compound playing a more and more important role in the oxidation process is hydrogen peroxide. As the oxidant it does not cause the environmental contamination, and the reaction with its contribution produces water besides the major product. An additional advantage of the application of hydrogen peroxide in various chemical processes is associated with its relatively low price. Due to good oxidative properties, hydrogen peroxide found the application in many processes, displacing other, particularly so-called chemical oxidants, the application of which is associated with the formation of wastes. The most important processes [1], in which the oxidative action of hydrogen peroxide is being used comprise the oxidation of unsaturated compounds of the ethylene type to the alkene oxides (oxiranes). In the recent years the catalytic systems which selectively activate hydrogen peroxide are used. The catalysts used for the oxidation by means of hydrogen peroxide include titanium silicalites such as: TS-1, TS-2, and Ti-Beta. They replaced more dangerous acid catalysts (HF, HCl, H_2SO_4). Their additional advantage is associated with frequent elimination of the intermediate stages, which contributes to the reduction of the waste amounts. As a result of heterogeneity they can be easily separated from the reaction environment and subjected to regeneration. One of the advantages is the possibility of multiple regeneration and a lack of corrosion of apparatus. The application of titanium silicalite catalyst in the processes of alkenes epoxidation causes a limitation or elimination of the formation of the by-products, which are usually formed in the conventional epoxidation processes. The titanium-silicalite zeolites are used not only during the epoxidation of alkenes [2—7], but also for the oxidation of alcohols to aldehydes and ketones [8—10], for monoepoxidation of dienes [11], stereoselective epoxidation of *cis*- and *trans*-isomers [12], and for the oxidation of vinylbenzenes to corresponding aldehydes [13].

The application of titanium silicalite catalysts and hydrogen peroxide in the synthesis processes causes an improvement of the selectivity of transformation and the yield. Simultaneously, the processes can be carried out under mild conditions, which results in the reduction of operating costs of the installations [14].

As a result of the epoxidation of methallyl chloride (MAC) with 30 % hydrogen peroxide over the titanium silicalite catalyst β-methylepichlorohydrin (MECH) is obtained. This compound finds many useful applications. Primarily, MECH is used in the production of epoxy resins. After hardening these resins are characterized by good mechanical and dielectric properties and they exhibit a good heat resistance and durability. The resins based on MECH have the applications in the electrical industry (among others, for the electrical equipment) and building industry (for the manufacture of floor mix, chemically resistant compositions used as floor coverings) and in the production of laminates. The other applications include: adhesives, foil packages, lacquers, printer's inks, bind-

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ing agents, mineral matter binders, fillers, and dyes [15, 16].

The objective of this work is to investigate the influence of the technological parameters on the epoxidation of MAC by 30 % hydrogen peroxide over the TS-1 catalyst, the selection of the method for process running between the pressure and nonpressure processes.

EXPERIMENTAL

The following raw materials were used: methallyl chloride (MAC) (97 mass %, Fluka), hydrogen peroxide (30 %, P.O.Ch., Gliwice, Poland), methanol (anal. grade, P.O.Ch., Gliwice, Poland). The TS-1 catalyst was prepared by the method described by *Thangaraj et al.* [17]. Characterization of the catalyst was performed by different conventional techniques (XRF, XRD, IR, UV VIS, and SEM). The catalyst composition (mainly the content of Ti) was determined by X-ray fluorescence (XRF). The TS-1 catalyst contained 2.1 mass % of TiO_2. The crystalline structure of TS-1 was confirmed by the XRD method. The IR and UV VIS spectra presented the absorption bands ($\tilde{\nu} = 960$ cm^{-1} and $\lambda = 220$ nm) confirming the incorporation of titanium into the crystal structure of silica. The size of crystallites of TS-1 catalyst amounted to 0.3 μm (hexagonal lumps).

Epoxidation

The epoxidation was carried out by two methods: at atmospheric pressure (nonpressure method, glass reactor) and under increased pressure (pressure method, in the autoclave). In the nonpressure method the glass reactor was equipped with a reflux condenser, thermometer, mechanical stirrer, and dropping funnel. The reagents: MAC, solvent (methanol), and the catalyst were consecutively placed in the reactor. Hydrogen peroxide was added dropwise at the moment when the process temperature was reached and during a rapid mixing. In the pressure method a stainless-steel 7 cm^3 autoclave, equipped with PTFE insert was used. The reagents were placed in the autoclave in the following sequence: unsaturated compound, 30 % hydrogen peroxide, methanol, and the catalyst. The autoclave was fixed in a shaker holder and immersed in the oil bath the temperature of which was maintained by a thermostat. (The checking of the autoclave seal was performed by its weighing before and after the procedure.)

The studies were performed over the following ranges of variations of process parameters: the mole ratio of MAC to hydrogen peroxide 0.5—10:1, methanol content 5—90 mass %, the TS-1 catalyst content 0.1—2.0 mass %, reaction time 30—300 min. In the case of the pressure method, the temperature changes ranged between 20—120 °C, however in the case of nonpressure method a temperature range was lower due to a relatively low boiling point of solvent (64.5 °C) and amounted to 20—60 °C. The content of organic compounds in the post-reaction mixture was determined by gas chromatography (GC) on a Chrom-5 apparatus equipped with a flame-ionization detector (FID). Analyses were performed using a column 3 m long and 4 mm in diameter filled with Chromosorb 101 ("60/100 mesh"). Unreacted hydrogen peroxide was determined by iodometric titration [18]. After the mass balance was performed, the parameters characterizing the process (selectivity of transformation to MECH and to 1-chloro-2-methylpropane-2,3-diol (CMPD) in relation to MAC consumed, yield of MECH and CMPD, and the conversion of MAC and hydrogen peroxide) were calculated.

RESULTS AND DISCUSSION

The principal and side reactions proceeding during the epoxidation of MAC with hydrogen peroxide is presented in Scheme 1.

As a result of the epoxidation MECH was obtained as the major product, and further the following compounds were identified in the post-reaction mixture: CMPD and β-methylglycerol. In some experiments methallyl alcohol and 2-methylacrolein were found in the trace amounts. Within the studied ranges of technological parameters variations the occurrence of the above-mentioned remaining compounds was not found. The initial technological parameters of the syntheses were the following: mole ratio of MAC to hydrogen peroxide $n(MAC)/n(H_2O_2)$ 1:1, methanol content 40 mass %, the TS-1 content 1 mass %, and the reaction time was 180 min.

Changes of the selectivity of transformation to MECH and CMPD in relation to MAC consumed as a function of temperature are shown in Fig. 1. As temperature was increased, a decrease of selectivity of transformation to MECH with simultaneous increase of the selectivity of transformation to CMPD was observed in both methods. In the pressure method MECH was formed with the selectivity about 5 mole % in the temperature range from 80 to 120 °C, whereas the above-mentioned diol was the major compound. For each temperature from the studied range β-methylglycerol is formed in both the pressure and nonpressure methods. The selectivity of transformation to this compound in relation to consumed MAC is practically constant and amounts to about 2 mole %.

A decrease of the selectivity of transformation to MECH with increasing temperature and pressure results from a considerable reactivity of the oxirane ring. The vicinity of the methyl group additionally facilitates ring opening. The highest selectivity of transformation to MECH in relation to consumed MAC is achieved at 20 °C. At this temperature and above-mentioned remaining parameters the selectiv-
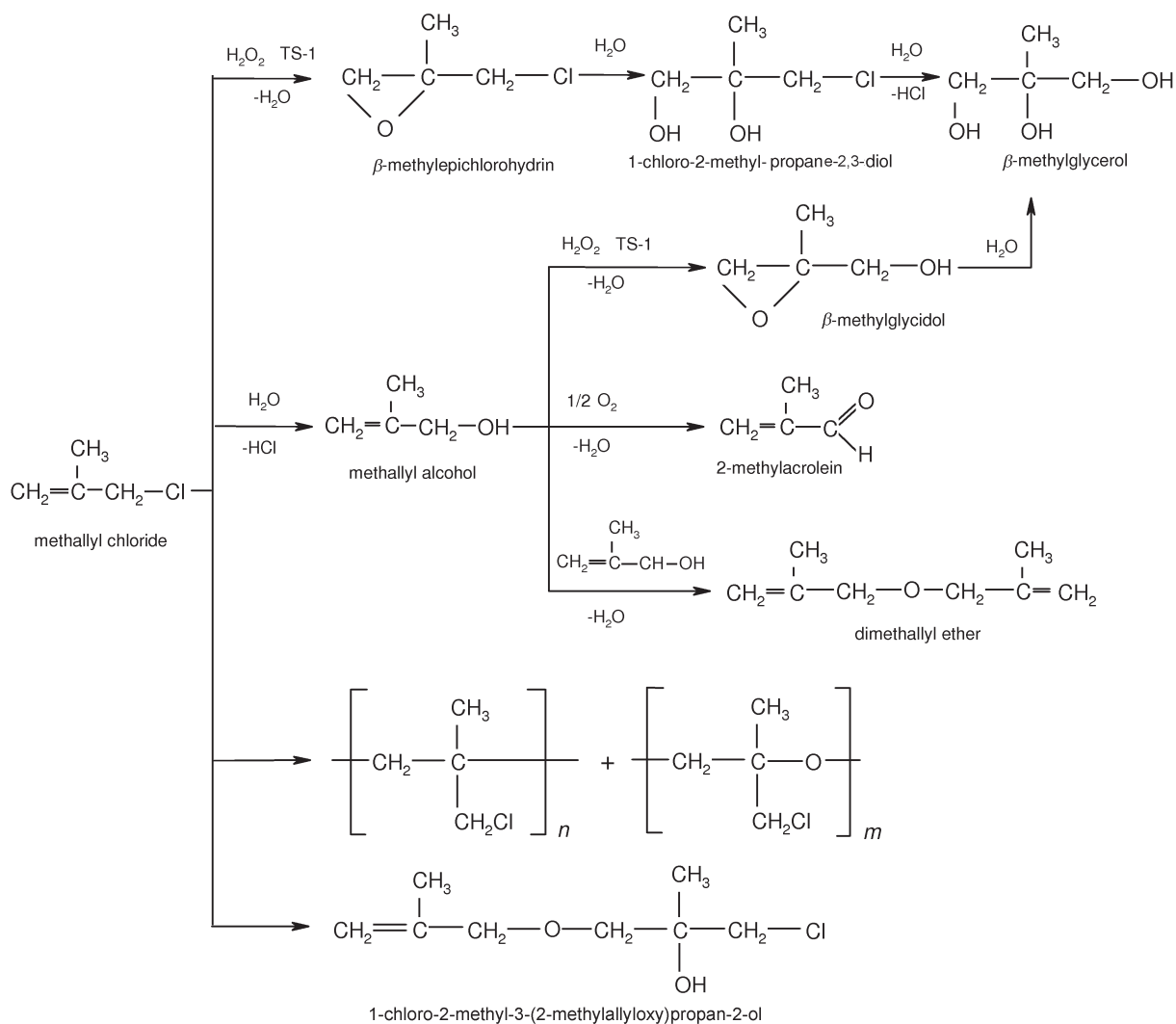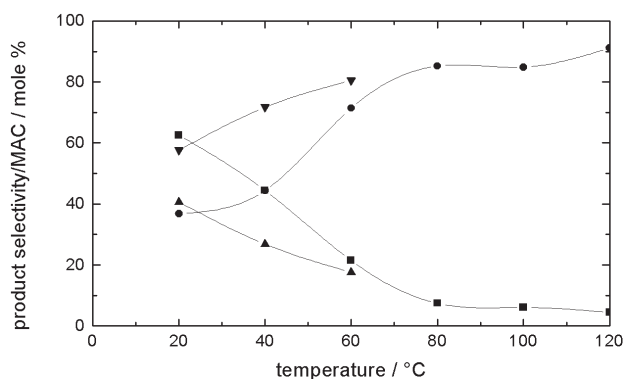
Scheme 1

Fig. 1. Influence of temperature on the selectivity of transformation to MECH (▲ nonpressure method, ■ pressure method) and CMPD (▼ nonpressure method, ● pressure method) in relation to MAC consumed.

ity of transformation to MECH in relation to MAC consumed in the nonpressure method amounts to 41 mole % with the conversion of MAC and hydrogen peroxide amounting to 51 mole % and 97 mole %, respectively. In the pressure method, the selectivity of transformation to MECH amounts to 63 mole % at the conversion of MAC of 7 mole % and hydrogen peroxide conversion of 98 mole %.

The influence of MAC/H$_2$O$_2$ mole ratio on the selectivity of transformation to MECH and CMPD in relation to MAC consumed is shown in Fig. 2. The studies were carried out at temperature of 20 °C. The influence of this parameter is similar independently of the method (pressure, nonpressure). Initially, the selectivity of transformation to MECH increases with an increase of the mole ratio of MAC/H$_2$O$_2$ reaching a maximum at the mole ratio of MAC/H$_2$O$_2$ 1:1 (41 mole % in the nonpressure method, 62 mole % in the pressure method), then the selectivity was found to decrease with increasing mole ratio. In the case of the nonpressure method, for the mole ratio of MAC/H$_2$O$_2$ 2:1, the selectivity of transformation to MECH amounts to about 5 mole % and it remains at the same level during a further increasing of the

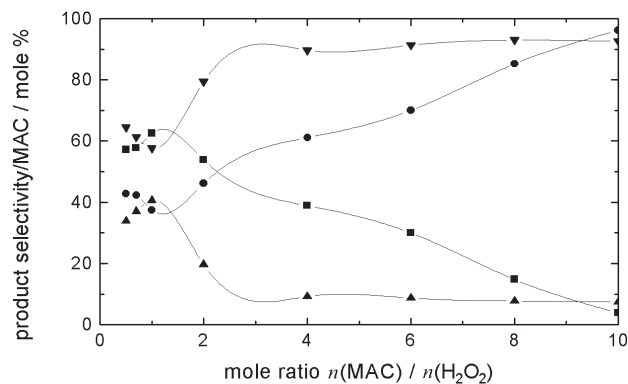**Fig. 2.** Investigation of the effect of MAC/H_2O_2 mole ratio on the selectivity of transformation to MECH (▲ nonpressure method, ■ pressure method) and CMPD (▼ nonpressure method, ● pressure method) in relation to MAC consumed.

Fig. 4. Investigation of the effect of TS-1 catalyst on the selectivity of transformation to MECH (▲ nonpressure method, ■ pressure method) and CMPD (▼ nonpressure method, ● pressure method) in relation to MAC consumed.
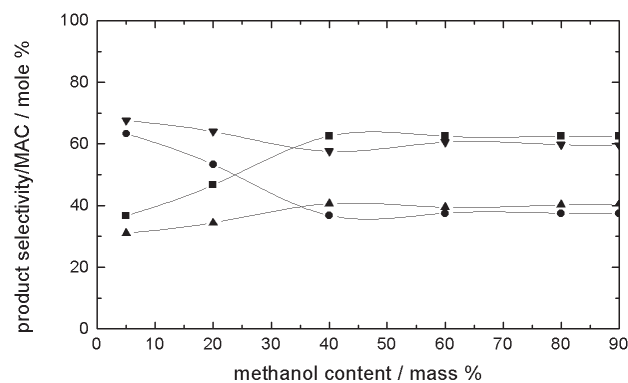

Fig. 3. Investigation of the effect of methanol on the selectivity of transformation to MECH (▲ nonpressure method, ■ pressure method) and CMPD (▼ nonpressure method, ● pressure method) in relation to MAC consumed.

MAC/H_2O_2 mole ratio up to 10:1. A decrease of the selectivity of transformation to MECH with the increase of the MAC/H_2O_2 mole ratio is also observed in the pressure method, however, this decline is gradual. A decrease of the selectivity of transformation to MECH is associated with a decrease of the conversion of MAC and H_2O_2. With increasing of MAC concentration in the reaction mixture the H_2O_2 concentration decreases. A dilution of the reactions environment causes a decline of the epoxidation rate. Simultaneously, the formed MECH relatively easily undergoes hydration to CMPD. In the studied range of changes of the MAC/H_2O_2 mole ratio, the highest selectivity of transformation to MECH was achieved at the MAC/H_2O_2 1:1. The conversion of MAC in the nonpressure method at this mole ratio amounts to 51 mole %, whereas in the pressure method it is 7 mole %.

The effect of methanol concentration on the selectivity of transformation to MECH and CMPD in relation to MAC consumed is shown in Fig. 3. In this case,
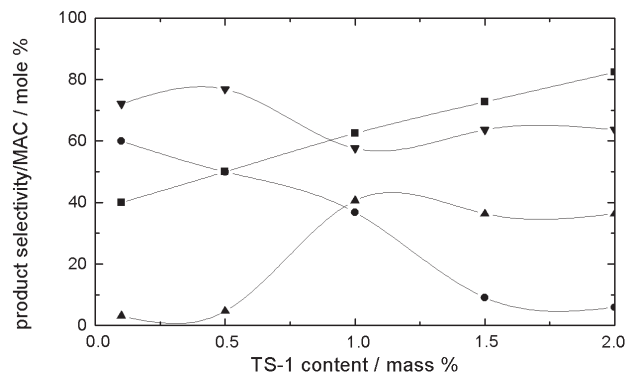
the selectivity of transformation to MECH as a function of the methanol concentration varies in a similar way for both methods. An increase of methanol concentration to 40 mass % in the nonpressure method causes an increase of the selectivity of transformation to MECH to 40 mole %, whereas to 62 mole % in the pressure method. Above the methanol content of 40 mass % no variation in the selectivity of transformation to MECH in relation to MAC consumed was observed. Under these conditions the MAC conversion amounted to 51 mole % in the nonpressure method, whereas to 7 mole % in the pressure method. A similar behaviour is exhibited by a function of the selectivity of transformation to CMPD. Initially, the selectivity of CPMD decreases, and then it remains at the constant level of 59 mole % and 37 mole % in the nonpressure and pressure method, respectively after exceeding the methanol content amounting to 40 mass %. In accordance with the mechanism presented by *Adam et al.* [19] methanol besides H_2O_2 performs a key role in the formation of an active adduct with the active centres of catalyst (Ti^{4+} ions). In this case one can speak about a boundary concentration of H_2O_2, above which no influence of H_2O_2 concentration on the course of epoxidation can be observed. Most probably this results from the fact that no more active adducts can be formed due to a limited content of Ti in zeolite (up to 2 mole %).

Changes of the selectivity of transformation to MECH and CMPD in relation to MAC consumed during a variation of the TS-1 catalyst concentration are presented in Fig. 4. The selectivity of transformation to MECH significantly increases with increasing content of the catalyst up to 1 mass % for both methods, whereas a simultaneous decrease of the selectivity of transformation to CMPD is observed. An exceeding of the catalyst content amounting to 1 mass % does not cause changes in the selectivity of transformation to MECH and to CMPD for the nonpressure

Table 1. Result of MAC Epoxidation with 30 % Hydrogen Peroxide over the TS-1 Catalyst Obtained by the Pressure and Non-pressure Method

Quantity		Nonpressure method	Pressure method
Temperature	$\theta/°C$	20	20
Mole ratio MAC/H_2O_2		1.0	1.0
Methanol content	w/mass %	40	40
TS-1 content	w/mass %	1.0	2.0
Reaction time	t/min	120	120
Mole fraction (x_i)			
$S_{MECH/MAC}$	x/mole %	94	93
$S_{CMPD/MAC}$	x/mole %	6	7
$Y_{MECH/MAC}$	x/mole %	25	14
$Y_{CMPD/MAC}$	x/mole %	2	1
K_{MAC}	x/mole %	26	16
$K_{H_2O_2}$	x/mole %	95	99

$S_{MECH/MAC}$ – selectivity of transformation to MECH in relation to consumed MAC, $S_{CMPD/MAC}$ – selectivity of transformation to CMPD in relation to consumed MAC, $Y_{MECH/MAC}$ – yield of MECH in relation to MAC introduced into the reactor, $Y_{CMPD/MAC}$ – yield of CMPD in relation to MAC introduced into the reactor, K_{MAC} – conversion of MAC, $K_{H_2O_2}$ – conversion of hydrogen peroxide.
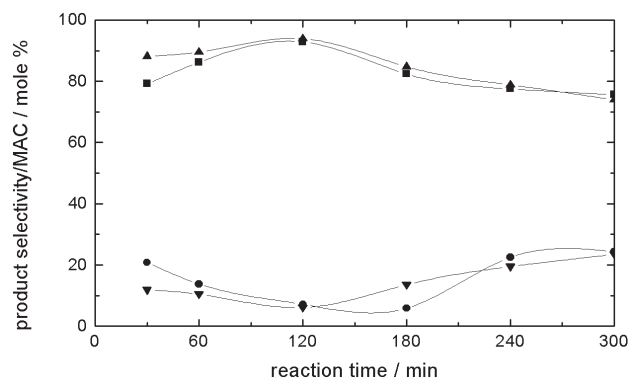

Fig. 5. Investigation of the effect of reaction time on the selectivity of transformation to MECH (▲ nonpressure method, ■ pressure method) and CMPD (▼ nonpressure method, ● pressure method) in relation to MAC consumed.

method. The values 38 mole % and 61 mole %, respectively were maintained. However, in the pressure method, the selectivity of transformation to MECH increases along with a further increase of catalyst content achieving 80 mole % for the TS-1 content of 2.0 mass %, the selectivity of transformation to CMPD decreases to 19 mole % with increasing content of the TS-1 catalyst to 2.0 mass %. The most favourable content of TS-1 in the nonpressure method amounts to 1.0 mass %, whereas 2.0 mass % in the case of pressure method. In the first case the conversion of MAC amounts to 51 mole %, whereas in the second one to 19 mole %. The investigations of the effect of TS-1 catalyst concentration demonstrate that the catalyst has a significant influence on the selectivity of transformation to MECH.

At the study of the effect of the reaction time the TS-1 content of 1.0 mass % in the pressure method

and 2.0 mass % in the nonpressure method was used. The experimental results are shown in Fig. 5. For both methods the selectivity of transformation to MECH initially increased when the reaction time was prolonged achieving a maximum after 120 min. However, after 120 min the selectivity decreases from 95 mole % to about 75 mole %. Moreover, the selectivity of transformation to CMPD is similar in both methods, and it increases with increasing the reaction time from ≈10 mole % after 30 min to ≈25 mole % after 300 min. The time equal to 120 min can be recognized as optimal for both methods of the epoxidation. Under the given technological conditions the MAC conversion after such time amounted to 26 mole % in the nonpressure method, whereas to 16 mole % in the pressure method. However, shorter reaction times (30 to 60 min) do not allow to achieve sufficiently high conversion of MAC in spite of the high selectivity.

The performed studies determined the optimum technological parameters of the process running at the epoxidation of MAC with a 30 % H_2O_2 over the TS-1 catalyst in the nonpressure method and pressure method. These parameters are shown in Table 1. Under the optimum conditions, the formation of by-product CMPD was practically not observed, and the selectivity of transformation to MECH in relation to MAC consumed amounted to about 90 mole %.

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