Influence of Solvent on the Epoxidation of Allyl Alcohol by Hydrogen Peroxide over Titanium Silicalite Catalysts

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The epoxidation of allyl alcohol by 30 mass % hydrogen peroxide over titanium silicalite catalysts in the environment of protic and aprotic solvents has been investigated. The influence of the titanium silicalite catalysts TS-1, TS-2, and Ti-Beta and a protic solvent (methanol) and aprotic solvents (acetonitrile and methyl ethyl ketone) on the allyl alcohol epoxidation was studied. The catalyst solvent system, namely TS-2—methanol, allowing to achieve glycidol with the highest selectivity has been determined.

The course of epoxidation of unsaturated compounds of the ethylene type is affected by several factors, primarily by the nature of used oxidant catalyst and solvent. Hydrogen peroxide is used more and more frequently among the oxidants. Hydrogen peroxide is environmentally friendly, effective and efficient and is characterized by a relatively low price. The effectiveness of hydrogen peroxide application can be significantly enhanced by the catalysts. The titanium silicalite catalysts are of the greatest importance among the catalysts used for this purpose. In many low-tonnage oxidation processes hydrogen peroxide is used instead of tert-butyl hydroperoxide and ethylbenzene and chemical oxidizing agents, such as: NaClO, $NaClO_2$, HNO_3, $KHSO_5$, and $NaIO_4$. The application of the latter compounds leads to the formation of by-products, loading the environment.

Adam and Corma [1, 2] have found that the mechanism of allyl alcohol epoxidation relies on the formation of five-membered active adduct among the cata-

lyst, hydrogen peroxide, and protic solvent. The solvent molecule (ROH) is included in the composition of five-membered active adduct and it stabilizes the formed complex owing to the formation of the hydrogen bond. The formation of this structure explains an advantageous influence of the protic solvents in the case of the epoxidation of any unsaturated compound, using hydrogen peroxide in the presence of the titanium silicalite catalysts.

The five-membered active adduct is also formed in the case of application of aprotic solvent, where the position of solvent is occupied by the water molecule. Water is introduced into the reaction medium with a 30 mass % solution of H_2O_2 and is formed during the reaction.

The previous studies [2] revealed that the reactivity of this structure is higher in the case of the TS-1 and TS-2 catalysts, whereas in the case of Ti-Beta catalyst the structure with contribution of water is more active. This results from the fact that the Ti-Beta catalyst is more hydrophilic in comparison with TS-1 and TS-2. A literature survey reveals that in the case of the protic solvents the requirement of such type of process is fulfilled best by methanol, ethanol, and tert-butyl alcohol [3]. It was found that the reactivity of the active adduct of the above structure in the case of these solvents decreases in the following order: methanol, ethanol, tert-butyl alcohol. The authors of
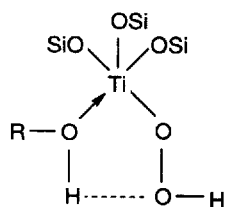
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this paper have noticed that the reactivity is in accordance with decreasing relative permittivity of these solvents (32.7, 24.5, and 10.9, respectively) and with an increase of the solvent molecule size. In our opinion, a decrease of the acidity of alcohols in the mentioned order: methanol pKa $= 15.54$, ethanol pKa $= 16.00$, and tert-butyl alcohol pKa $= 18.00$ is also an essential fact. Methanol is considered to be the best solvent for the epoxidation of unsaturated alcohols due to a good solubility of the substrates and products and a high reaction rate. However, the application of methanol is associated with a hazard of methanolysis. Moreover, the oxidation of methanol to formaldehyde [4] may proceed under extremely unfavourable conditions. The epoxidation is also affected by the molecular structure of solvent. A large molecule of protic solvent incorporated into the composition of the active adduct impedes the accessibility of unsaturated compound to oxygen from this adduct [3]. It is particularly apparent in the case of tert-butyl alcohol, where the three methyl groups increase the electron density on the tert-carbon atom (induction effect) and cause the formation of steric hindrances [2].

In the case of aprotic polar solvents the ability of epoxidation over the Ti-Beta catalyst decreases along with decreasing relative permittivity in the following order: acetonitrile (37.5), acetone (20.7), methyl ethyl ketone (18.5). This can be explained by increasing of the role of water in the formation of five-membered active adduct. An increase of solvent polarity increases the concentration of unsaturated compound in the hydrophilic pores of the Ti-Beta catalyst, thereby the reaction rate. On this basis acetonitrile was recognized as the best solvent in the case of Ti-Beta catalyst. The acidity of aprotic solvents is higher in comparison with those of protic solvents. The acetone acidity (pKa $= 19.30$) is at a level of tert-butyl alcohol, whereas acetonitrile acidity is even lower, pKa $= 25.00$. A decrease of solvent acidity should facilitate the formation of active adducts with the contribution of the water molecules [2], particularly in the case of Ti-Beta catalyst.

On the basis of the literature data the allyl alcohol (AA) epoxidation was carried out in the environment of methanol, acetonitrile, and methyl ethyl ketone. In the performed experiment the influence of the following parameters was investigated: temperature, mole ratio of AA to hydrogen peroxide (AA/H$_2$O$_2$), solvent concentration, catalyst concentration, and reaction time. The magnitudes describing the epoxidation process were as follows: the selectivity of transformation to glycidol in relation to consumed AA ($S_{glyc/AA}$) and hydrogen peroxide (S_{glyc/H_2O_2}), conversion of AA (K_{AA}) and hydrogen peroxide ($K_{H_2O_2}$). In the assumed method of calculations, the yield of glycidol in relation to allyl alcohol or hydrogen peroxide introduced into the reactor is a product of respective conversions and selectivities.

EXPERIMENTAL

The following reagents were used in the syntheses: allyl alcohol (99 % Fluka), hydrogen peroxide (30 mass % aqueous solution, P.O.Ch. Gliwice); the catalysts: TS-1, TS-2, and Ti-Beta (prepared in the Institute of Organic Chemical Technology, Technical University of Szczecin according to the methods described in the literature [5—8]); the solvents methanol (anal. grade, P.O.Ch, Gliwice), acetonitrile, methyl ethyl ketone (both anal. grade, Reanal, Hungary).

Characterization of the catalysts was performed by different conventional techniques (XRF, XRD, IR, UV VIS, SEM). The catalyst composition was determined by X-ray fluorescence (XRF). The catalysts contained the following amounts of Ti (expressed in w_i/mass % of TiO$_2$): TS-1 – 4.1, TS-2 – 4.2, and Ti-Beta – 1.1. The crystalline structures of samples were 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 for both TS-1 and TS-2 amounted to ≈ 0.3 μm, whereas for Ti-Beta to 50—80 μm.

Epoxidation

The reaction was carried out in a pressure reactor, equipped with PTFE insert of 7 cm^3 capacity. Determined amounts of the substrates were introduced into a dry autoclave in the following sequence: allyl alcohol, hydrogen peroxide, solvent, and a catalyst. The amount of substrates was selected so that the degree of autoclave filling did not exceed 80 vol. % with maintaining the process parameters. The autoclave was screwed and then placed in a shaker holder and immersed in the oil bath, the temperature of which was controlled by a thermostat. After starting the shaker, the reaction was carried out for the time appropriate for a given experiment. After the reaction was completed, the autoclave was cooled in a freezer for about 15 min and emptied. A post-reaction solution was weighed in order to balance the process. A post-reaction mixture was analyzed to determine the amount of unreacted hydrogen peroxide (iodometric method [9]) and glycerol (periodate method [10]). The remaining compounds (allyl alcohol, glycidol, 1-methoxy-2,3-propanediol, 2-methoxy-1,3-propanediol) were determined by a gas chromatography method [11, 12] on a Chrom 5 apparatus equipped with a flame-ionization detector (FID). Analyses were performed with a stainless steel column (3 m × 4 mm) packed with 10 mass % Triton 100 on Chromosorb W "60/80 mesh". The parameters of chromatographic separation were as follows: the flow rate of air – 400 cm^3 min^{-1}, hydrogen – 30 cm^3 min^{-1}, nitrogen – 30 cm^3 min^{-1}, the temperature of the sample chambers and the detector was 200 °C.

The thermostat temperature was changed gradually according to the program: isothermally 50 °C for 6 min, with an increase of temperature at the rate of 15 °C min^{-1}, isothermally 140 °C for 6 min, with an increase of temperature at the rate of 20 °C min^{-1}, isothermally 142 °C for 2 min and cooling to 50 °C.

The influence of technological parameters was studied within the following ranges: temperature 20—120 °C, the mole ratio $n(AA)/n(H_2O_2)$ 1:1—10:1, solvent concentration 5—90 mass %, catalyst content 0.1—2.0 mass %, reaction time 15—600 min.

RESULTS

Table 1 presents the most advantageous technological parameters and corresponding to them results of allyl alcohol epoxidation with a 30 mass % hydrogen peroxide over the catalysts TS-1, TS-2, and Ti-Beta in the environment of methanol. This series of studies demonstrate that the technological conditions under which the high selectivities of transformation to glycidol were achieved over each of the tested catalyst were the same, only the catalyst concentrations were different. Catalyst concentration in this range has a small influence on the epoxidation results (conversions of alcohol and hydrogen peroxide, selectivity of transformation in relation to each of the substrates). A comparison of the results obtained at these parameters reveals that the selectivity of transformation to glycidol in relation to allyl alcohol consumed exceeds 80 mole % over each of the catalysts. The H_2O_2 conversion is almost identical and does not exceed 95 mole %. The epoxidation process proceeds fast (60 min) in methanol, at a high degree of conversion of allyl alcohol and hydrogen peroxide over all the catalysts. The highest values of the magnitudes describing the process were achieved over the TS-2 catalyst.

The results of the epoxidation in the environment of acetonitrile are presented in Table 2. The optimum conditions of epoxidation over each of the studied catalysts in this case were also similar. The best catalyst is TS-2 similarly like in the presence of methanol. The optimum reaction time necessary to achieve these magnitudes amounts to 90 min and is slightly longer in comparison with the process carried out in the environment of methanol.

The results of the epoxidation in the presence of methyl ethyl ketone are presented in Table 3. The optimum parameters of the epoxidation over the consecutive catalysts are practically the same. A small difference concerns the $n(AA)/n(H_2O_2)$ mole ratio, which amounts to 2:1 in the case of TS-1 and Ti-Beta, whereas for TS-2 it amounts to 1:1. The remaining optimum parameters are the same for all the catalysts. The TS-2 catalyst acts the most selectively also in this case. The magnitudes describing the process in the case of methyl ethyl ketone are lower in comparison with those obtained in the presence of methanol or

acetonitrile. The highest selectivity of transformation to glycidol in relation to consumed allyl alcohol was achieved with the TS-2 catalyst and it amounted to 67.6 mole %. Simultaneously the complete consumption of allyl alcohol takes place in this case.

The optimum parameters and corresponding to them results of AA epoxidation in the studied sol-

Table 1. The Optimum Conditions of AA Epoxidation with 30 mass % H_2O_2 over the Titanium Silicalite Catalysts in the Methanol Medium

Parameter	TS-1	TS-2	Ti-Beta
Temperature/ °C	20	20	20
Mole ratio $n(AA)/n(H_2O_2)$	1:1	1:1	1:1
Methanol concentration/mass %	80	80	80
Catalyst concentration/mass %	1.0	0.1	0.5
Reaction time/min	60	60	60
$S_{glyc/AA}$/mole %	93.6	88.4	82.3
S_{glyc/H_2O_2}/mole %	67.5	73.1	74.4
K_{AA}/mole %	68.9	97.7	87.7
$K_{H_2O_2}$/mole %	95.6	95.7	95.5

Table 2. The Optimum Conditions of AA Epoxidation with 30 mass % H_2O_2 over the Titanium Silicalite Catalysts in the Acetonitrile Medium

Parameter	TS-1	TS-2	Ti-Beta
Temperature/ °C	20	20	20
Mole ratio $n(AA)/n(H_2O_2)$	1:1	1:1	2:1
Acetonitrile concentration/mass %	90	90	90
Catalyst concentration/mass %	1.0	1.0	0.1
Reaction time/min	180	90	180
$S_{glyc/AA}$/mole %	78.6	94.4	100.0
S_{glyc/H_2O_2}/mole %	25.0	25.6	27.0
K_{AA}/mole %	73.7	94.8	51.4
$K_{H_2O_2}$/mole %	95.2	88.9	88.9

Table 3. The Optimum Conditions of AA Epoxidation with 30 mass % H_2O_2 over the Titanium Silicalite Catalysts in the Methyl Ethyl Ketone (MEK) Medium

Parameter	TS-1	TS-2	Ti-Beta
Temperature/ °C	20	20	20
Mole ratio $n(AA)/n(H_2O_2)$	2:1	1:1	2:1
MEK concentration/mass %	90	90	90
Catalyst concentration/mass %	1.0	1.0	1.0
Reaction time/min	240	240	240
$S_{glyc/AA}$/mole %	60.9	67.6	81.7
S_{glyc/H_2O_2}/mole %	19.1	13.0	14.4
K_{AA}/mole %	63.9	100.0	41.9
$K_{H_2O_2}$/mole %	89.5	90.0	90.0

vents over the TS-2 catalyst are given in the middle columns of Tables 1—3. With comparable parameters or less significant differences in their values with regard to the influence on the values describing the process (conversion, selectivity) TS-2 was found to be the best catalyst. It can be seen from a comparison of the results of the reaction over the TS-2 catalyst in the presence of mentioned solvents that the lowest selectivity of transformation to glycidol in relation to allyl alcohol and in relation to H_2O_2 with the conversion of allyl alcohol and hydrogen peroxide similar to those for the remaining solvents was achieved in methyl ethyl ketone. Moreover, one can speak about an equivalence of methanol as the protic solvent and acetonitrile as the aprotic solvent. In both cases comparable and relatively high selectivities of transformation to glycidol in relation to allyl alcohol, respectively 90.4 mole % and 94.4 mole % were achieved. The conditions under which the above values were achieved are identical as for the temperature and the $n(AA)/n(H_2O_2)$ mole ratio, respectively 20 °C and 1:1. In the case of solvent the optimum methanol concentration amounts to 80 mass %, however, the application of 90 mass % (as in the case of acetonitrile) does not change the values of magnitudes describing the process. The recognition of methanol concentration amounting to 80 mass % as optimum results only from the possibility of recirculation of its smaller amount. Likewise it is in the case of catalyst concentration. In the presence of methanol the highest values of conversion and selectivity were achieved in the range of catalyst concentration 0.1—1.0 mass %. Therefore, a lower concentration was recognized as optimum. The prolongation of reaction time from 60 to 90 min in methanol does not cause significant changes of these magnitudes.

CONCLUSION

Among the studied titanium silicalite catalysts the most active was TS-2 independently of the nature of the used solvent. The high values of the conversion of allyl alcohol and hydrogen peroxide and the selectivity of transformation to glycidol in relation to allyl alcohol

and hydrogen peroxide were achieved using this catalyst. There are no significant differences in the course of the epoxidation process of allyl alcohol in the presence of the protic solvent – methanol and aprotic one – acetonitrile. The selection of methanol as the reaction medium can be justified by the possibility of application of slightly milder technological parameters in comparison with acetonitrile: lower concentration of solvent and catalyst and shorter reaction time. This will be associated with a smaller consumption of solvent and catalyst in the industrial solutions, therefore a better economics of production. However, this requires an accurate maintenance of parameters recognized as optimum. An increase of temperature above optimum, prolongation of the reaction time over 90 min causes the formation of products of oxirane ring methanolysis.

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