Obtaining Titanium-Containing Zeolite and Studying Its Catalytic Properties in the Epoxidation of Allyl Alcohol

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Abstract

Results are presented concerning the optimization of composition and conditions for obtaining titanium-containing zeolite, a catalyst for allyl alcohol liquid-phase epoxidation by an aqueous solution of hydrogen peroxide in the methanol environment. The composition and conditions for catalyst preparation were revealed to provide a maximum yield of glycidol.

Key words: titanium zeolite, allyl alcohol, glycidol, epoxidation, catalytic activity

INTRODUCTION

Glycidol (1,2-epoxypropanol) is an important product of the organic synthesis. Exhibiting a high reactivity, it can readily interact with different classes of compounds, which allows obtaining on this basis a number of products used in many industries (epoxy resins, paints, varnishes, adhesives, synthetic fibres, ion exchange resins, rubbers characterized by high oil and the heat resistance and gas impermeability, *etc.*). In addition, a non-chlorine process for the synthesis of glycerol, based on the hydrolysis of glycidol, remained for a long time the main method for producing synthetic glycerol [1].

The main methods for preparing glycidol are as it follows: dehydrohalogenation of the glycerol monochlorohydrin, the hydrolysis of epichlorohydrin, the interaction between allyl alcohol and perbenzoic acid. However, these methods have a number of significant disadvantages, including a low yield of the target product, the formation of a large number of difficult-to-recovery reaction by-products, waste water, *etc.*

The analysis of the methods for producing glycidol we performed demonstrated that the most promising method for the synthesis is based on a liquid-phase oxidation of allyl alcohol by hydrogen peroxide in an organic solvent on the heterogeneous catalyst such as titanium-containing zeolite. The distinctive feature of the process consists in the fact that the process is carried out at moderate temperature values (30–60 °C), and at a low pressure values (1–2 atm), being thus attractive from the environmental point of view. In this connection, of special urgency are the questions associated with obtaining the catalyst (titanium-containing zeolite) as well as with studying on its catalytic activity.

The object of investigation in this study was presented by the process of optimizing the composition and the conditions for obtaining titanium-containing zeolite used as a catalyst for liquid-phase epoxidation of allyl alcohol by aqueous solutions of hydrogen peroxide in the methanol environment.

The analysis of data published demonstrated that the most convenient method for obtaining titanium-containing zeolite consists in the syn-

thesis *via* using a sol-gel technology [2], based on the hydrolysis of the solutions of silicon and titanium alkoxides in the presence of a structure-forming base such as tetrapropylammonium hydroxide. The promise of this method consists in the possibility of interconnected controlling the composition and microstructure of titanium-containing zeolites at the molecular level as well as of forming the material shaped as powder, different size and shape granules with preset catalytic properties.

For the process of the preparation of titanium-containing zeolite, one could roughly distinguish the following stages: mixing the initial reactants, hydrothermal processing, washing, drying and calcination of titanium-containing zeolite crystals. The conditions for carrying out each stage and the initial ratio between the reagents affect to a considerable extent the activity of the catalyst obtained. However, there is almost no information available from the literature concerning the impact of these factors on the catalytic properties of titanium-containing zeolite used in the liquid-phase epoxidation of allyl alcohol by the aqueous solution of hydrogen peroxide. This paper presents the results of optimizing the composition and conditions for obtaining titanium-containing zeolite used in the synthesis of glycidol in the environment of methyl alcohol. As the optimization criterion for the catalyst obtained we used the yield of the target product − glycidol − calculated for the hydrogen peroxide converted. The yield of glycidol was assessed according to the results of testing the samples of titanium-containing catalyst zeolite. Along with the formation of glycidol, side reactions occur resulting in the formation of glycerol and other unidentified impurities in small amounts.

EXPERIMENTAL

In this work, we used the following reagents: analytical grade methanol (State Standard GOST 2222−95), pure grade glycidol, technical specifications TU 6-09-14-2635−79), 33−34 % hydrogen peroxide (high pure quality, TU 2611-069-05807977−2006), allyl alcohol (technical specifications TU 6-01-753−77), tetrabutoxytitanium (TBOT, TU 6-09-2738−89), tetraethoxysilane

(TEOS, TU 2435-419-05763441−2003), tetrapropylammonium hydroxide (TPAH).

The titanium-containing zeolite was prepared *via* mixing tetraethoxysilane and tetrabutoxytitanium in a glass reactor. Further, under vigorous stirring, was added tetrapropylammonium hydroxide. In order to complete the hydrolysis and distillation of the resulting alcohols the reaction mixture was heated. The gel obtained was subjected to hydrothermal treatment, which was performed using an autoclave, fixed on a shaker with reciprocating motion, the frequency being of $2 s^{-1}$ with the amplitude of 0.05 m and the temperature ranging within 130−200 °C, during 19−100 h, under stirring. After cooling the resulting suspension of titanium-containing zeolite, a solid substance obtained was washed until the washing water exhibit pH ranging within 7−8, dried for 12 h at 120 °C under vacuum (20 mm Hg). The sample was then calcined at 350−750 °C during 6 h in a muffle furnace.

The catalytic testing of the samples of titanium-containing zeolite was carried out using a laboratory set-up of cyclical operation at 40 °C, at the molar ratio allyl alcohol: hydrogen peroxide equal to 3.0, and the mass fraction of solvent being of 80.5 %. The content of titanium-containing zeolite remained constant in all the experiments and amounted to 4.9 g/L.

The analysis of the components of the reaction mixture was carried out using GLC by means of a Tsvet 500 chromatograph equipped with a flame ionization detector, with the help of the method of absolute calibration. We used a stainless steel column 3 mm in diameter and 2 m long, filled with Chromaton-N-AW-DMCS (0.2−2.25 mm) carrier, where on a chromatographic phase Reoplex-400 was deposited in an amount of 15 % of the carrier mass. The structure and morphology of the titanium-containing zeolite samples were studied by means of transmission electron microscopy, using Hitachi a S-2500 electron microscope, by means of IR spectroscopy using a Perkin Elmer 221 spectrometer employing KBr pellets within the range of 400−4000 cm^{-1}. XRD patterns were registered on a Shimadzu LAB XRD-6000 diffractometer (CuK_α, Ni filter, voltage 30 kV, current 30 mA) under a continuous rotation of a cuvette with the sample. The speed of the counter amounted to 2 deg^{-1}, the diffraction patterns were registered for angles ranging within $2\theta = 5−80°$.

RESULTS AND DISCUSSION

Effect of TBOT/TEOS ratio

In order to evaluate the effect of TBOT/ TEOS ratio we obtained a series of samples of titanium-containing zeolite synthesized at an initial molar ratio of reactants TEOS/TBOT/ TPAH/H_2O = 1 : (0.02, 0.04, 0.06, 0.08) : 0.5 : 25, which corresponds to the theoretical mole fraction of TiO_2 equal to 1.96, 3.85, 5.66, 7.41 %, respectively.

The analysis of the IR spectra for the samples (Fig. 1) demonstrated that increasing the initial ratio TBO/TEOS results in an increase in the relative intensity of the characteristic absorption band for the titanium-containing zeolite at the wave number of 960 cm^{-1} (asymmetric vibration of Ti−O−Si fragment). This indicates an increase in the content of titanium atoms in the crystal lattice of the zeolite those are in the tetracoordinated state. The presence of bands at the wave number of 550 cm^{-1} is connected with the vibrations of double five-membered rings (the building unit of the pentasil family of zeolites), indicating the formation of zeolite with MFI structure. Furthermore, the presence of bands at 800 cm^{-1} in the IR spectrum characterizes the occurrence of the symmetric (Si−O−Si) vibrations, the bands within the wave number range of 1100−1210 cm^{-1} correspond to asymmetric (Si−O−Si) vibrations, where-
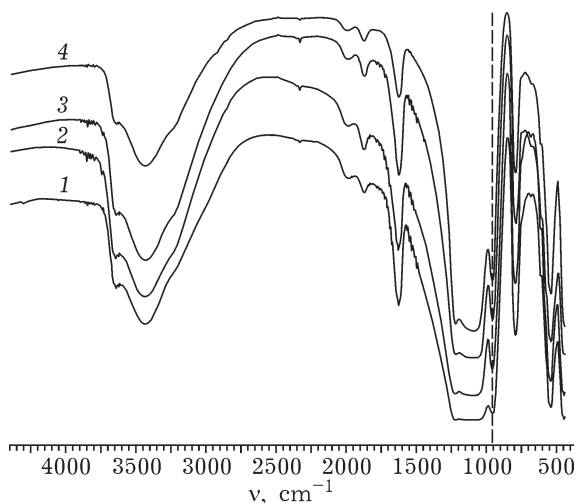
as those within in the region of ~3400 cm^{-1} are inherent in Si−OH stretching vibrations.

However, it should be noted that with increasing the content of titanium in the initial gel higher than 4−5 mol. % there is no adequate increase in its amount observed in the samples of solid catalyst. To all appearance, the amount of titanium, which can be incorporated into the zeolite framework in the tetracoordinated state is limited by the possibility of obtaining titanium-containing zeolite with MFI structure of. In addition, the increase in titanium content in the crystal lattice of the zeolite results in decrease the rate of titanium inclusion into the zeolite framework [3]. It is important to note that the excess titanium not included in the framework of the zeolite remains in the form of TiO_2 such as anatase that exhibits no catalytic activity, but could accelerate adverse reactions (e. g., the reaction of H_2O_2 decomposition).

The regularities established were confirmed by the results of catalytic testing of the samples. Figure 2 demonstrates the main parameters of the process of obtaining glycidol depending on the initial molar TBOT/TEOS ratio in the structure of the zeolite.

It is seen that the maximum yield of the target product is achieved at the TBOT/TEOS molar ratio equal to 0.04. The further increase in the ratio is impractical because there is a significant anatase impurity appearing in the catalyst samples, which results in the misuse

Fig. 1. IR spectra of samples prepared at different TBOT/ TEOS molar ratio: 0.02 (1), 0.04 (2), 0.06 (3), 0.08 (4).
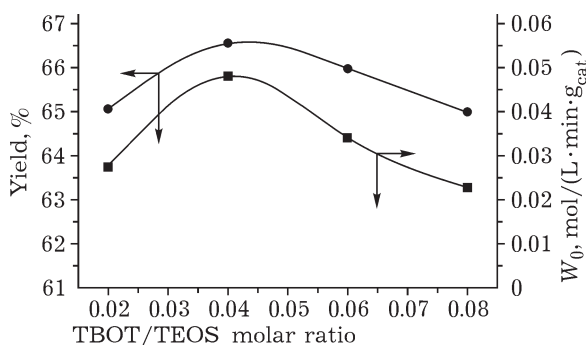

Fig. 2. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) and the initial rate of glycidol formation depending on the initial TBOT/TEOS molar ratio.
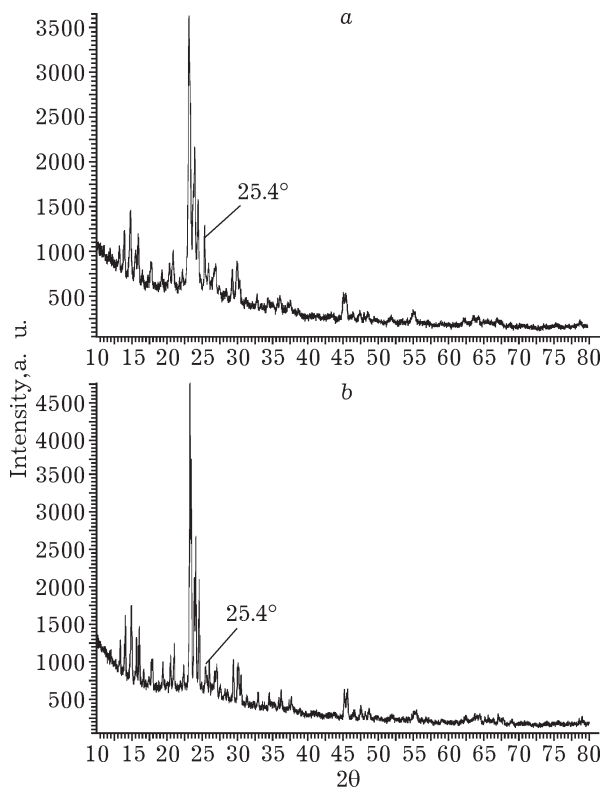
Fig. 3. XRD patterns for the catalyst samples obtained at TPAH/TEOS molar ratio equal to 0.0833 (*a*) and 0.25 (*b*).
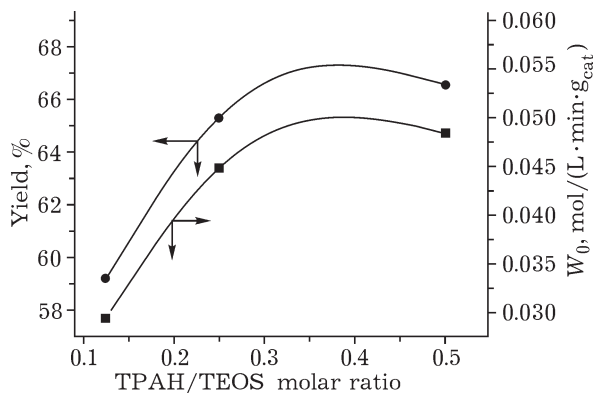

Fig. 4. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) and the initial rate of glycidol formation depending on the initial TPAH/TEOS molar ratio.

of hydrogen peroxide and, consequently, in decreasing the yield of glycidol.

Effect of TPAH/TEOS ratio

In order to assess the influence of the TPAH/TEOS ratio we obtained a series of samples of titanium-containing zeolite with initial molar ratio between reactants TEOS/TBOT/TPAH/H_2O = 1 : 0.04 : (0.083, 0.125, 0.25, 0.5) : 25.

The analysis of the samples obtained demonstrated that the use of different amounts of the structure-forming agent (TPAH) exerts a significant effect both on the structure and on the morphology of the titanium-containing zeolite under obtaining. Thus, at a molar ratio TPAH/TEOS equal to 0.083, the IR spectrum of the sample exhibits the characteristic band corresponding to tetracoordinated titanium atom at 960 cm^{-1} having ill-defined shape, whereas the ratio between the intensities of the bands 960 and 550 cm^{-1} is close to zero. This indicates the fact that the titanium-containing zeolite with MFI structure is formed in very small amounts. The analysis of the sample by means of pow-

der X-ray diffraction revealed an increase in the intensity of the reflexes at $2\theta = 25.4°$ (Fig. 3, *a*) indicating a high content of TiO_2. At the same time, the other samples did not demonstrate any increase in the intensity of the band under consideration, and they remain almost identical (see Fig. 3, *b*).

This allows one to conclude that the lack of the sufficient amount of the structure-forming agent which provides a way to build a regular structure of titanium-containing zeolite results in the formation of an amorphous TiO_2 and SiO_2 mixture.

Comparing the key indicators of the catalytic activity of the samples (Fig. 4) obtained at different initial TPAH/TEOS molar ratio demonstrated that the glycidol yield increases with increasing the ratio from 0.125 to 0.25. The further increase in the TPAH/TEOS ratio to 0.5 does not result in an adequate increase in the yield of glycidol, and this value remains almost constant.

For the sample obtained at the initial molar ratio TPAH/TEOS = 0.083, glycidol is formed in small amounts (1.5 %) due to a low content of Ti atoms in the tetracoordinated state in this sample those exhibit catalytic activity.

Effect of stirring at the stage of hydrothermal treatment

In order to evaluate the effect of stirring at the stage of the hydrothermal treatment of the catalyst obtained, we obtained a series of samples with the molar ratio between the re-

actants TEOS/TBOT/TPAH/H_2O = 1 : 0.04 : 0.5 : 25, without stirring and under stirring.

For characterizing the morphology of the catalyst samples synthesized we obtained micrographs using the method of transmission electron microscopy. According to the data of the comparative analysis of two electron-microscope images, it can be concluded that the presence or absence of stirring in the course of the stage of hydrothermal treatment affects the size of the catalyst particles obtained.

It is established that the presence of the stirring at the stage of hydrothermal treatment results in the fact that the particle size of the catalyst is more homogeneous. In addition, the average particle size obtained without stirring is to a considerable extent larger than that for the particles prepared under stirring. This is connected with the fact that in the absence of stirring required for an intense nucleation and uniform growth of crystals in the reactor, a temperature gradient appears which affects the equilibrium solubility. In a more "hot" area the solubility of small particles exceeds the solubility of large particles, thus the precipitation of dissolved forms in the "cold" zone intensifies the total change in particle size, resulting in an increase in the growth of already existing sol particles (Ostwald ripening [4]).

For the samples of catalysts prepared with stirring and without stirring, the yield of glycidol amounts to 66.03 and 58.19 %, respectively, whereas the initial rate of glycidol formation is equal to 0.026 and 0.019 mol/(L $\cdot$ min $\cdot$ g$_{cat}$), respectively.

These data allow one to conclude that in order to obtain a maximum yield of glycidol the hydrothermal treatment should be carried out under stirring.

Effect of temperature
at the stage of hydrothermal treatment

In order to evaluate the effect of temperature at the stage of hydrothermal treatment we obtained a series of the catalyst samples at a molar ratio between reactants TEOS/TBOT/TPAH/H_2O = 1 : 0.04 : 0.25 : 25 at the temperature values amounting to 130, 150, 170, 200 °C.
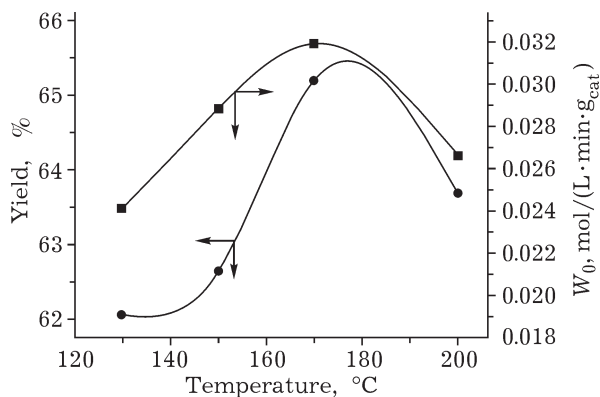

Fig. 5. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) and the initial rate of glycidol formation depending on the temperature of hydrothermal treatment.

The catalytic testing carried out for the samples obtained demonstrated that the yield of glycidol depending on the temperature of the hydrothermal treatment of the catalyst samples exhibits an extreme character (Fig. 5).

According to IR spectroscopy, the temperature increase at the stage of hydrothermal treatment within the range 130–200 °C results in an increase in titanium content in the crystal lattice of the zeolite obtained. As a consequence, an increase in the catalytic activity of the samples is observed to cause an increase in the glycidol yield. At the same time, a decrease in the catalytic activity is observed for the sample whereto the hydrothermal treatment was performed at the temperature of 200 °C. To all appearance, this could be explained by the fact that there are titanium compounds formed in extraskeletal hexacoordinated state those do not exhibit catalytic activity [5]. In addition, the decomposition of the structure-forming agent (TPAH) and the formation of amorphous silicon in significant amounts at high temperature values also results in decreasing the glycidol yield.

Effect of hydrothermal treatment duration

In order to evaluate the effect of the duration of the stage of hydrothermal treatment we synthesized a series of the catalyst samples at a molar ratio between reactants TEOS/TBOT/TPAH/H_2O = 1 : 0.04 : 0.25 : 25 with different exposure time (19, 40, 62, 83 h).
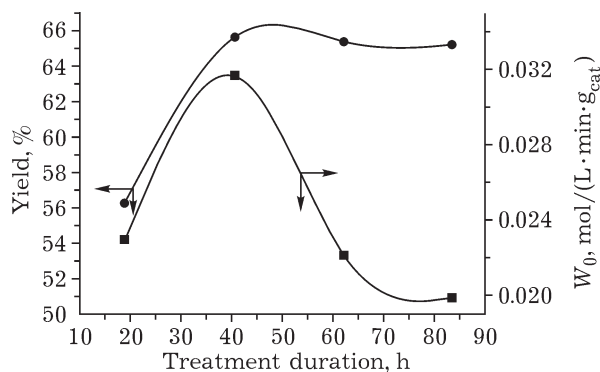
Fig. 6. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) and the initial rate of glycidol formation depending on the duration of hydrothermal treatment.

Fig. 7. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) depending on washing the catalyst by methanol (*1*), water (*2*), isopropanol (*3*), acetone (*4*), hydrochloric acid and hydrogen peroxide a mixture (*5*), hydrochloric acid (*6*) hydrogen peroxide (*7*).

All the samples obtained were characterized according to the XRD phase analysis by a high level of crystallinity (close to 100 %). However, even with a high crystallinity, but a low duration of hydrothermal treatment the activity of the samples is less than the activity of the samples with the same crystallinity and greater exposure. This could be explained by the fact that the introduction of titanium into the framework of the zeolite takes place gradually, as it is indicated by an increase in the relative intensity of corresponding bands in the IR spectra of the samples with increasing exposure time at the stage of hydrothermal treatment.

The regularities revealed are in a good agreement with the results of catalytic testing the samples (Fig. 6). Increasing the hydrothermal treatment duration results in an increase in the glycidol yield which remains almost constant with exposing the samples during more than 40 h.

Effect of the nature of washing liquid

In order to reveal the most efficient solvent used at the washing stage, we obtained a series of the catalyst samples at a molar ratio between reactants $TEOS/TBOT/TPAH/H_2O = 1 : 0.02 : 0.43 : 25$, wherein the conditions of washing differed from each other. As a washing solvent we choose acetone, water, isopropanol, methanol, 3 % hydrogen peroxide, the mixture of 3 % hydrogen peroxide with 3 % HCl solution.
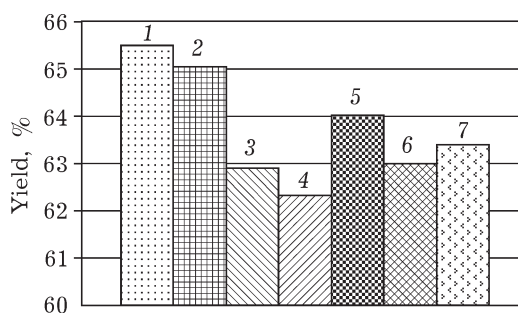
Figure 7 demonstrates data concerning the catalytic activity of the catalyst samples obtained using different solvents at the washing stage.

The differences in the catalytic activity of the samples, to all appearance, could be caused to a considerable extent by different levels of liberating the pores from the organic structure-forming base.

For the series of solvents such as acetone, isopropanol, water, methanol one observe an increase in the yield of glycidol, which is, to all appearance, connected with the size of solvent molecules as well as with the ability of washing out a structure-forming agent and impurities adsorbed by the crystals of titanium-containing zeolite in the course of the hydrothermal treatment. However, water that exhibits the smallest molecular size in the series under consideration, due to the hydrophobicity of the titanium-containing zeolite surface has less wettability and, consequently, a lower wetting ability comparing to methanol.

It is known [6] that hydrogen peroxide can react with TiO_2, resulting in the formation of orthotitanic acid H_4TiO_4 soluble in water and dilute acids. In this connection, in order to enhance the catalytic activity of the samples and for a more complete removal of the anatase and the structure-forming agent residue from the pores of the catalyst, we studied aqueous solutions of hydrogen peroxide, hydrochloric acid, and their mixtures as the washing liquid. It was found that such treatment does not increase the catalytic activity of titanium-containing zeolite. Similar results were obtained for the aqueous
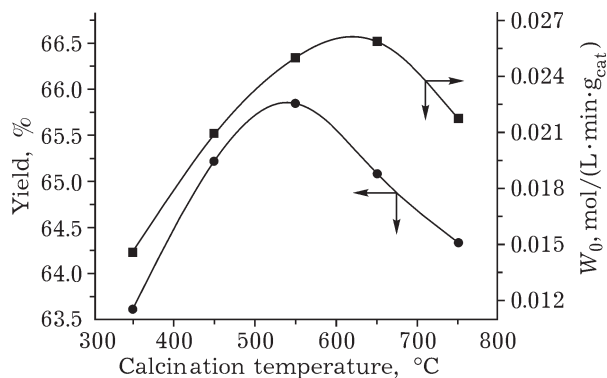
Fig. 8. Yield of glycidol (the conversion level of hydrogen peroxide being equal to 70 %) and the initial rate of glycidol formation depending on the calcination temperature titanium-containing zeolite.

Fig. 9. IR spectra for the catalyst samples prepared by calcination at 550 (*1*) and 750 °C (*2*).

solution of hydrochloric acid and the aqueous solution of hydrochloric acid and hydrogen peroxide. Thus, the use of water with the addition of hydrogen peroxide, hydrochloric acid, or their mixtures as a washing agent does not increase the catalytic activity of the samples.

Effect of calcination temperature

In order to determine the optimal temperature maintained at the stage of the catalyst calcination, we obtained a series of titanium-containing zeolite samples with a molar ratio between reactants TEOS/TBOT/TPAH/H_2O = 1 : 0.025 : 0.43 : 25, with different annealing temperatures (350, 450, 550, 650, 750 °C).

The results for the catalytic testing of the samples are demonstrated in Fig. 8.

The low yield of glycidol for the samples obtained without calcination or at a relatively low calcination temperature could be caused, to all appearance, by an insufficient removal of the structure-forming agent from the inner surface of the catalyst. With increasing the calcination temperature, the yield of the target product increases, but at the temperatures higher than 550 °C again a decrease of the glycidol yield is observed. The latter is due to the phase transitions in the structure of the catalyst resulting in its partial destruction with the formation of an inactive form of TiO_2 such as rutile.

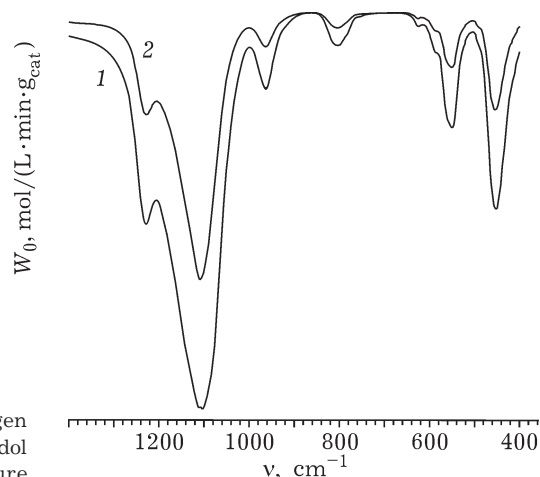In addition, the decrease of the amount of tetra-coordinated titanium was also confirmed

by data obtained by IR spectroscopy. Figure 9 demonstrates the IR spectra of the catalyst samples calcined at 550 and 750 °C. Decreasing the intensity of the absorption band at 960 cm^{-1} for the second sample indicates a decrease in the amount of titanium incorporated into the crystal lattice of the zeolite.

In addition, with increasing the calcination temperature, the formation of agglomerates is observed due to the coalescence of particles through one or more faces.

CONCLUSION

The analysis of the results of studies concerning the stages of titanium-containing zeolite preparation allowed us to determine the optimum conditions for the synthesis of titanium-containing zeolite as it follows: the initial molar ratio tetrabutoxytitanium: tetraethoxysilane being equal to 0.04–0.06, the molar ratio tetrapropylammonium hydroxide : tetraethoxysilane being equal to 0.25–0.5, the temperature and duration of hydrothermal treatment carried out in the course of mixing being equal to 170 °C and 40–60 h, respectively. The process of cleaning titanium-containing zeolite should be performed either with the use of demineralised water, or by means of methanol. The calcination temperature should be equal to 550 °C.

The samples of titanium-containing zeolites obtained under these conditions, exhibit a high

catalytic activity and they could be recommended for industrial applications.

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