Article

Epoxidation of 1,5,9-Cyclododecatriene with Hydrogen Peroxide over Ti-MCM-41 Catalyst

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Abstract: This work presents the results of our research on the epoxidation of 1,5,9-cyclododecatriene (CDT) with hydrogen peroxide over the Ti-MCM-41 catalyst. The influence of the following parameters on the course of the process was investigated: temperature, CDT:H_2O_2 molar ratio, solvent composition and its type, and catalyst content. The highest selectivity of CDT transformation to 1,2-epoxy-5,9-cyclododecadiene (ECDD)—approximately 100 mol%, the highest yet reported—was obtained at the CDT conversion of 13 mol% and with the following parameter values: a catalyst content of 5 wt%; a molar ratio of CDT:H_2O_2 = 2; isopropyl alcohol (i-PrOH) as the solvent, with a composition of 80 wt% in the reaction mixture; a temperature of 80 °C; and a reaction time of 240 min. The highest conversion of CDT (37 mol%) was obtained at the ECDD selectivity of 56 mol% and using the following process parameters: a catalyst content of 5 wt%; a molar ratio of CDT:H_2O_2 = 0.5; i-PrOH used as the solvent, with solvent composition of 80 wt%; a temperature of 80 °C; and a reaction time of 60 min. It should be emphasized that the CDT conversion obtained in the current study is higher (by 9 mol%) than that described in the literature on heterogeneous catalysts.

Keywords: 1,5,9-cyclododecatriene; 1,2-epoxy-5,9-cyclododecadiene; hydrogen peroxide; Ti-MCM-41

1. Introduction

1,2-Epoxy-5,9-cyclododecadiene (ECDD) is obtained by epoxidation of 1,5,9-cyclododecatriene (CDT). Due to the high degree of functionalization of the molecule, ECDD can be used in the production of cross-linked polymers. Polymers obtained with the use of ECDD are used in the production of batteries [1–4], capacitors [5], cross-linked acrylic rubbers [6], antistatic coatings [7], and antibacterial coatings [8]. As an intermediate, this compound is used in the production of monomers, such as laurolactam and decanedicarboxylic acid (dodecanedioic acid, DDA) [9]. DDA has found applications as a raw material for several types of resins (polyurethane, polyester, and polyamide), and also as a curing agent for acrylic powder paints. During the reaction of DDA with various alcohols and diamines, polyester and polyamide resins with excellent performance are obtained, especially in terms of hydrolytic resistance, flexibility, and heat stability. Moreover, DDA is used as the raw material for obtaining synthetic musk fragrances, in a variety of organic synthesis processes, and is also used as a rust-preventive in cutting oil. Interestingly, though it is a valuable industrial compound, UBE Industries is the sole manufacturer of DDA in Japan [10].

One of the most appealing areas of possible applications of ECDD is in the perfume industry. According to the Fankhauser patent from the Firmenich company, ECDD can

be used as an ingredient in perfumes with an earthy and musky scent [11]. In addition, ECDD can be isomerized, and as a result 4,8-cyclododecadienone is obtained (Figure 1)—a compound used as the ingredient in perfumes with a woody-musky scent [12]. A summary of ECDD applications is presented in Figure 2. Applications of ECDD.
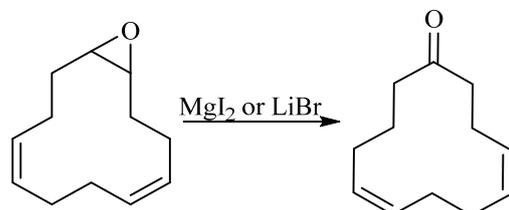

Figure 1. 1,2-Epoxy-5,9-cyclododecadiene (ECDD) isomerization to 4,8-cyclododecadienone.
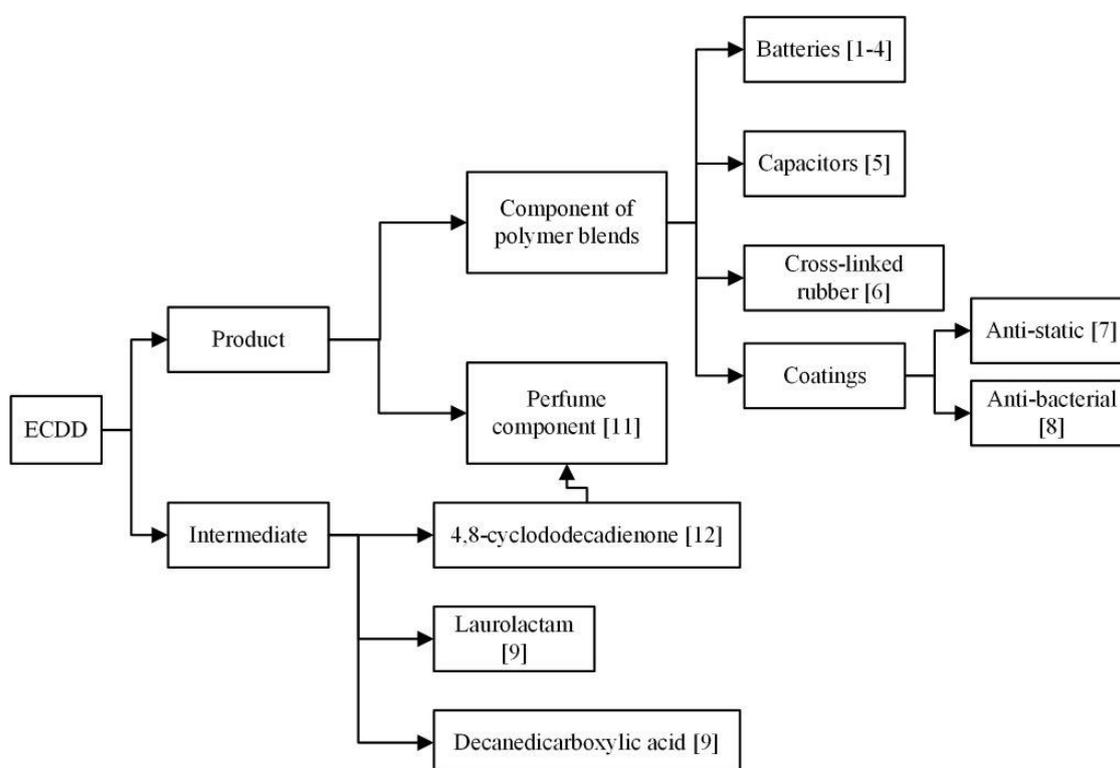

Figure 2. Applications of ECDD.

Studies on CDT epoxidation were performed mainly with the use of homogeneous catalysts. Many methods have been developed for the preparation of ECDD under the conditions of traditional homogeneous catalysis, as well as under the conditions of phase transfer catalysis (PTC). On the other hand, research on CDT epoxidation with the participation of heterogeneous catalysts, e.g., titanium silicate catalysts, is conducted less frequently.

Under homogeneous conditions, ECDD can be obtained as a result of the reaction of CDT with acetic peracid ex situ [13] or in situ [14]. Another possibility is the use of hydrogen peroxide and lithium compounds as a catalyst [15]. This process can also be performed with the use of tert-butyl hydroperoxide and homogeneous molybdenum catalysts under batch [16] or continuous conditions using a cascade of reactors [17].

The presence of two mutually incompatible phases is characteristic of the oxidation reactions carried out under PTC conditions. The first is the aqueous phase, containing water and hydrogen peroxide. The second phase includes the solvent, CDT, and the products ECDD and diECDD. The PTC oxidation catalyst consists of two parts: the first is responsible for interphase transport (most often it is the onium salt), and the second is responsible for

oxidation (often these are compounds formed as a result of the reaction of tungsten acid or its salt with hydrogen peroxide). There is already a large amount of information available in the literature on the obtainment of ECDD under these conditions [9,18–20].

Titanium silicates (catalysts TS-1 and TS-2) have been known since the 1990s and still enjoy the unflagging interest of scientists. The result of further research on these catalysts was the synthesis of such titanium silicate catalysts as Ti-MCM-41, Ti-MWW, Ti-SBA-15, and Ti-SBA-16. Another direction of research on titanium silicate catalysts currently being developed, is the modification of their methods of synthesis in order to obtain materials with greater durability, containing pores of larger diameter, containing more titanium (the active center of the catalyst), and thus more active in oxidation processes involving hydrogen peroxide. In the case of TS-1 zeolite, an example of modification of its synthesis is the addition of starch to the crystallization gel, which reduces the amount of anatase (this compound blocks the pores of the catalyst) and, consequently, increases the activity of the catalyst [21]. Another example of TS-1 modification may be the addition of non-ionic surfactants to the crystallization gel, such as Triton X-100 [22], Pluronic P123, or F127 [23]. Performing the crystallization in the presence of these surfactants results in the formation of larger agglomerates of TS-1 crystals and the production of additional mesopores. Research is also being conducted on the modification of the synthesis methods of the mesoporous Ti-MCM-41 catalyst by, for example, modifying its structure so as to lead to the production of additional mesopores. This was achieved by adding Amberlite IRA-900 ion exchange resin [24,25] to the crystallization gel, or by desilication and subsequent titanation [26].

The first reports on the possibility of epoxidation of CDT over titanium silicate catalysts were published in 2010 by the Lin research group [24]. The publication concerned the preparation and characterization of the titanium silicate catalyst obtained with the addition of Amberlite IRA-900 ion exchange resin to the crystallization gel. The catalyst modified in this way showed a higher catalytic activity, which resulted from the presence of macropores with a diameter of approximately 40–50 nm, created as a result of the use of this resin. The presence of such large pores in the resulting material allowed epoxidation of larger olefins, such as CDT. Catalytic experiments enabled the conversion of CDT to reach 11.3 mol%, while the selectivity of transformation to ECDD was equal to 95.6 mol%. The reaction was performed with the CDT/H_2O_2 molar ratio of 2:1 (H_2O_2 was used as 50 wt% aqueous solution) at a temperature of 60 °C for 5 h and using acetonitrile as the solvent.

Another publication regarding the possibility of using titanium silicate catalysts in CDT epoxidation was the use of the titanium silicalite catalyst, also obtained with the addition of Amberlite IRA-900 resin, but with the use of other raw materials [25]. The authors of the publication did not specify exactly what type of catalyst they modified; however, from the raw materials used, it can be concluded that it was similar to Ti-MCM-41. This catalyst made it possible to obtain higher CDT conversion (25.2 mol%) with comparable selectivity of transformation to ECDD (96.8 mol%) under reaction conditions similar to those in the previous tests (the concentration of H_2O_2 used was 35 wt%). The use of the standard Ti-MCM-41 (without modification by the resin) under similar conditions resulted in the very low conversion of CDT equal to 7.3 mol%, however, the selectivity of transformation to ECDD reached 97.3 mol%.

The next reports on the synthesis of the large olefin epoxidation catalyst were also the work of the previously mentioned Lin group [26]. This time, a desilicated and then titanated MCM-41 catalyst was used. Such modification resulted in a significant increase in the pore size of this material compared to the standard Ti-MCM-41 (12.7 and 2.7 nm, respectively). Using this catalyst, it was possible to obtain a CDT conversion of 28.2 mol%. For standard Ti-MCM-41, the conversion was 20.8 mol%. The epoxidation conditions were similar to those used in the studies described above.

Recent published research on CDT epoxidation using titanium silicalite catalysts is also from the Lin group [27]. This time the TS-1 catalyst modified by adding Amberlite IRA-900 resin to the crystallization gel was used. The catalyst modified in this way had micropores with a diameter of about 0.54 nm occurring in the structure of the standard

TS-1, and macropores with a diameter of 20–100 nm derived from the ion exchange resin. Using this catalyst under reaction conditions similar to those described in the previous studies (shaking was used instead of a magnetic stirrer), the authors achieved the CDT conversion of 15.6 mol% and the ECDD selectivity of 97.0 mol%.

A major problem in the reaction producing ECDD is the formation of diECDD as a result of the subsequent epoxidation of the second double bond (Figure 3). The formation of diECDD is the main cause of lowering the selectivity of transformation of CDT to ECDD. In order to obtain a high selectivity for ECDD it is necessary to carry out the CDT epoxidation process with low CDT conversion.
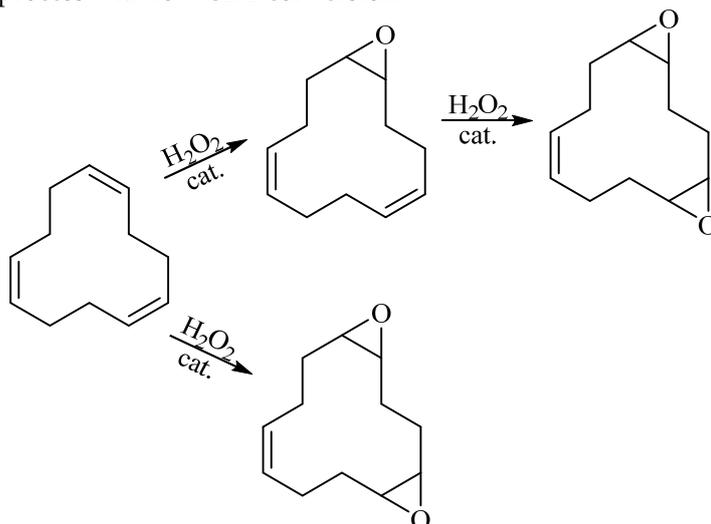

Figure 3. Schematic diagram of the 1,5,9-cyclododecatriene (CDT) epoxidation process.

Currently, there are only a few reports on the preparation of ECDD over titanium silicate catalysts and there is no research on the influence of parameters such as temperature, amount of catalyst, or reaction time on the course of the epoxidation process. Therefore, in this work, we decided to check the possibilities of CDT epoxidation over the Ti-MCM-41 catalyst. It is a mesoporous material, which is one of the most commonly used catalysts in the epoxidation of large organic molecules. In this publication we present the results of the first series of our studies on the influence of selected parameters, such as temperature, molar ratio of CDT:H_2O_2, solvent content and type, and catalyst content on the course of CDT epoxidation over the Ti-MCM-41 catalyst.

2. Results

After obtaining the Ti-MCM-41 catalyst, we first determined its characteristics using appropriate instrumental methods (N_2-sorption, XRD, SEM, EDX, UV-Vis, and FT-IR), and then we conducted research on the activity of this catalyst in the CDT epoxidation. Figure 4 shows the EDX spectrum of the Ti-MCM-41 catalyst.
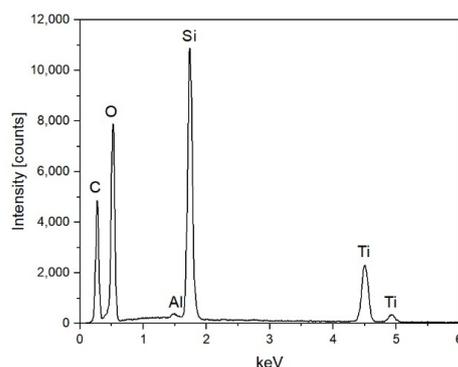

Figure 4. EDX spectrum of Ti-MCM-41.

The Ti content estimated on the basis of the EDX spectrum was equal to 4.5%. The presence of C is caused by the carbon tape and that of Al by the SEM specimen stub.

Figure 5 presents the N_2 adsorption/desorption isotherm and pore size distribution curve of Ti-MCM-41.
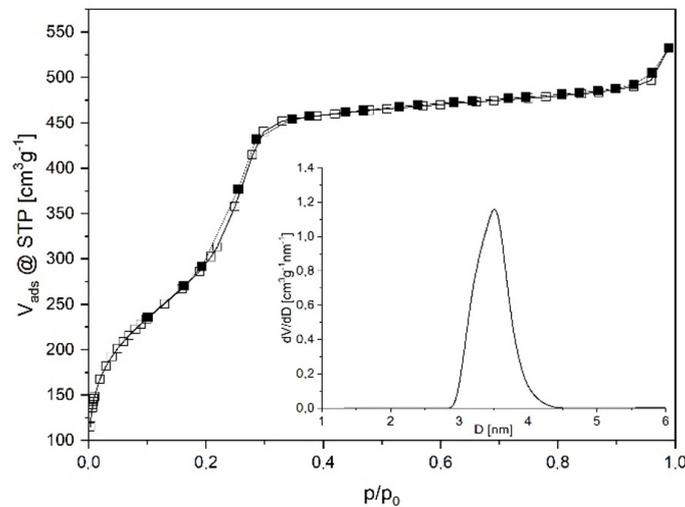

Figure 5. The N_2 adsorption/desorption isotherm and pore size distribution curve of Ti-MCM-41.

The N_2 adsorption/desorption isotherm (Figure 5) represents a type IV isotherm according to the IUPAC classification with a sharp inflection at a relative pressure of about 0.3, which is characteristic of capillary condensation within uniform mesopores. A very narrow H1 type hysteresis loop is observed in the relative pressure range of 0.18–0.34. This indicates the very regular mesoporous channels. The DFT pore size distribution curve confirms narrow pore size distribution between 3 and 4 nm. The BET surface area was equal to 1071 m^2/g and the total pore volume was 0.826 cm^3/g.

Figure 6 presents the XRD diffraction patterns of Ti-MCM-41.

Figure 6. XRD diffraction patterns of Ti-MCM-41.

The small and high angle XRD patterns of Ti-MCM-41 are presented in Figure 6. The small angle XRD investigations show an intense peak at $2\theta = 2.43$ (100) characteristic of the mesostructure and MCM-41 materials. The typical pattern of the well-ordered hexagonal mesoporous material with space group p6mm is a strong peak about 2.1 (100) and three weak ones about 3.56, 4.08, and 5.4° that correspond to (110), (200), and (210) reflections [28–30]. The shift of (100) reflections and absence of the weak signals suggests

a decrease of the spatial regularity compared with the typical structure of MCM-41. The high angle XRD investigations show a very wide peak at about 2θ = 23.11° due to the amorphous nature of Ti-MCM-41. This signal is typical for amorphous silica [31].

Figure 7 shows the SEM image of Ti-MCM-41. SEM investigations reveal the spherical morphology of Ti-MCM-41, and the average diameter was equal to 420 nm.
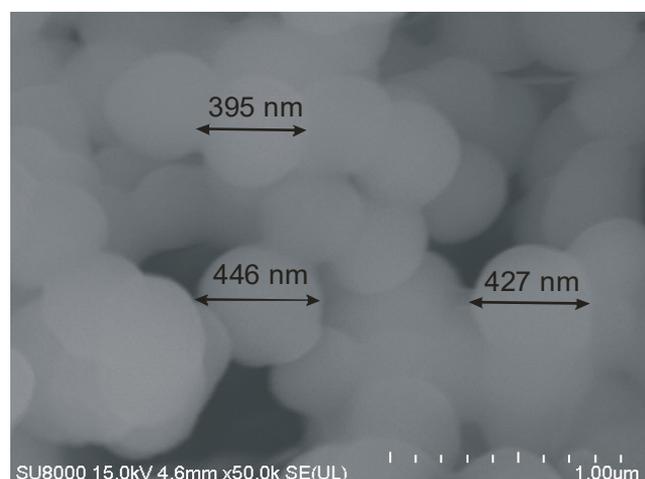

Figure 7. SEM image of Ti-MCM-41.

The results of the tests of the Ti-MCM-41 catalyst using the UV-Vis method are shown in Figure 8.

Figure 8. The UV-Vis spectrum of the Ti-MCM-41 catalyst.

The UV-Vis spectrum for the Ti-MCM-41 catalyst is characterized by an intense absorption band for the 255 nm wavelength and two weak absorption bands for the 290 and 350 nm wavelengths. The literature data show that the absorption for wavelengths < 260 nm is caused by the presence of tetrahedral titanium in the silica structure [32]. The bands 255–260 nm and 290 nm are assigned to titanium, whose atoms are tetrahedrally coordinated in the structure of silica, to which also one or two water molecules were coordinated. However, some literature data described the widening and shifting of the absorption bands towards higher wavelengths and this was thought to be caused by the presence of clustered titanium ions and TiO$_2$, as found for the Ti-SBA-15 catalyst [33,34]. There are some theories

showing the way of coordinated of titanium in the silica lattice [35]. Possible methods of binding the titanium in the Ti-MCM-41 catalyst are presented in Figure 9.

Figure 9. Possible methods of titanium binding in the Ti-MCM-14 catalyst: (**a**) Ti is bounded in the silica structure in the same manner as Si, (**b**) Ti is present in the form of Ti=O groups (titanyl groups), (**c**) Ti is present in the form of hydrated titanyl groups, (**d**,**e**) possible dimeric structures of titanium on the surface of the catalyst.

Figure 10 shows the FT-IR spectrum of the Ti-MCM-41 catalyst used in our research.

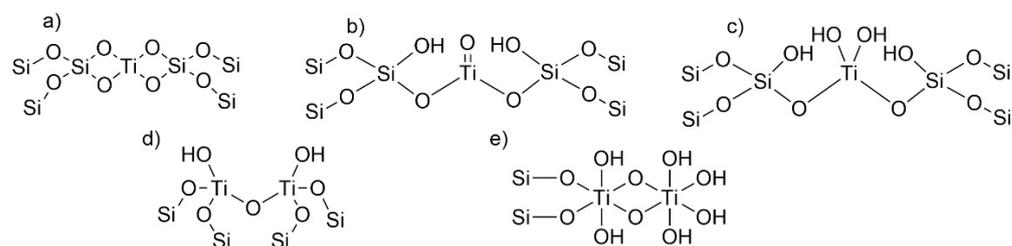**Figure 10.** FT-IR spectrum of Ti-MCM-41 catalyst.

In the FT-IR spectrum of the Ti-MCM-41 catalyst there are absorption bands at 440 and 800 cm^{-1}, which correspond to deformation vibrations of the Si–O–Si groups. The band at 960 cm^{-1} is related to the isomorphic substitution of Si by Ti, and it confirms the incorporation of Ti into the catalyst structure. The band in the range of 1000–1300 cm^{-1} corresponds to the Si–O–Si bonds present in the silica structure—the band characteristic of silicate materials. The bands around 3500 cm^{-1} correspond to water adsorbed on the catalyst surface, and the band at 2350 cm^{-1} corresponds to adsorbed CO_2 [36].

In the first stage of the catalytic tests of the Ti-MCM-41 catalyst, the influence of temperature on the course of CDT epoxidation was investigated. The range of temperature

changes was 60–90 °C. The tests were carried out in a range of reaction times from 15 to 240 min. The results of these tests are presented in Figure 11 and in Table 1.

Figure 11. Conversion of CDT and selectivity of transformation of CDT to ECDD as a function of time for reactions performed at different temperatures. Reaction conditions: i-PrOH solvent, 80 wt%; catalyst, 5 wt%; CDT:H_2O_2 molar ratio, 1:1; mixing speed, 500 rpm.
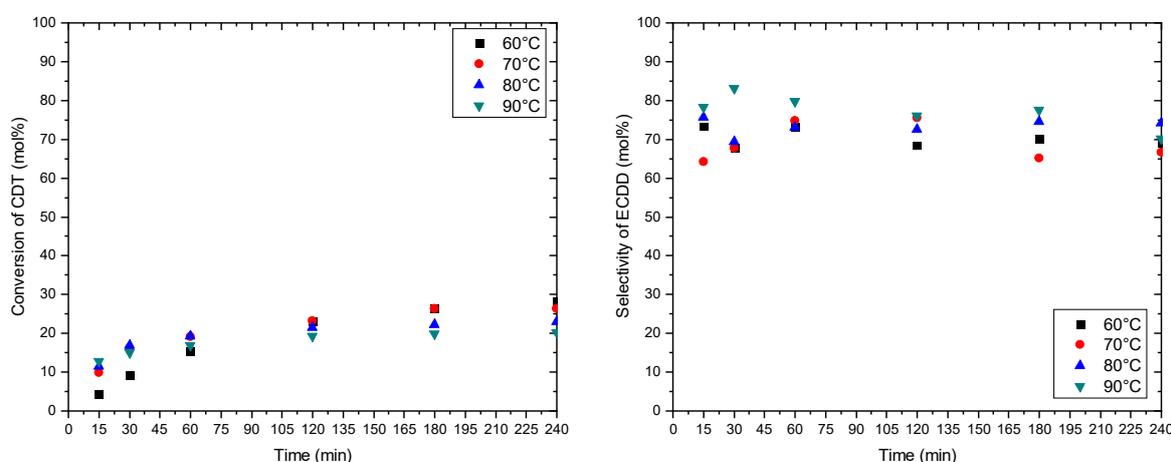
Table 1. Values of the conversion of H_2O_2 and selectivity of transformation of H_2O_2 to ECDD obtained after 4 h of performing the reaction at different temperatures. The reaction conditions were as described in Figure 11.

Temperature, °C	Conversion of H_2O_2, mol%	Selectivity of Transformation of H_2O_2 to ECDD, mol%	Blank Test H_2O_2 Conversion, mol%
60	68	29	80
70	81	22	98
80	89	20	98 (12 without catalyst)
90	93	16	99

Figure 11 shows that the temperature only slightly influences the results of the epoxidation process. The upward trend in CDT conversion is most evident when comparing the value of this function describing the process at 60 °C with its values at higher temperatures. For the reaction time up to 30 min, the CDT conversion is then approximately two times lower at 60 °C with respect to the other tested temperatures. After 60 min, the increase in CDT conversion stops at temperatures of 80 and 90 °C, while the value of this process function increases at temperatures of 60 and 70 °C. Most likely, the differences between the individual maximum CDT conversion values for the tested temperatures are the results of H_2O_2 depletion due to its ineffective degradation.

The selectivities of ECDD formation from CDT (Figure 11) are relatively constant throughout the reaction. The constant value of the selectivity of transformation to ECDD, maintained at the level of about 70 mol%, may indicate that some of the side reactions taking place are parallel. The analysis of the chromatograms of the tested samples of the reaction mixtures showed that the reaction also produced a number of by-products, which, however, we were unable to identify due to their very low concentrations in the reaction mixture. However, it can be assumed that among them were oxidation products of allylic carbons in the CDT molecule (2,6,10-cyclododecatrienol and 2,6,10-cyclododecatrienone).

Reactions with the participation of hydrogen peroxide are characterized by the ineffective decomposition of H_2O_2. It can occur under the influence of temperature, as a result of reaction with active centers of titanium on the surface of the catalyst and in its pores in the Ti-MCM-41 structure, and hydrogen peroxide can also accumulate in the pores of the catalyst. Hence, in this work, we used the titration method to determine the amount

of hydrogen peroxide that remained in the reaction mixture after the completion of the reaction. On this basis, we calculated the total conversion of hydrogen peroxide, which is then presented in Tables 1–5. On the basis of the number of moles of ECDD obtained, we calculated what part of hydrogen peroxide was transformed to ECDD. In Tables 1–5 this was presented as selectivity of transformation of hydrogen peroxide to ECDD—it is a value related to the effective conversion of hydrogen peroxide. Thus, the remaining part of the hydrogen peroxide reacted ineffectively, i.e., it decomposed under the influence of temperature and in the active centers of titanium in the catalyst, or it remained in the pores. It can be assumed that the latter phenomenon is least responsible for the ineffective conversion of hydrogen peroxide. When it comes to the influence of temperature on the decomposition of hydrogen peroxide and its decomposition in the active centers of the catalyst, it appears that the decomposition of hydrogen peroxide in the active centers should be of greater importance here than the temperature of the epoxidation process. The increased temperature may accelerate the hydrogen peroxide decomposition process in the active centers of the catalyst. Table 1 presents the parameters describing the utilization of H_2O_2 in the tested process. It can be seen that with increasing temperature, the conversion of H_2O_2 increases, and at the same time the selectivity of its transformation to ECDD decreases.

Having hypothesized that the differences in CDT conversions are mainly due to the decomposition of H_2O_2, we decided to examine the CDT:H_2O_2 molar ratio as another important process parameter (Figure 12, Table 2).

Table 2. Values of the conversion of H_2O_2 and selectivity of transformation of H_2O_2 to ECDD obtained after 4 h of performing the reaction with different molar ratios of CDT:H_2O_2. The reaction conditions were as described in Figure 12.

Molar Ratio CDT:H_2O_2	Conversion of H_2O_2, mol%	Selectivity of Transformation of H_2O_2 to ECDD, mol%
0.5	86	12
1	89	20
2	91	30

Figure 12. Conversion of CDT and selectivity of transformation of CDT to ECDD as a function of time for reactions performed with different CDT:H2O2 molar ratios. Reaction conditions: i-PrOH solvent, 80 wt%; catalyst, 5 wt%; temperature, 80 °C; mixing speed, 500 rpm.

When analyzing the results presented in Figure 12, it can be seen that, in contrast to changes in temperature, a change in the CDT:H_2O_2 molar ratio significantly affects each of the two tested functions describing the course of the CDT epoxidation process. As the excess CDT is reduced, a significant increase in CDT conversion can be seen, accompanied

by a decrease in the selectivity of transformation to ECDD. The decrease in the selectivity of transformation to ECDD is most evident when changing the ratio from two to one, and its further reduction does not cause such a significant decrease in the value of this function. It is worth noting that in this series of tests it was possible to obtain the highest values of two examined functions of the process: selectivity of transformation to ECDD at about 100 mol%, and conversion of CDT reaching a maximum of 37 mol% after 240 min of reaction.

The results presented in Table 2 indicate that the reduction of the CDT:H_2O_2 molar ratio causes a significant increase in side reactions, resulting in a significant decrease in the selectivity of the transformation of H_2O_2 to ECDD. Conversely, the conversion of H_2O_2 depends on the molar ratio of reactants only to a very small extent. The results obtained in this series of tests seem to confirm the proposed hypothesis that the reaction is largely limited by the decomposition of H_2O_2.

Figure 13 and Table 3 present the results of studies on the influence of solvent (i-PrOH) concentration on the course of the CDT epoxidation.

Table 3. Values of the conversion of H_2O_2 and selectivity of transformation of H_2O_2 to ECDD obtained after 4 h of performing the reaction with different i-PrOH solvent compositions. Reaction conditions were as given for Figure 13.

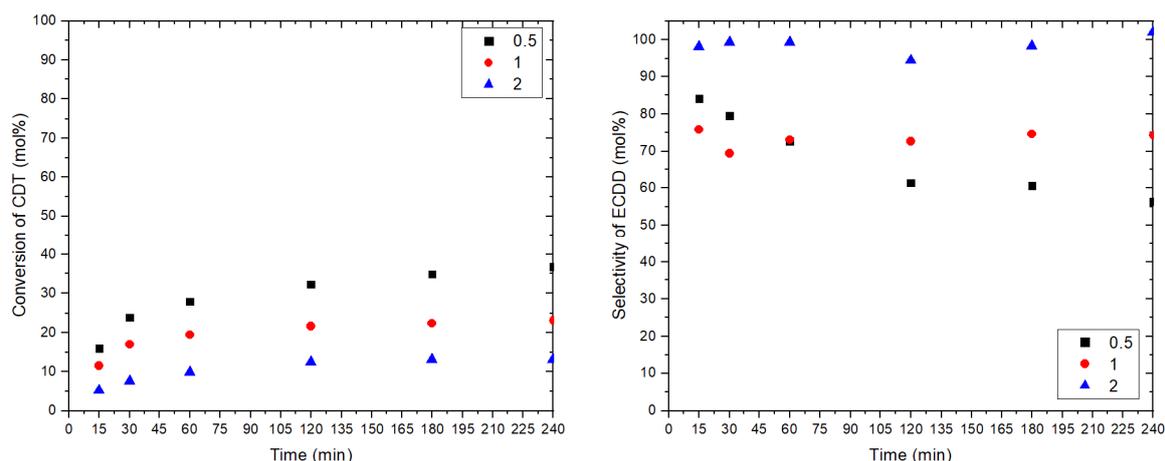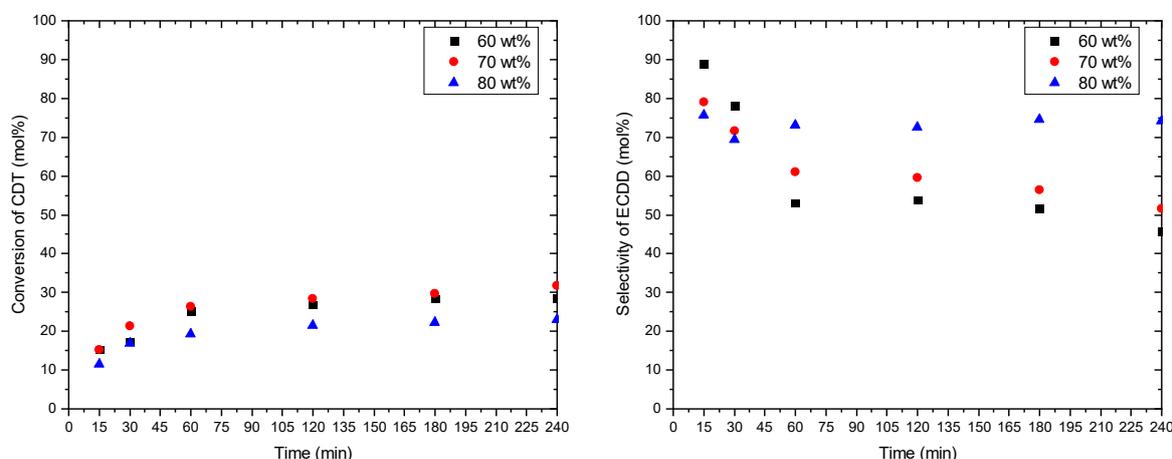| Solvent Content, wt%	Conversion of H_2O_2, mol%	Selectivity of Transformation of H_2O_2 to ECDD, mol%
60	90	15
70	85	20
80	89	20

Figure 13. Conversion of CDT and selectivity of transformation of CDT to ECDD as a function of time for reactions performed with different solvent compositions. Reaction conditions: i-PrOH solvent; CDT:H_2O_2 molar ratio, 1:1; catalyst, 5 wt%; temperature, 80 °C; mixing speed, 500 rpm.

In this series of tests, the aim was to check what effect the gradual concentration increase of the reaction mixture has on the results of the epoxidation process. When planning the research, we decided that we would gradually reduce the proportion of solvent in the reaction mixture by 10% until there were problems with solubility. They occurred at a solvent composition of 50 wt% in the reaction mixture. Therefore, the tests were performed only for solvent concentrations of 60, 70, and 80 wt%. For the current research, we chose isopropanol based on the preliminary research that we conducted, though acetonitrile is typically used by researchers in the process we are investigating, as discussed in detail in the introduction to this article.

From Figure 13, which shows the changes in the main functions describing the process as a function of reaction time, it can be concluded that the reduction of the solvent content in the reaction mixture from 80 to 70 wt% has the greatest impact on the results. This causes a slight increase in conversion of CDT from the beginning of the reaction and a decrease in the selectivity of the transformation to ECDD after 60 min. Further lowering of the solvent content no longer increases the conversion of CDT; only the selectivity of transformation to ECDD is slightly decreased.

The results presented in Table 3, describing the use of H_2O_2 in the tested reaction, seem to be slightly dependent on the solvent content.

Figure 14 and Table 4 present the results of studies on the influence of the type of solvent—isopropanol (i-PrOH) or acetonitrile (MeCN)—on the course of CDT epoxidation.

Table 4. Values of the conversion of H_2O_2 and selectivity of transformation of H_2O_2 to ECDD obtained after 4 h of reaction with two tested solvents. Reaction conditions were as given for Figure 14.

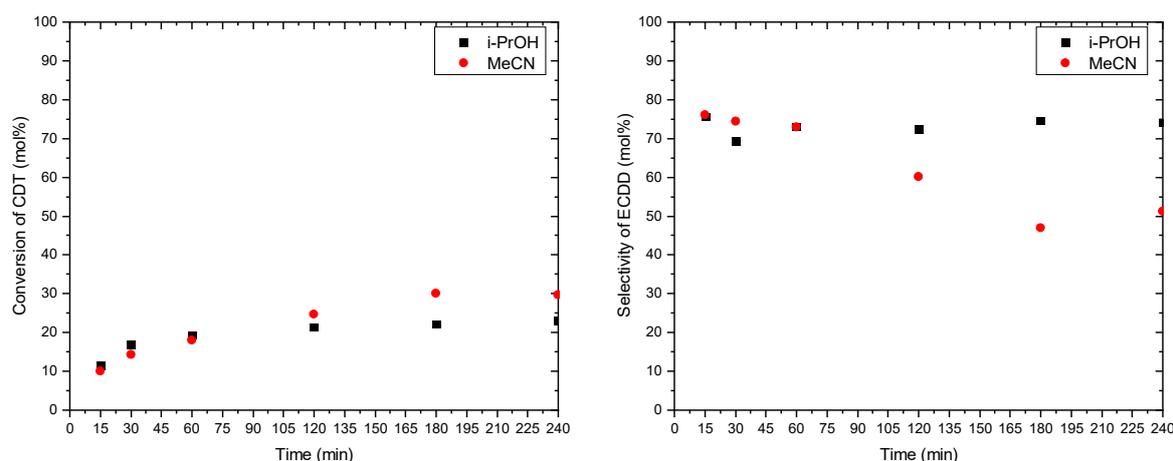| Solvent	Conversion of H_2O_2, mol%	Selectivity of Transformation of H_2O_2 to ECDD, mol%	Blank Test H_2O_2 Conversion, mol%
i-PrOH	89	20	98
MeCN	86	18	

Figure 14. Conversion of CDT and selectivity of transformation of CDT to ECDD as a function of time for reactions performed with different types of solvents. Reaction conditions: solvent concentration, 80 wt%; CDT:H_2O_2 molar ratio, 1:1; temperature, 80 °C; catalyst, 5 wt%; mixing speed, 500 rpm.

In the case of the CDT conversion and the selectivity of transformation to ECDD (Figure 14), it can be seen that up to the reaction time of 60 min, both processes are almost identical. Differences only begin to appear after the reaction time of 120 min. It is noticeable that an approximately 5% higher conversion of CDT is achieved with acetonitrile. On the other hand, the selectivity of transformation to ECDD is definitely higher, about 25% higher with isopropanol. The results of these studies show that isopropanol is a better solvent in the process that we are investigating.

The values of the functions describing the use of H_2O_2 in the epoxidation process (presented in Table 4) indicate that after 4 h these functions are independent of the type of solvent used. However, it is possible that the lower CDT conversion in the reaction performed with i-PrOH is due to slightly higher (though inefficient) rates of H_2O_2 decomposition.

Figure 15 and Table 5 present the results of studies on the influence of catalyst content on the course of CDT epoxidation.

Table 5. Values of the conversion of H_2O_2 and selectivity of transformation of H_2O_2 to ECDD obtained after 4 h of performing the reaction with different catalyst contents. Reaction conditions were as given for Figure 15.

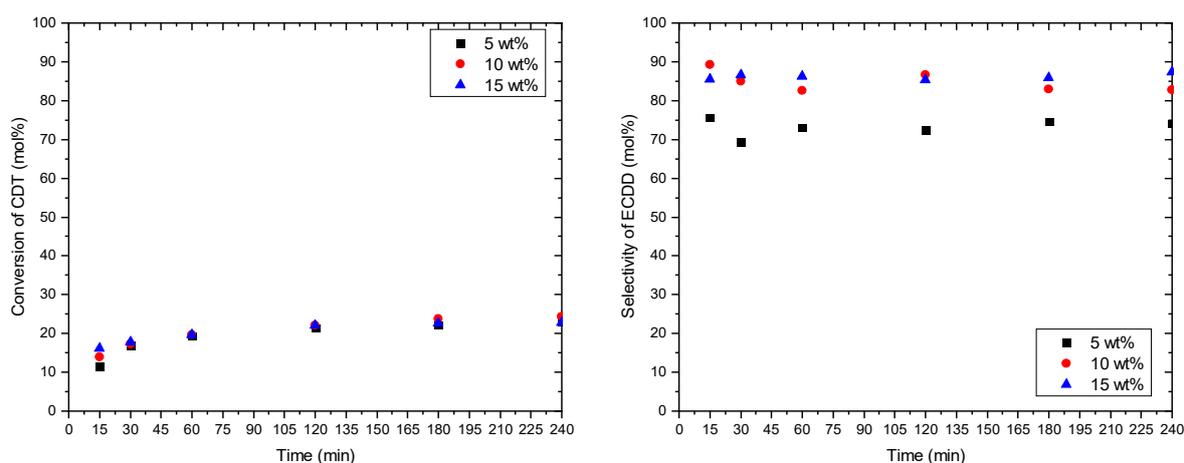| Catalyst Content, wt%	Conversion of H_2O_2, mol%	Selectivity of Transformation of H_2O_2 to ECDD, mol%
5	89	20
10	96	22
15	99	21

Figure 15. Conversion of CDT and selectivity of transformation of CDT to ECDD as a function of time for reactions conducted with different catalyst contents. Reaction conditions: i-PrOH solvent, 80 wt%; CDT:H_2O_2 molar ratio, 1:1; temperature, 80 °C; mixing speed, 500 rpm.

It is interesting to note from Figure 15 that the conversion of CDT is independent of the amount of catalyst, and the selectivity of the transformation to ECDD increases by about 10 mol% with the increase in catalyst content from 5 to 10 wt%. On the other hand, a further increase in the catalyst content in the reaction mixture (to 15 wt%) does not result in a further increase in the selectivity of transformation to ECDD. The independence of the conversion of CDT from the catalyst content indicates that the reaction rate is limited in a way other than by diffusion. In the case of diffusion limitation, increasing the amount of catalyst should result in increasing the CDT conversion rate. Increasing the value of the selectivity of ECDD with an increase in catalyst content from 5 to 10 wt% shows that it is not the catalyst itself that is responsible for the formation of the by-products. If surface groups from the catalyst were responsible for their formation, increasing its amount would result in lowering the ECDD selectivity value.

The process functions presented in Table 5, concerning the use of H_2O_2 in the tested process, are only slightly dependent on the catalyst content. The conversion of H_2O_2 increases with the increase in catalyst content, reaching its highest value during the entire tests of 99 mol% for the catalyst content of 15 wt%. The selectivity of the transformation of hydrogen peroxide to ECDD, in turn, is independent of the catalyst content. It can be assumed that during the epoxidation process, hydrogen peroxide molecules and CDT molecules compete with each other in accessing the pores where the active centers of titanium are located. The results presented in this study show that in the active centers of titanium, the ineffective hydrogen peroxide decomposes more easily than the formation of active complexes with hydrogen peroxide, from which oxygen is then transferred to a double bond. The limitations in CDT diffusion into the pores are mainly related to the particle size of this unsaturated cyclic compound and the steric limitations in the pores due to the size and shape of the CDT molecule. Perhaps only a part of the CDT molecule

with one double bond enters the pores, which would explain the epoxidation of only one double bond and the formation of CDT. On the other hand, if the entire CDT molecule enters the pores, perhaps steric obstacles and the inability to rotate the CDT molecule in the pores cause only one bond to be epoxidized. Tetrahedral titanium in the silica structure is involved in the formation of active complexes in Ti centers. On the basis of the UV-Vis spectrum shown in Figure 8, it can be concluded that this form of titanium is the most numerous in the Ti-MCM-41 catalyst we used. The UV-Vis spectrum also shows weak bands indicating the presence of Ti tetrahedrally coordinated into which also one or two water molecules were coordinated. In such a case, active Ti centers having additionally coordinated water molecules may be even less accessible to CDT molecules due to even larger spatial obstacles. There are also solvent particles in the pores, and their presence may also affect the diffusion of CDT into the pores and the ease of access of this compound to Ti active sites. It should also be taken into account that part of the hydrogen peroxide will decompose already on the catalyst surface, where there are dimeric titanium structures (Figure 9d,e), the presence of which, in a small amount, can be confirmed on the basis of the UV-Vis spectrum presented in Figure 8.

3. Materials and Methods

3.1. Raw Materials

In the Ti-MCM-41 catalyst synthesis the following raw materials were used: hexadecyltrimethylammonium bromide (≥97%, Merck, Poznań, Poland); ammonia (30 wt% aqueous solution, pure for analysis, Chempur, Piekary Śląskie, Poland), tetrabutyl-ortotitanate (≥97,0%, Fluka, Poznań, Poland); tetraethyl silicate (98%, Aldrich, Poznań, Poland); anhydrous ethanol (pure for analysis, POCh, Gliwice, Poland).

In the epoxidation reactions the following raw materials were used: trans-,trans-,cis-1,5,9-cyclododecatriene (98%, Aldrich, Poznań, Poland), hydrogen peroxide (60 wt% aqueous solution, Chempur, Piekary Śląskie, Poland); isopropanol, i-PrOH (pure for analysis, POCh, Gliwice, Poland); acetonitrile (pure for analysis, Chempur, Piekary Śląskie, Poland); and ethylbenzene (98.8%, pure, Acros Organics, Poznań, Poland).

3.2. Method of the Synthesis of the Ti-MCM-41 Catalyst

The Ti-MCM-41 catalyst was obtained according to the method described in our previous publication [36], and the molar ratio Si/Ti in the crystallization gel was 30:1.

The catalyst has been characterized using the following instrumental methods: N_2-sorption analyses, X-ray diffraction (XRD) (X'Pert–PRO, Panalytical, Almelo, The Netherlands, 2012), and Scanning Electron Microscopy (SEM) (SU8020 Ultra-High Resolution Field Emission Scanning Electron Microscope; Hitachi Ltd, Japan, 2012).

The N_2 adsorption/desorption at 77 K investigations were performed on a Quadrasorb evo™ Gas Sorption analyzer (Anton Paar, St Albans, UK; previously Quantachrome Instruments, USA, 2014). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The density functional theory (DFT) method was applied to generate pore size distribution curves. The total pore volume was estimated on the basis of nitrogen volume adsorbed at p/p_0 equal to 0.99.

The XRD spectra were obtained using an X'Pert PRO diffractometer with CuKa radiation. Diffractions in the range $2\theta = 1–5°$ and $12–50°$ were recorded.

The SEM images were obtained using UHR FE-SEM Hitachi SU8020 equipped with energy dispersive X-ray spectroscopy (EDX) for the estimation of Ti content. The sample was grounded and mounted on carbon tape.

3.3. Method of the CDT Epoxidation

The studies on CDT epoxidation were performed in such a way that specific amounts of CDT, H_2O_2, i-PrOH (or acetonitrile, MeCN), and ethylbenzene (internal standard) were successively added to a glass reactor with a capacity of 10 cm^3. After adding the catalyst, the reactor was placed in an oil bath at the set temperature. The reactor contents were

stirred at 500 rpm with a magnetic stirrer. The influence of the following parameters was investigated during the studies on the epoxidation of CDT: temperature (60–90 °C), the molar ratio of CDT:H_2O_2 (0.5–2.0), solvent concentration (60–80 wt%), type of solvent (i-PrOH or MeCN) and catalyst content (5–15 wt%). Samples of the reaction mixture were taken after the appropriate reaction time (15, 30, 60, 120, 180, 240 min), and next centrifuged, diluted with isopropanol (1–1 *v/v*) and subjected to chromatographic analyses. After the studies on a given epoxidation process were completed, the contents of the reactor were poured into a plastic tube and centrifuged, then the H_2O_2 composition was determined using the iodometric method.

In order to avoid errors related to the change in the mass of the reactor charge, this was calculated as 8 g for each experiment. Additionally, to avoid errors related to the excessive content of the internal standard ethylbenzene (EB), this was always 5 wt% of the sum of the masses of solvents; for example, when it was necessary to use 1 g of solvent for the reaction, this mass was divided into 0.95 g of i-PrOH and 0.05 g of EB.

A blank H_2O_2 conversion test was performed by replacing the CDT with the same mass of ethylbenzene.

3.4. Conditions for Chromatographic Analyses

A Thermo Focus GC chromatograph with a Restek RTX-5 (Thermo Scientific, Waltham, MA, USA, 2012), 30 m, 0.32 mm ID, 0.25 μm column was used for gas chromatographic analyses. The quantitative analysis was performed using the internal standard method (ethylbenzene). The method of calculating the results is presented below:

Component content in the reaction mixture:

$$c_i = \alpha_i * \frac{A_i}{A_s} * \frac{m_s}{m_p} * 100\% \tag{1}$$

where α_i = directional factor of the calibration curve of component "*i*"; A_i, A_s = peak areas of component "*i*" and standard, respectively; and m_s, m_p = masses [g] of standard and sample, respectively.

Conversion of CDT and H_2O_2:

$$K_i = \frac{n_{0,i} - n_i}{n_{0,i}} * 100\% \tag{2}$$

where $n_{0,i}$, n_i = number of moles (mmol) of component "*i*", initially and at the time of measurement, respectively,

Selectivity of ECDD:

$$S_{ECDD} = \frac{n_{ECDD}}{n_{0,CDT} - n_{CDT}} * 100\% \tag{3}$$

where $n_{0,CDT}$, n_{CDT} = number of moles (mmol) of CDT, initially and at the time of measurement, respectively; and n_{ECDD} = number of moles (mmol) of ECDD at the time of measurement.

4. Conclusions

Summarizing the results presented in this work, it can be stated that the highest selectivity of CDT transformation to 1,2-epoxy-5,9-cyclododecadiene (approximately 100 mol%) was obtained at the CDT conversion of 13 mol% and with the following values for the tested process parameters: catalyst content, 5 wt%; molar ratio of CDT:H_2O_2 = 2; isopropyl alcohol (i-PrOH) as the solvent, and with the content of this solvent in the reaction mixture at 80 wt%; temperature, 80 °C; and reaction time, 240 min. The highest conversion of CDT (37 mol%) was obtained at ECDD selectivity of 56 mol% and using the following process parameters: catalyst content, 5 wt%, molar ratio of CDT:H_2O_2 = 0.5; i-PrOH used as the solvent, and the composition of this solvent was 80 wt%; temperature, 80 °C; and reaction time, 60 min.

The studies presented in this work showed that increasing the temperature in the range of 60–90 °C did not significantly affect the results of CDT epoxidation. Increasing the excess of H_2O_2 in relation to CDT causes an increase in the conversion of CDT and a decrease in the selectivity of transformation to ECDD. Lowering the solvent content in the reaction mixture from 80 to 70 wt% results in an increase in the CDT conversion rate and a decrease in the selectivity of the transformation to ECDD. On the other hand, a further reduction of the solvent content in the reaction mixture does not cause any major changes in the values of the main functions describing this process. The initial rate of increase in the conversion of CDT for MeCN and i-PrOH is very similar; after 60 min this increase stops for i-PrOH, while for MeCN the conversion continues to increase. The selectivity of transformation to ECDD is higher with i-PrOH. Increasing the catalyst content in the reaction mixture does not change the conversion of CDT. On the other hand, increasing the catalyst content in the reaction mixture from 5 to 10 wt% results in an increase in the selectivity of transformation to ECDD by about 10 mol%, while further increasing the catalyst content no longer increases the selectivity of the transformation to ECDD.

Table 6 shows a comparison of the results of CDT epoxidation described in the literature with the results obtained in this work, which produced the most favorable parameters for obtaining the maximum selectivity of ECDD and the most favorable parameters for attaining the maximum conversion of CDT.

Table 6. Comparison of literature data on the results of the CDT epoxidation reaction with the results obtained in this work.

Data Source	Catalyst	Conversion	Selectivity
[23]	TiSil-HPB-60	11.3	95.6
[24]	BMB-TiSil	25.2	96.8
[24]	Ti-MCM-41	7.3	97.3
[25]	BM-Ti-MCM-41	28.2	-
[25]	Ti-MCM-41	20.8	-
[26]	HPB-TS-1	15.6	97.0
[37]	PTC	72.3	75.9 (calculated from yield and conversion)
[this work]	Ti-MCM-41	13	100
[this work]	Ti-MCM-41	37	56

Table 6 shows that the maximum selectivity of ECDD obtained in the current work is somewhat higher than those obtained by other research groups, and that the conversion of CDT obtained is the highest among those presented so far for heterogeneous catalysts. The conversion of CDT obtained under PTC (homogeneous) conditions significantly exceeds the conversion of CDT obtained with heterogeneous catalysts.

Most likely, the results of CDT epoxidation and the fact that we only obtained ECDD (the epoxidation product of one double bond in the CDT molecule) are influenced by the size and shape of the CDT molecule. The steric effects limit the ability of CDT molecules to move through the pores. It should also be taken into account that in the pores there are also solvent and oxidant molecules—hydrogen peroxide, which additionally make it difficult for CDT molecules to access active centers. The results obtained in our research also indicate that we are dealing with two competing reactions: the decomposition of hydrogen peroxide in Ti active centers and the transfer of oxygen from the peroxide bond to the CDT double bond. Of these two reactions, the first contributes significantly more. Further research on the CDT epoxidation process should focus on increasing the selectivity of the transformation of H_2O_2 to ECDD. In this work, the maximum value of this function is only 30 mol%. Such a low efficiency of using H_2O_2 means that in order to obtain a higher conversion of CDT, an excess of oxidant should be used in the epoxidation process. This, in turn, would increase the water content of the reaction mixture and enhance ECDD hydrolysis, reducing the selectivity of the compound. Another way to improve the selectivity of the transformation of hydrogen peroxide to ECDD could be to use a

different catalyst that would not be so active in catalyzing the decomposition of hydrogen peroxide, or to reduce the forms of Ti in the catalyst used that cause the decomposition of hydrogen peroxide. However, these proposals, the latter in particular, require further detailed studies.

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