

# Studies on the deactivation of Ti-MCM-41 catalyst in the process of allyl alcohol epoxidation

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The synthesis of Ti-MCM-41 catalyst was performed. The obtained catalyst was characterized by the following instrumental methods: UV-vis, IR spectroscopy, XRD, and X-ray microanalysis. The activity of the obtained catalyst was tested in the process of allyl alcohol epoxidation with 30 wt.% hydrogen peroxide in methanol as a solvent and under atmospheric pressure. In the next stage, recovery of Ti-MCM-41 catalyst from the post-reaction mixture and its regeneration by washing with appropriate solvents and drying were conducted. In the case of total loss of the activity of the catalyst, calcination of the catalyst was also carried out. The loss of titanium from the structure of Ti-MCM-41 catalyst and a partial collapsing of the structure of this catalyst can be the main reason of the decrease the activity of the catalyst what was mainly visible in the decrease of the values of two functions of this process: the allyl alcohol conversion and conversion of hydrogen peroxide to organic compounds.

**Keywords:** titanium silicate Ti-MCM-41 catalyst, deactivation of Ti-MCM-41catalyst, regeneration of Ti-MCM-41catalyst.

## INTRODUCTION

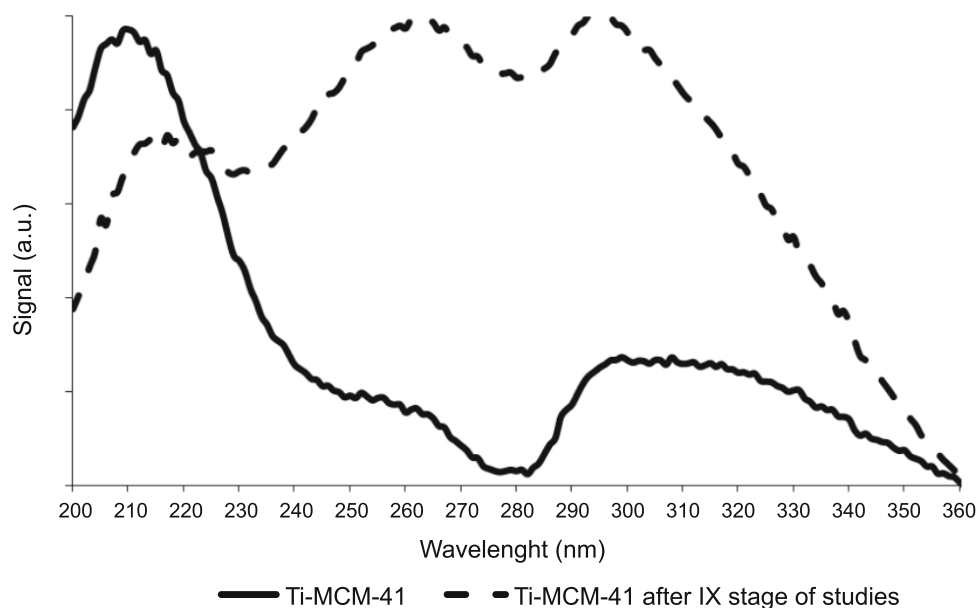
A well-known mesoporous catalyst from the M41S family is Ti-MCM-41 catalyst. The structure of MCM-41 material is characterized by one-dimensional hexagonal, elliptical or spherical parallel channel systems, whose diameter can be even up to 10 nm. The thickness of pore walls is from 0.8 up to 1.2 nm. It crystallizes in the hexagonal system and the particles have a length of 10–20  $\mu\text{m}$  and a width of 2  $\mu\text{m}$ <sup>1-2</sup>.

The process of allyl alcohol (AA) epoxidation over titanium silicalite catalysts was in detail studied in the literature – also the studies on the influence of the technological parameters on the epoxidation of allyl alcohol over Ti-MCM-41 catalyst were shown in the literature<sup>3-7</sup>. On the other hand, the studies on the deactivation and regeneration of the titanium silicalite catalysts are not completed and mainly relate to TS-1 catalyst used in the process of propylene epoxidation and phenol hydroxylation<sup>8-9</sup>. These studies showed that titanium silicate catalysts used in the epoxidation processes in the presence of hydrogen peroxide as an oxidizing agent are characterized by titanium leaching from their structures. The loss of titanium decreases the activity of the catalyst and deactivates it in the later stages of epoxidation. Ti-MCM-41 is stable at raised temperatures in air or oxygen, but in the presence of even low water amount (introduced into the reaction medium with hydrogen peroxide and formed during the epoxidation process from hydrogen peroxide) and triol (formed during the process of AA epoxidation by hydration of epoxide ring) silicalite hydrolysis can occur which causes the changes in the catalyst structure. Sheldon<sup>10</sup> et al. have proposed two types of reaction mechanisms of metal leaching from the structure of titanium silicate catalysts. The first mechanism consists in leaching inactive metal as a homogeneous catalyst and hence there is no effect of the dissolved metal complex on the course of the catalyzed reaction. In the second mechanism, the dissolved metal complex is an active, homogeneous oxidation catalyst

and in this case, homo- and heterogeneous processes compete with each other<sup>11-13</sup>. If the catalyst is exposed to the activity of water that is introduced to the reaction medium along with 30 wt. % hydrogen peroxide, Ti<sup>4+</sup> ions (I) (derived from tetrahedral titanium bonded permanently with the surface of the catalyst) change their coordination to Ti<sup>6+</sup> (II) (two water molecules are bonded additionally with active centre of Ti), while preserving bindings Ti-O-Si in the mesoporous structure of the catalyst. They permanently bond with the catalyst surface. When the reaction medium includes glycerol, hydrolysis of bindings Ti-O-Si (III) takes place which leads to a permanent loss of titanium from the catalyst structure (IV)<sup>11-13</sup> – Figure 1.

The scientific literature compared the leaching of titanium from the structure of TS-1 and Ti-MCM-41 but the epoxidized compound was not allyl alcohol but crotyl alcohol<sup>12, 14</sup>. These compounds have close structure but not the same and epoxidation process proceeds a bit differently for them. However, the results can be partially taken into account during interpretation of the results of allyl alcohol epoxidation over Ti-MCM-41 catalyst. There was observed in the process of crotyl alcohol epoxidation over TS-1 and Ti-MCM-41 that TS-1 catalyst was more stable than Ti-MCM-41. Moreover, in case of TS-1 catalyst for the leaching of Ti both triol and hydrogen peroxide were required. For Ti leaching from Ti-MCM-41 just hydrogen peroxide was needed.

Another reason for the loss of the activity of the catalyst is a pore blocking by deposition of oligomeric products (tars). The third reason the loss of the activity of the titanium silicate catalysts can be the instability of their structures in the water environment and at raised temperatures (mainly it relates to mesoporous titanium silicalite catalysts). The methods of the regeneration of TS-1 catalyst used in the process of propylene epoxidation and phenol hydroxylation relay on: calcination at temperatures 300–700°C in the presence of air, vapor and inert gas, oxidation by hydrogen peroxide, ozone, organic peroxides at temperatures lower than 100°C and



**Figure 1.** The mechanism of titanium leaching from the Ti-MCM-41 catalyst structure<sup>13</sup>

washing by different solvents at temperatures 140–240°C (mainly methanol). The methods of the regeneration of TS-1 catalyst are often time-consuming, they need large amounts of energy and use very expensive reagents (solvents, oxidizing agents). These methods also require very expensive equipment, for example – autoclaves<sup>8-9</sup>.

The results obtained during the studies on the deactivation and regeneration of the TS-1 catalysts are not always true for all titanium silicalite catalysts because these catalysts differ in: the amount of Ti in the structure, the kind of the structure and the stability of this structure in water solution at raised temperatures and the pore size. The aim of the paper was to check the activity length of Ti-MCM-41 in the epoxidation of allyl alcohol and to develop methods for regeneration of this catalyst after the epoxidation process by washing with appropriately chosen solvents, drying and calcination.

## EXPERIMENTAL

### The synthesis of Ti-MCM-41 catalyst and the characteristic of the obtained material

Titanium silicate catalyst Ti-MCM-41 was obtained by a direct precipitation from crystallization gel<sup>15</sup>. The obtained Ti-MCM-41 catalyst was characterized by the following instrumental methods: the XRD method - in order to confirm the structure of the obtained material (the studies were carried out on XPERT PRO diffractometer at an angle of 2 theta from 0 up to 10° using a copper lamp with a wavelength of 0.154 nm), by the UV-vis method – to confirm the inclusion of Ti into the MCM-41 structure (the studies were carried out with SPECORD M40 apparatus), by IR spectroscopy – also

to confirm the inclusion of titanium into the mesoporous silica structure (JASCO FT/IR-430 apparatus was used in these studies) and by X-ray microanalysis method – to determine the amount of Ti included in the MCM-41 structure (Oxford X-ray analyzer ISIS 300 was used in these studies).

### The studies on the deactivation of Ti-MCM-41 catalyst in the process of AA epoxidation

The studies on the deactivation of Ti-MCM-41 catalyst were performed in the process of allyl alcohol epoxidation with 30 wt.% hydrogen peroxide and in methanol as the solvent under conditions that had been determined by Wróblewska et al.<sup>16</sup>: a temperature of 40°C, molar ratio of allyl alcohol to hydrogen peroxide of 2:1, concentration of solvent (methanol) 80 wt.%, catalyst amount (Ti-MCM-41) 1 wt.%, reaction time of 120 min, and intensity of stirring of 650 rpm. The AA epoxidation process was carried out in a glass reactor with a capacity of 1000 cm<sup>3</sup>. The substrates were introduced into the reactor in the following order – catalyst Ti-MCM-41 (22.5 g, obtained in ITChO ZUT), AA (73.6 g, 98%, Fluka) and methanol (582.0 g, analytical grade, POCh Gliwice). Then, during the intensive stirring, the 30 wt.% aqueous solution of hydrogen peroxide (72.0 g, P.O.Ch. Gliwice) was added drop by drop and the epoxidation process was carried out for a given period of time. After the process, the post-reaction mixtures were weighed, filtered and subject to chromatographic analyses. The chromatographic analyses were taken at the following parameters: helium pressure – 50 kPa, sample chamber temperature – 200°C, detector temperature – 250°C, the temperature of the thermostat increased according to the

following program: isothermally 40°C for five minutes, temperature increase at a rate of 5°C/min, isothermally 250°C for five minutes, cooling to 40°C, sensitivity – 10, dosed sample volume – 0.2 µl. The analyses were conducted using FOCUS apparatus equipped with FID detector and with Quadrex capillary column of 30 m x 250 µm x 0.25 µm and an autosampler. The concentration of unreacted hydrogen peroxide was determined using an iodimetric method<sup>17</sup>, whereas the potentiometric method was used to mark the content of glycerol<sup>18</sup>.

After each epoxidation process (after each stage), the Ti-MCM-41 catalyst was washed two times with deionized water (two portions with the capacity of 250 cm<sup>3</sup>), and then two times with methanol (two portions with the capacity of 125 cm<sup>3</sup>) on the filter and then dried in a dryer (at the temperature of 100°C for 6 h). The prepared (washed and dried) catalyst was then used in the next epoxidation process (the next stage). This procedure was repeated until the conversion of AA did reach a value of 0 mol%. Six stages were conducted in the first study cycle (stages I-VI). After this time, the catalyst was washed on the filter, dried in a dryer, and additionally calcined in an oven (550°C, 5 hours) to remove organic compounds occluded in the catalyst pores. Then, the material was used for the next epoxidation process (the stages of the II cycle). Three stages were conducted in the second study cycle (stages VII-IX). Generally, nine stages were carried out in cycles I and II, after which the Ti-MCM-41 catalyst (after calcination) was subject to instrumental studies: XRD, IR, UV-vis and X-ray microanalysis.

## RESULTS AND DISCUSSION

Nine stages were conducted in the process of allyl alcohol epoxidation: six stages were carried out in the first cycle, whereas the second cycle included three stages. Table 1 presents the results obtained during the studies on recovery and regeneration of Ti-MCM-41 catalyst. This table shows that in I cycle the decrease in Ti content from 2.57 to 1.33 wt.% took place. In the second cycle the amount of titanium decreased from 1.33. to 0.71 wt.%. In the first cycle the selectivity of glycidol increased from 49 mol% to 96 mol% (stages

I to V) and decreased to 0 mol%, on the other hand, the selectivity of glycerol decreased from 51 mol% to 0 mol%. It shows that during the stages I to V glycerol took part in formation of soluble complexes of Ti and was detected in lower amount in post-reaction mixtures. Simultaneously, in cycle I, the conversion of AA decreased from 28 mol% to 0 mol%. On the other hand, the Table 1 shows that during the stages of I to VI the conversion of hydrogen peroxide was practically constant and high – above 90 mol% but the conversion of hydrogen peroxide to organic compounds decreased from 55 to 21 mol% and next to 0 mol%. It shows that an ineffective decomposition of hydrogen peroxide considerable predominate at stages IV to IV. At stages I to III more than 50% of hydrogen peroxide was transformed to glycidol and glycerol (the function of selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed). In the II cycle (after regeneration of the catalyst) only three stages were carried out (stages VII to IX). The selectivity of glycidol raised from 62 mol% to 78 mol% and decreased to 0 mol%, and the selectivity of glycerol decreased from 38 mol% to 0 mol%. It shows that the molecule of glycidol was not so stable as at the first cycle of studies and in a part glycidol was transferred to glycerine. The conversion of AA in II cycle was lower than in I cycle, it decreased from 17 mol% to 0 mol%. On the other hand, the conversion of hydrogen peroxide was very high (more than 90 mol%) but a main part of hydrogen peroxide was ineffective decomposed (more than 60%).

The results presented in Table 1 shows that the most important influence on the process of AA epoxidation over Ti-MCM-41 catalyst have probably two phenomenon's: the leaching of titanium from the structure of the catalyst (the decrease of the active centers of the catalyst) and the collapsing the structure of the catalyst at raised temperatures in water solution. This two phenomenon's cased in the II cycle the lowering of the number of stages to three (stages VII – IX). The consequence of leaching of Ti from the structure of the catalyst and destroying the structure of the catalyst was the decrease the conversion of allyl alcohol and the increase of ineffective decomposition of hydrogen peroxide. The third phenomenon – formation tars and

**Table 1.** The results of the epoxidation of allyl alcohol over the Ti-MCM-41 catalyst

Cycle	Stages	S <sub>GLY/AA</sub> [mol%]	S <sub>GLI/AA</sub> [mol%]	C <sub>AA</sub> [mol%]	C <sub>H<sub>2</sub>O<sub>2</sub></sub> [mol%]	C <sub>H<sub>2</sub>O<sub>2</sub>/org.comp.</sub> [mol%]	S <sub>H<sub>2</sub>O<sub>2</sub>/org.comp.</sub> [mol%]	Ti content [wt. %]
I	I	49	51	28	94	55	59	2.57
	II	53	47	25	94	51	54	–
	III	53	47	26	94	52	56	–
	IV	95	5	12	97	23	24	–
	V	96	4	10	94	21	22	–
	VI	0	0	0	91	0	0	1.33
Calcination of Ti-MCM-41 catalyst (550°C, 5 h)								
II	VII	62	38	17	90	34	38	1.33
	VIII	78	22	13	82	25	31	–
	IX	0	0	0	92	0	0	0.71
Calcination of the used Ti-MCM-41 catalyst (550°C, 5 h) and instrumental studies: XRD, IR, UV-vis and X-ray microanalysis								
*S <sub>GLY/AA</sub> – the selectivity of transformation to glycidol in relation to AA consumed, *S <sub>GLI/AA</sub> – the selectivity of transformation to glycerol in relation to AA consumed, *C <sub>AA</sub> – AA conversion, *C <sub>H<sub>2</sub>O<sub>2</sub></sub> – the total conversion of hydrogen peroxide, *C <sub>H<sub>2</sub>O<sub>2</sub>/org.comp.</sub> – the conversion of hydrogen peroxide to organic compounds S <sub>H<sub>2</sub>O<sub>2</sub>/org.comp.</sub> – the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed *Ti content – The titanium content in the sample of the catalyst determined by the X-ray microanalysis.								

blocking of pores had probably a minor influence on the course of epoxidation (mainly at stages V–VI and VIII–IX). It can be connected with the temperature of the process which was very low (40°C).

Studies on the catalyst made with help of the UV-VIS spectroscopy (Fig. 2) show that the initial sample of catalyst Ti-MCM-41 includes a very intense absorption band at a wavelength of about 210 nm, and two weak bands at a wavelength of about 260 and 300 nm. The band at a wavelength of 210 nm is considered as a direct evidence of the presence of tetrahedral titanium atoms in the skeleton of mesoporous silica (this band is assigned to the ligand-to-metal charge transfer from oxygen to Ti an isolated tetrahedral species). However, two bands – 260 and 300 nm – are attributed to titanium in an impaired five fold and six fold coordination in the structure of mesoporous silica. There is no band at a wavelength of 330 nm which proves that there is no extra-skeletal titanium in the form of anatase (TiO<sub>2</sub>). The UV spectrum of the used Ti-MCM-41 catalyst shows a change in the coordination of titanium from tetrahedral to five fold and six fold coordination after the ninth stage of the studies on the regeneration of this catalyst. This phenomenon occurs under the influence of water introduced into the reaction medium along with hydrogen peroxide and formed during the process of allyl alcohol epoxidation<sup>19–20</sup>.

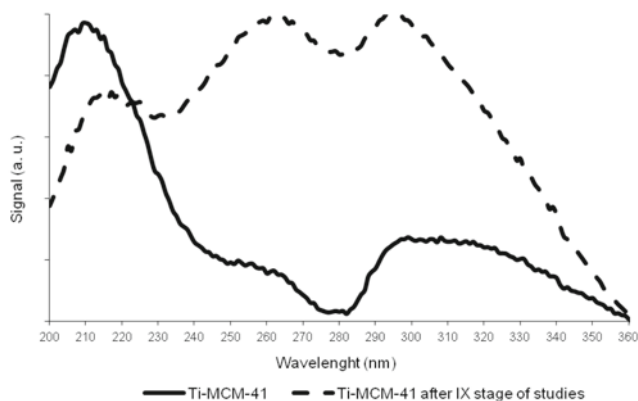


Figure 2. The UV-VIS spectra's of the Ti-MCM-41 catalyst

The IR spectroscopy (Figure 3) confirmed the presence of tetrahedral titanium in the structure of Ti-MCM-41 – the presence of the band at a wavelength of 960 cm<sup>-1</sup>. After the ninth stage of the studies, the intensity of this band decreased, which is associated with a decreased the amount of titanium in the silicalite structure<sup>19–20</sup>.

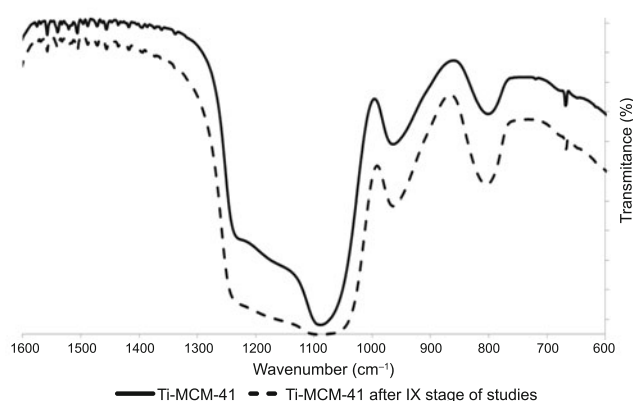


Figure 3. The IR spectra's of the Ti-MCM-41 catalyst

A diffraction pattern for Ti-MCM-41 catalyst shows one very intense diffraction peak (100) that is characteristic for a 2-d hexagonal structure and two weak diffraction peaks (110, 200). It was observed that with the decrease of titanium content in the catalyst structure, the peak (100) shifts towards lower values of the angle 2-theta. Moreover, the decrease of the intensity of this peak was observed. It shows that during the cycles of I to II a partial collapsing of the mesoporous structure took place (Fig. 4)<sup>19–20</sup>.

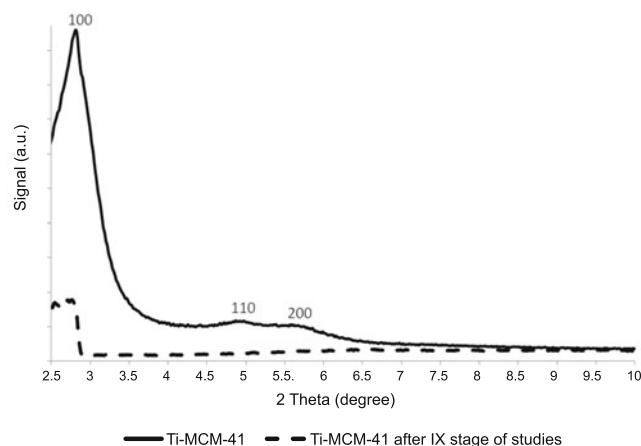


Figure 4. The XRD patterns of the Ti-MCM-41 catalyst

## CONCLUSIONS

The research showed that the most important influence on the process of AA epoxidation over Ti-MWW catalyst can have two phenomenon's: the leaching of titanium from the structure of the catalyst (the decrease of the active centers of the catalyst) and the collapsing the structure of the catalyst at raised temperatures in water solution. This two phenomenon's cased the lowering the values of the two main factions of the process of AA epoxidation: the conversion of allyl alcohol and the conversion of hydrogen peroxide to organic compounds. Simultaneously, the increase of ineffective decomposition of hydrogen peroxide was observed. The third phenomenon – formation tars and blocking of pores had probably a minor influence on the course of epoxidation (mainly at stages V–VI and VIII–IX). It can be connected with the temperature of the process which was very low (40°C).

The proposed method of the regeneration of ti-MCM-41 catalyst does not require the complex equipment, reduces the number of unit operations and simplifies the process of the catalyst regeneration.

The comparison the results obtained at the I stage of I cycle (initial sample of the catalyst) for the process of AA epoxidation over Ti-MCM-41 catalyst (Table 1) with our previous results obtained for TS-1 catalyst in the same process<sup>6</sup> shows that the TS-1 catalyst is more active in the process of AA epoxidation. The epoxidation over TS-1 was performed at close conditions as over Ti-MCM-41 catalyst: the temperature of 20°C, the molar ratio of AA/H<sub>2</sub>O<sub>2</sub> = 2:1, the methanol concentration of 90 wt.%, the catalyst concentration of 1 wt.% and a very short time of 30 minutes. Despite the four time shorter time of the reaction over TS-1 catalyst the selectivity of glycidol was 100 mol%, the conversion of AA amounted to 43 mol% and the selectivity of transformation to organic



compounds in relation to hydrogen peroxide consumed 97 mol%. The absence of glycerol (triol) in the post-reaction mixture can cause that TS-1 catalyst will be more stable in the process of AA epoxidation and also active for a longer time but it needs detailed studies.

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