Epoxidation of methyl oleate over various amorphous Ti–SiO₂ catalysts

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Abstract
The epoxidation reaction of the vegetable oil derivative methyl oleate with tert-butyl hydroperoxide in the presence of amorphous Ti–SiO₂ catalysts prepared by different methods using various silica sources was carried out. The reaction conditions were optimized. The relation between the properties of the catalysts such as specific surface area as well as titanium dispersion and the catalytic performance was in focus of the investigation. Based on the catalytic results in small batch reactors, the reaction was scaled up in a larger 4 L batch-reactor. Thereby similar conversions and selectivities were obtained in comparison with the small scale experiments.

Keywords Epoxidation · Methyl oleate · Tert-butyl hydroperoxide · Amorphous Ti–SiO₂

Introduction
The past century has shown that polyvinyl chloride (PVC) is the world’s second largest volume and most versatile plastic. The world demand of PVC is expected to grow with faster speed in coming years. However, PVC resins have a poor heat stability and high coefficient of friction at the temperature of processing. These features of PVC initiated the development of a wide variety of chemical additives, such as stabilizers and lubricants [1, 2]. The used lubricants are traditionally based on mineral oil. Therefore, lubricants produced from mineral oil are commonly used due to their well-established, good
technical performance and low cost [3]. Nevertheless, due to the increase of environmental issues like waste disposal problems, non-biodegradable resources, greenhouse effect, etc. and also the reduction of petroleum resources, renewable oils from vegetable origin have become an important issue [4]. Many evidences prove that the substitution of renewable instead of crude oil resources can be of sustainable development. In our days, some lubricants produced from renewable-harvestable resources can be successfully applied [3].

In general, vegetable oils have many advantages like high flash point, high viscosity index, high lubricity and low evaporative loss besides eco-compatible, renewable non-toxic and biodegradable. But there are still some limitations that wide spread application could not be overcome, i.e. low resistance towards oxidative degradation at high temperature and poor low temperature properties [5].

Epoxidation of the double bond is one of the interesting chemical modification methods because it opens up a wide variety of further reactions carried out under mild conditions [6]. Normally, the formed epoxide is an intermediate which can be converted to various products by the addition of nucleophiles to form suitable lubricants due to the kind of nucleophiles. In industry, the epoxidation of plant oils has been already carried out homogeneously using percarboxylic acids, such as peracetic acid and performic acid, obtained by oxidation with hydrogen peroxide, using mineral acid, like sulfuric acid as catalyst [7]. However, there are several drawbacks in such processes: (i) high selectivity of epoxidation is not achieved due to acid-catalyzed oxirane ring opening; (ii) the separation of acidic by-products is difficult; (iii) the handling of concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems and additionally, they are environmentally harmful [8]. Thus, recently, a lot of interest arose to develop heterogeneously catalyzed processes in order to avoid these disadvantages.

Typically, the heterogeneous catalysts used in epoxidation reactions are based on metal materials [9]. Metals have low oxidation potentials, but a high Lewis acidity in their highest oxidation states. Typical representatives are titanium-containing silica materials which are reported to be efficient heterogeneous catalysts for the epoxidation of a wide variety of substances under environmentally friendly conditions [6, 10–12]. There are many types of titanium-containing zeolite catalysts such as TS-1 [13, 14], Ti-β [15, 16], Ti-MCM-41 [6], etc. However, when steric effects due to the small pore size of such materials, high preparation costs and long time consuming synthesis come in consideration, mesoporous amorphous Ti–SiO2 catalyst are highly regarded for the epoxidation of large size substances.

In this work, the heterogeneously catalyzed epoxidation of the vegetable oil derivative oleic acid methyl ester was investigated in both small as well as larger scale batch-reactors. This includes the preparation and analysis of amorphous Ti–SiO2 catalysts using different silica sources and different preparation methods.
Experimental

Catalysts and reactants preparation

Amorphous Ti–SiO₂ prepared according to method ‘a’

The amorphous Ti–SiO₂ materials were prepared according to the procedure described by Rios et al. [6]. In this so called method ‘a’, five different catalysts, Ti–SiO₂₁a, Ti–SiO₂₂a, Ti–SiO₂₃a, Ti–SiO₂₄a and Ti–SiO₂₅a, were prepared. The number in the name denotes the different silica sources: 1 Aerosil200 [Degussa]; 2 Aerosil380 [Evonik]; 3 Davicat SI 1404 [Grace Davison]; 4 PD10012 [PQ Corporation]; 5 PD10013 [PQ Corporation]. The catalysts were prepared as follows: 2.7 g silica were carefully mixed with 142.17 g H₂O and 25.6 g tetraethylammonium hydroxide (Fluka 40 wt% in H₂O). Then, 0.435 g of ammonium pentafluoroperoxytitanates ((NH₄)₃[Ti(O₂)F₅]) (synthesized via ref. [17]) were added into the mixture. The mixture was then stirred for 1 h. Afterwards the mixture was stirred under addition of 11.75 g silica for 5 h. The mixture was placed in a Teflon-lined autoclave and allowed to crystallize at 100 °C for 7 days. The gel product was separated by a centrifugation and washed by distilled water three times. The solid product was dried at room temperature overnight before calcination. The calcination was carried out under nitrogen atmosphere first in temperature programming:

\[
20 °C \rightarrow 120 °C \rightarrow 120 °C \text{ for 2 h } \rightarrow 540 °C \rightarrow 540 °C \text{ for 6 h } \rightarrow 200 °C \text{ with a heating rate of 1 °C/min. The same program was repeated under air flow conditions. After calcination, the powder was immediately put into a glass bottle and dried at 150 °C overnight before use.}
\]

Amorphous Ti–SiO₂ prepared according to method ‘b’

The method ‘b’ for the amorphous Ti–SiO₂ (b) was based on the following procedure [18]: 0.15 g of titanium isopropoxide (TIP) was dispersed in 150 ml of cyclohexanol. The solution was heated up to 150 °C under stirring and then 3.91 g of silica was added. The solid was filtrated under vacuum and washed with cyclohexanol. It was dried at 150 °C and calcined at 500 °C under air for 5 h with heating rate of 1 °C/min.

Preparation of anhydrous tert-butyl hydroperoxide

The anhydrous tert-butyl hydroperoxide (TBHP) used as oxidant in the epoxidation was prepared by mixing of 14.29 g TBHP (Sigma-Aldrich, 70 wt% in H₂O) with 30 g of toluene and 25 g of dried molecular sieve (UOP type 3A). This mixture was stored in the fridge for at least 2 days before use under mild shaking conditions.

Catalyst characterization

The titanium content of the catalysts was analyzed by inductive coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro-Flame D. The measurement was
carried out after 30 mg of the sample are dissolved in the mixture of 40 ml 10% solution of HF, 8 ml of water and 2 ml sulfuric acid (98%).

The specific surface area (according to Brunauer Emmet Teller (BET) method) was measured based on nitrogen adsorption isotherm analysis using a Micrometrics ASAP2010 at 77.3 K with relative pressure (P/P0) range of 0.05–0.25.

X-ray powder diffraction (XRD) was measured in a Siemens D 5000 with the wavelength of 1.5405 Å (Cu Kα1).

Diffuse reflectance UV/Vis spectroscopy (DR-UV) was recorded on a Lambda 7 instrument produced by Perkin-Elmer. The sample was simply measured in the wavelength range of 190–500 nm after putting the powder sample on the T-shaped sample plate. BaSO₄ was used as reference.

Fourier-transformed infrared spectroscopy (FT-IR) analysis was conducted by means of a Nicolet Protégé 460. The small amount of sample were ground and mixed with KBr and pelleted by Grasby Specac 15 t press. The spectra was taken at room temperature under dry air flow.

**Epoxidation reaction**

The epoxidation reactions of methyl oleate (MO) were carried out in a 50 ml two-neck round-bottom flasks placed in an oil bath. Stirring was accomplished by using a Teflon-lined magnetic stirrer. For the scale up in a 4 L reactor, a mechanical stirrer was applied. Before adding the reaction mixture into the reactor, temperature was adjusted. The reaction mixture was prepared using the following ratios: TBHP/MO = 1.1 mol/mol, MO/Catalyst = 20 g/g, toluene/MO = 1 g/g. The used pure MO (ca. 95% purity) was kindly provided by Fuchs Europe Schmierstoffe GmbH, Mannheim. The first sample for the initial contents of reactants and product was taken before starting the reaction. Finally, the reaction was started and kept running for 24 h.

Different reaction conditions were applied, such as initial reactant concentration, different catalyst loading, etc. Reactions in the larger scale have been conducted under different amounts of materials.

**Product analysis**

The reaction mixtures were analyzed by gas chromatography on a Hewlett Packard HP 6890 equipped with a flame ionization detector using 60 m of the slightly polar column FS-SE54.

1 µl of sample was injected and the temperature of detector was 250 °C. Methyl undecanoate (Alfa Aesar, 99%) was used as the external standard.
Results and discussion

Catalyst characterization of Ti–SiO₂ (a)

Preparation of amorphous Ti–SiO₂ catalysts using different silica sources (a)

All catalysts were prepared with same amount of titanium precursor. Assuming that the complete titanium content is incorporated in the silica surface, 0.8 mol% \((\text{MolTi}/\text{MolSi} \times 100)\) of each sample was expected. However, the titanium loading of each sample, which was analyzed by ICP-AES, is slightly different because of a loss of silica or titanium during catalyst synthesis (Table 1).

Nitrogen adsorption analysis was carried out to determine some physical parameters of the catalysts such as pore size and Specific surface area. All catalyst samples showed the typical hysteresis for the nitrogen adsorption isotherm which is observed due to capillary condensation in mesopores (Fig. 1). The surface areas of their original silica sources and those of the prepared catalysts were compared. The analytical details are shown in Table 1. Comparing the specific surface area of the original silica sources and of the catalysts, it is clearly demonstrated that the specific surface area was decreased during preparation. The reason for this is the agglomeration of the particles during the experiments in the autoclave.

To find out more about the Ti species in the catalyst framework, FT-IR and DR-UV/Vis analysis were carried out. The UV/Vis spectroscopy is one of the most useful techniques for evaluating the titanium environment [19]. The UV/Vis absorption spectra show that the visible absorption spectra of the catalysts prepared by method ‘a’ (Fig. 2). The plot of anatase (non modified) is added into the figure as a reference. In particular, the absorption band edges of the prepared catalysts (Ti–SiO₂1a–4a) are slightly shifted to visible light region at around 450 nm compared to anatase (425 nm). The Ti–SiO₂5a catalyst has an absorption band edge of approximately 390 nm.

In addition, the band gap energy of these compounds can be estimated from the plots of the Kubelka Munk Function (Eq. 1) versus photon energy where \(R_{\infty}\) is the measured absolute reflectance of the sample \((R_{\text{sample}}/R_{\text{standard}})\) [20].

| Catalyst | Ti [wt%] | Ti [mol%] | Silica source BET* [m²/g] | Catalyst BET* [m²/g] | Pore radius [nm] |
|----------|----------|-----------|---------------------------|----------------------|-----------------|
| Ti–SiO₂1a | 0.58 | 0.77 | 200 | 132.7 | 11.85 |
| Ti–SiO₂2a | 0.88 | 1.22 | 380 | 157.3 | 9.93 |
| Ti–SiO₂3a | 0.59 | 0.76 | 500 | 210.27 | 5.75 |
| Ti–SiO₂4a | 0.75 | 1.00 | 535 | 199.78 | 6.45 |
| Ti–SiO₂5a | 0.87 | 1.17 | 657 | 200.79 | 6.87 |

*Specific surface area determined by the Brunauer Emmet Teller (BET) method
The value of anatase band gap energy is 3.1 eV and similar to those reported in the literature [21]. The range of the band gap energies of the prepared catalysts are around 2.9 eV for Ti–SiO$_2$4a and 3.2 eV for Ti–SiO$_2$1a. However, the UV/Vis band at around 210 nm indicates isolated Ti(IV) sites in tetrahedral coordination and high dispersion of Ti. The band at ca. 340–400 nm indicates the presence of free TiO$_2$ like anatase in the sample [6, 18, 19, 22, 23]. The presence of highly isolated tetrahedral Ti(IV) sites plays an important role in both Ti(IV)-peroxo complexes intermediates and the interaction between these oxidizing species and organic materials [27]. None of the samples have a strong absorption around 340–400 nm like anatase, but Ti–SiO$_2$1a and Ti–SiO$_2$2a have a small band and others contain broad shoulders in that range of the wavelengths which rules out the presence of non-isolated Ti. This indicates the existence of both isolated and non-isolated Ti in the catalysts framework. However, it can be clearly recognized which catalyst contains more isolated Ti sites by comparing the plots because a lower wavelength for the position of the absorption band is linked to a higher Ti

\[
\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = F(R_{\infty})
\]  

Fig. 1 $\text{N}_2$ adsorption isotherms for amorphous Ti–SiO$_2$ catalysts (a)
dispersion. Therefore, the result demonstrates that the Ti dispersion of Ti–SiO$_2$3a and Ti–SiO$_2$5a is higher than in the other cases.

FT-IR spectroscopy results are presented in Fig. 3. The peak centered at about 810 cm$^{-1}$ is an indication of the symmetric stretching and bending of Si–O–Si bridges. The band at about 1085 cm$^{-1}$ is due to the asymmetric stretching of Si–O–Si. The band at about 960 cm$^{-1}$ is known as the specific peak for Si–OH stretching vibrations as in the case of pure amorphous silica. For Ti-containing silica materials, a band at this wavenumber is generally taken as a proof of the incorporation of the metal into the framework, Si–O–Ti asymmetric stretching [6, 22, 24, 25].

According to Fig. 2, the bands of all samples at 960 cm$^{-1}$ are weak. Thus, these bands seem to be shoulders rather than peaks. This can be possibly explained by the titanium source used in the preparation. Triammoniumpentfluoroperoxotitanate ((NH$_4$)$_3$[Ti(O$_2$)F$_5$]) has the advantage that it is well soluble in water. This makes the synthesis much easier and it lowers the risk of having to dispose of the gel or the product because of the presence of titanium oxide species. A drawback of this compound as the titanium source might be the presence of fluoride. It was reported that fluoride leads to the formation of octahedral framework titanium which is not active or is leading production of by-products in the epoxidation reaction [26, 27].

**Influences on specific surface area of the catalyst (a)**

In the case of Ti–SiO$_2$5a, the specific surface area is only about 200 m$^2$/g, although its silica source has the specific surface area higher than 600 m$^2$/g. Due to the highly
decreased specific surface area of amorphous Ti–SiO$_2$ catalysts prepared by method ‘a’, some tests were conducted.

First, the specific surface area after each step of catalyst preparation of Ti–SiO$_2$5a was measured to find out the specific surface area decreasing step. A comparison of the specific surface at each step is given in Table 2.

It was found that the calcination is not the only step in which the specific surface area is decreased. Also the crystallization in the autoclave is crucial. Comparing the

Table 2 Specific surface area after each step of catalyst preparation of Ti–SiO$_2$5a

| Catalyst (Ti–SiO$_2$5a) | Ti [wt%] | Ti [mol%] | Surface area [m$^2$/g] | Pore radius [nm] |
|-------------------------|----------|-----------|------------------------|------------------|
| Silica source PD10013 [PQ corporation] | –        | –         | 657                    | –                |
| Ti–SiO$_2$5a as-synthesized | 0.68     | 1.11      | 335.3                  | 6.56             |
| Ti–SiO$_2$5a after calcination (T: 540 °C) | 0.83     | 1.13      | 199.0                  | 6.87             |
| Ti–SiO$_2$5a 2nd calcination after used in epoxidation | –       | –         | 164.1                  | 7.65             |
specific surface area of the silica source, PD10013 (PQ Corporation), and the as-synthesized Ti–SiO₂₅ₐ, almost half of it was decreased during the synthesis in the autoclave. This occurs due to some crystallization by adding the base mineraliser tetra-ethyl ammonium hydroxide when the catalyst solution was mixed before the reaction in the autoclave or due to the blocked pores resulted from agglomeration of the broken particles. Additionally, the specific surface area was decreased by the 2nd calcination after the reaction. It means that the calcination time is also important factor affecting specific surface.

The effect of the calcination temperature on the specific surface was also proved. The as-synthesized Ti–SiO₂₅ₐ catalyst was calcined at different temperatures (Table 3). The lower the calcination temperature, the higher the remaining specific surface area.

### Table 3 Specific surface area of catalysts, Ti–SiO₂₅ₐ, calcined at different temperatures

| Catalyst (Ti–SiO₂₅ₐ) | Ti [wt%] | Ti [mol%] | Surface area [m²/g] | Pore radius [nm] |
|-----------------------|----------|-----------|---------------------|-----------------|
| Ti–SiO₂₅ₐ (calc. T: 540 °C) | 0.81 | 1.13 | 197.7 | 5.67 |
| Ti–SiO₂₅ₐ (calc. T: 500 °C) | 0.83 | 1.15 | 256.3 | 4.99 |
| Ti–SiO₂₅ₐ (calc. T: 450 °C) | 0.84 | 1.18 | 275.6 | 5.10 |

### Table 4 Specific surface area and pore size of catalysts and elemental analysis (prepared by method ‘b’) |

| Catalyst Ti–SiO₂ (b) | Ti [wt%] | Ti [mol%] | Silica source BET* [m²/g] | Catalyst BET* [m²/g] | Pore radius [nm] |
|----------------------|----------|-----------|---------------------------|----------------------|-----------------|
| Ti–SiO₂₁₃b           | 0.45     | 0.60      | 200                       | 183.96               | 9.82            |
| Ti–SiO₂₂₃b           | 0.51     | 0.72      | 380                       | 365.57               | 14.02           |
| Ti–SiO₂₃₃b           | 0.46     | 0.61      | 500                       | 504.15               | 3.02            |
| Ti–SiO₂₄₃b           | 0.54     | 0.74      | 535                       | 555.75               | 8.17            |
| Ti–SiO₂₅₃b           | 0.54     | 0.76      | 657                       | 675.69               | 9.52            |

*Specific surface area determined by the Brunauer Emmet Teller (BET) method

Catalyst characterization of Ti–SiO₂ (b)

Preparation of amorphous Ti–SiO₂ catalysts using different silica sources (b)

Several amorphous Ti–SiO₂ catalysts were prepared by the impregnation method (method ‘b’). Specific surface area measurements by nitrogen adsorption analysis and elemental analysis were carried out (Table 4). According to the nitrogen adsorption isotherm all catalysts are mesoporous materials (Fig. 4). However, there are significant differences, for example, between Ti–SiO₂₅b and Ti–SiO₂₃b. Ti–SiO₂₅b has BJH desorption cumulative volume of pores 3.24 cm³/g, while 0.99 cm³/g of pore volume were obtained for Ti–SiO₂₃b. In contrast to the catalysts prepared via method ‘a’, the surface area of the silica sources are well maintained after the catalyst preparation.
The N\textsubscript{2} physisorption isotherm of all catalyst corresponds to type IV according to the IUPAC classification, while the hysteresis loop (H1) is characteristic of the capillary condensation that takes place in the mesopores. These hysteresis loops are often associated with porous materials consisting of well-defined cylindrical-like pore channels or agglomerates of approximately uniform spheres. However, the adsorption branch shows a very steep increase at the relatively pressure range of 0.8 < P/P\textsubscript{0} < 1.0, indicating a very uniform channel diameter. The gradients of the hysteresis loops (adsorption and desorption isotherms) of the catalyst (Ti–SiO\textsubscript{2}2b, Ti–SiO\textsubscript{2}4b, Ti–SiO\textsubscript{2}5b) prepared by method ‘b’ are higher compared to the ones of method ‘a’ (Ti–SiO\textsubscript{2}2a, Ti–SiO\textsubscript{2}4a, Ti–SiO\textsubscript{2}5a). This indicates the presence of additional or not blocked mesopores.

In other cases, with higher amount of titania loading titania nanoparticles can block the pores of silica, resulting in lower surface area. However, in this case the amount of titania is less than 1 wt%, which cannot make such remarkable changes in surface properties. The significant decrease of the surface area seems to occur during the catalyst preparation. The catalyst solution was mixed before the reaction in the autoclave and then blocked pores resulted from agglomeration of the broken particles leads to a total transformation and rearrangement of the pore structure.

DR-UV and FT-IR spectroscopy analysis were performed as it was described for the catalysts prepared by method ‘b’. Fig. 5 shows the DR-UV spectra of the Ti–SiO\textsubscript{2}
In particular, the absorption band edges of the prepared catalysts (Ti–SiO\textsubscript{2}1b–5b) are lower (310–375 nm) compared to anatase (425 nm). This results in higher band gap energies with values above 3.6 eV.

However, in all the samples there are no hints for the presence of anatase-like separated TiO\textsubscript{2} phase. That fact could be explained by the titanium source used in this preparation method ‘b’. It is reported that Ti(O\textsubscript{i}Pr\textsubscript{4}) supported on silica is an efficient catalyst for the epoxidation of olefins [28, 29]. Such a catalyst should have more active sites. In another report, it is claimed totally differently that titanium isopropoxide precursor yields tetrahedrally coordinated polymeric titanium species, which lower the efficiency of the catalyst [19]. As explained in the previous chapter, a higher wavelength for the position of the absorption band is linked to a lower dispersion of Ti in the framework. Therefore, better Ti dispersion on Ti–SiO\textsubscript{2}3b and Ti–SiO\textsubscript{2}5b can be assumed.

FT-IR spectrometer analysis was carried out as illustrated in Fig. 6. All samples show clearly the band at ca. 960 cm\textsuperscript{-1}. That is more pronounced than in the case of the catalysts prepared according to method (a), especially on Ti–SiO\textsubscript{2}4b and Ti–SiO\textsubscript{2}5b. This proves, not decisive, that more isolated tetrahedrally coordinated Ti species are present in the framework of these catalysts. However, the band at 960 cm\textsuperscript{-1} appears very weak in catalyst Ti–SiO\textsubscript{2}1b indicating a low dispersion of framework Ti.
Epoxidation of methyl oleate with amorphous Ti–SiO₂ catalysts (a)

Catalysts prepared according to method ‘a’ with different silica sources

The epoxidation reactions of methyl oleate with Ti–SiO₂ catalysts prepared using different silica sources were carried out. The catalytic results are presented in Fig. 7. The plots of selectivity were omitted because all the values are higher than 90% in this case. In the characterizations of these catalysts, there were no significant differences observed. However, for example, the specific surface area of Ti–SiO₂1a and Ti–SiO₂2a were lower than those of the other catalysts. Therefore lower activities were observed. Furthermore, dispersion of titanium causes higher conversions over Ti–SiO₂3a and Ti–SiO₂5a. The specific surface area of Ti–SiO₂4a is almost same with that of Ti–SiO₂5a. Nevertheless, the Ti–SiO₂5a is more active. That proves that the state of the titanium in the catalyst framework is the main factor which influences the activity of catalysts. After all, the catalyst Ti–SiO₂5a whose preparation is based on the silica source PD10013 from PQ corporation having both high specific surface area and high dispersion of Ti presented the best catalytic performance. Therefore, Ti–SiO₂5a is used in further investigations.
Temperature dependence

The effect of temperature on the reaction was checked (Fig. 8). Increasing temperature from 50 to 70 °C does not cause a decrease in selectivity but conversion increases about 10%. However, by further increasing temperature from 70 to 90 °C, ca. 30% of selectivity was lost while the conversion was increased from 24 to 61%. The GC results of the samples taken at 80 and 90 °C presented many unknown small peaks of by-products which could not be identified. Making a compromise between conversion and selectivity in the results, 70 and 80 °C are considered as optimal temperature for the epoxidation of methyl oleate with TBHP.

Reaction in larger vessel

The epoxidation reaction of methyl oleate in 4 L reactor over the catalyst Ti–SiO₂₅a was carried out. High purity methyl oleate (ca. 95 wt% ≤), which was kindly supported by Fuchs Europe Schmierstoffe GmbH, was used in the same manner as in small scale reaction. The results were quite different when the technical methyl oleate (ca. ≤ 80 wt%) was used as a substrate because the impurity of this liquid are fatty acid methylester containing C=C double bonds, such as ca. 10 wt% of methyl linoleate. The relative oxidation rate of these two double bonds in methyl linoleate is 10 times faster than the oxidation rate of a double bond in
methyl oleate [30]. This is the reason why much less epoxidized methyl oleate was resulted in the reaction in the 4 L reactor using the technical methyl oleate. The results of the epoxidation of high purity methyl oleate in small scale (50 ml) and larger scale presented on Figs. 9 and 10.

**Fig. 8** Conversion, Yield and Selectivity of epoxidation reactions with the catalyst at different temperatures. Catalyst = Ti–SiO$_2$5a, TBHP/MO = 1.1 mol/mol, MO/Catalyst = 20 g/g, Toluene/MO = 1 g/g, temperature = 50–90 °C, reaction time = 24 h

**Fig. 9** Conversion, Selectivity and Yield of epoxidation reaction of methyl oleate with the catalysts in 50 ml round-bottom flask. Catalyst = Ti–SiO$_2$5a, TBHP/MO = 1.1 mol/mol, MO/Catalyst = 20 g/g, Toluene/MO = 1 g/g, temperature = 80 °C, reaction time = 24 h
The last concentrations of produced epoxystearic methylester (ESME) in the small scale as well as in the larger scale reach almost the same conversion and selectivity, although the initial reaction rate was slightly different, maybe due to heat transfer. Even though the temperatures of both reactors are adjusted before the reaction mixture is added to the reactors, a larger amount of the added reaction mixture in a larger scale takes a longer time to reach the set temperature point than in the case of the smaller scale reactor. Nevertheless, these results prove that the scaling-up of this reaction is possible and it could have a potential for industrial use.

**Epoxidation of methyl oleate with amorphous Ti–SiO$_2$ catalysts (b)**

**Catalysts prepared according to method ‘b’ with different silica sources**

The epoxidation reactions of methyl oleate were carried out over Ti–SiO$_2$ catalysts prepared according method ‘b’ using different silica sources (Fig. 11). Surprisingly, all results show higher selectivity (> 90%) and conversion than the results in the presence of catalysts prepared by method ‘a’. This can be explained by a better dispersion of Ti and higher specific surface area of the catalysts (b). However, when only the results of the epoxidation reactions using catalysts (b) are compared, the differences of surface area and the dispersion of Ti do not play the important role in this case. Although conversion in the reaction over the catalyst Ti–SiO$_2$1b is somewhat lower than those obtained with other catalysts (b), it cannot be concluded that the productivity depends exactly on the properties of the catalysts, such as surface
area of the catalysts and the dispersion of the Ti. This can be proved also by comparing the results of catalysts prepared by method (a) and Ti–SiO$_2$1b. The catalyst Ti–SiO$_2$1b having no better catalytic features than catalysts (a) performs much better, yielding ca. 60% conversion. Therefore, more experimental work is necessary to find the decisive catalytic features influencing catalytic performance, and moreover optimal and economical Ti–SiO$_2$ catalyst for the epoxidation reaction would be found.

Right now, in conclusion it can be stated that the catalysts whose preparation are based on the silica sources, Aerosil 380 [Evonik], Davicat SI 1404 [Grace Davison], PD10012 [PQ Corporation], PD10013 [PQ Corporation] result in similar performance. This observation is completely different to the findings using catalysts prepared according to method (a).

**Temperature dependence (b)**

The epoxidation reactions of methyl oleate using Ti–SiO$_2$5b as the catalyst were carried out at different temperatures (Fig. 12). The following three observations were made in the previous catalyst characterization chapter 3.2: a well preserved specific surface area of catalysts prepared by method ‘b’, a clearer band at wavenumber 960 cm$^{-1}$ according to IR spectrometer results, and no band around 340 nm of the wavelength with regard to UV results. These features indicate that the titanium is well isolated and that there are

![Fig. 11](image-url)
more active sites. With these factors, a better epoxidation performance of Ti–SiO$_2$ was expected. As the result, this amorphous catalyst showed higher catalytic activity than the ones prepared by method ‘a’. The superior behavior of the Ti–SiO$_2$ catalyst could be explained not only by the higher specific surface area but also by better dispersion of isolated titanium in the framework of the catalyst.

It is shown that conversion and yield were increased from 31 to 85% and from 30 to 77% by increasing the reaction temperature from 50 to 90 °C. In contrast, the selectivities decreased from 98 to 90%. The highest yield was obtained at 90 °C, although the selectivity was decreased but still higher than 90% (90.31%). This high yield (77%) is lower than the yield (87.75%) reported by A. Campanella et al. who had carried out the epoxidation of soybean oil with hydrogen peroxide at 90 °C using the same catalyst preparation method (b) but with 0.3 wt% lower loading of titanium [8]. However, considering reaction running time (> 54 h) which was much longer than that in our study (24 h), 77% of the yield is reasonable and comparable.

Based on these results, 90 °C is applied in further experiments using catalysts (b).
Conclusions

In this study, amorphous Ti–SiO₂ materials are proved to be suitable catalysts for the selective epoxidation of methyl oleate using TBHP as oxidant. The properties, such as surface area or titanium dispersion on the surface, depend highly on the preparation method and on the silica source used. In contrast to the catalysts prepared according to method ‘a’, much better catalyst properties were obtained over catalysts prepared by impregnation method ‘b’. In this procedure, the surface areas of used silica sources were well conserved during the catalyst preparation and the dispersion of the isolated Ti(IV) was much better according to the results of UV/Vis and FT-IR spectroscopy. These characteristic features are strongly related to the catalytic performance in the epoxidation reaction. Although some factors for an optimal and economical epoxidation reaction, such as reaction time and titanium loading in the catalysts are not clearly found, the obtained high yield of epoxide over the non-ordered Ti–SiO₂5b made with PD10013 (PQ Corporation) as the silica source is a quite interesting finding. One more important finding is that the reactions in larger scale resulted in almost the same conversion and selectivity compared with the small scale reactions.

In conclusion, the best results achieved are 77.4% yield in the presence of Ti–SiO₂5b catalyst at 90 °C in 24 h reaction time.

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