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Synthesis and catalytic properties of titanium containing extra-large pore zeolite CIT-5

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ABSTRACT

Titanium containing extra-large pore zeolite CIT-5 (IZA code: CFI) was successfully prepared by direct synthesis using Cab-O-Sil M5 and titanium(IV) butoxide in the presence of LiOH. *N*-Methylsparteinium hydroxide was used as a structure directing agent. The product crystallized into thin plate crystals with an approximate size of 20 × 5 × 0.2 μm. The lowest achieved Si/Ti ratio was 23. The necessary duration of hydrothermal synthesis increased with increasing concentration of Ti in the reaction mixture from 11 days (Si/Ti = 63 in product) to 17 days (Si/Ti = 36) at 155 °C. Prepared Ti-CFI samples exhibit BET surface areas in the range of 308–346 m^2/g and micropore volumes of 0.094–0.097 cm^3/g. CFI possesses extra-large pores (14-ring, 7.2 × 7.5 Å) accessible for bulky molecules, therefore, Ti-CFI is a useful catalyst for epoxidation of double bonds in bulky molecules used in perfumery and pharmacy. The Ti-CFI samples proved to be catalytically active in epoxidation of 1-octene, cyclooctene, α-pinene, and norbornene with hydrogen peroxide as oxidation agent.

1. Introduction

Zeolites represent a rich family of porous crystalline aluminosilicates successfully applied as catalysts, adsorbents and ion exchangers [1,2]. The pore size of zeolites is defined by the number of atoms in the pore entrances. The larger pore, the larger molecules can access zeolite inner volume and diffuse to the active sites located mainly inside the pores. Zeolites having more than 12 tetrahedrally coordinated silicon or aluminium atoms in the entrance ring are called extra-large pore zeolites [3,4]. In contrast to aluminosilicate zeolites, a considerable breakthrough was the discovery of zeolite TS-1, having the MFI structure, by Taramasso et al. [5]. The TS-1 is widely used as catalyst in selective oxidations (epoxidations) with hydrogen peroxide providing low waste and being environmentally friendly [6]. Nowadays, the TS-1 is industrially applied by ENI in propylenoxide process [7]. Although the TS-1 is excellent epoxidation catalyst for small linear olefins, the access of larger molecules to the active sites is strongly restricted due to its narrow (10-ring) pores. The increase in accessibility of active sites in titanosilicates with larger pores [8,9] or layered Ti-containing materials was investigated [10] to prepare epoxides from bulky alkenes, cycloalkenes and terpenes. They are requested particularly in pharmacy and perfumery (e.g. α-pinene oxide is a precursor of fragrance ingredients trans-carveol and campholeic aldehyde [11]). Van der Waal reported synthesis of zeolite Ti-BEA and its catalytic behaviour in epoxidation of 1-octene [8] and subsequently of norbornene, camphene, and limonene [12]. Wu et al. reported that Ti-MWW is more active in epoxidation of linear alkenes than TS-1 and Ti-BEA [13]. Corma and co-workers prepared a delaminated MWW zeolite and introduced Ti into the structure to obtain Ti-ITQ-2 material combining the advantages of Ti-MWW structure and easy accessibility of the external surface in delaminated material [14]. However, the Ti-ITQ-2 exhibits high activities only with organic hydroperoxides as oxidants in the absence of water. Tatsumi et al. synthesized Ti-YNU-1 material (interlayer expanded MWW topology) [15], which is active even with aqueous hydrogen peroxide. Another promising material is specially designed TS-1 by Ryoo et al. prepared in the form of nanosheets [10]. This material exhibits activity similar to bulk TS-1 in epoxidation of 1-hexene, however, its activity is an order of magnitude higher in epoxidation of cyclooctene.

While several large-pore titanosilicates (e.g. Ti-BEA, Ti-MOR, Ti-ITQ-7) were synthesized, the only extra-large pore titanosilicate Ti-DON was reported up-to-now [16].

CIT-5 zeolite (IZA code: CFI) is an extra-large pore zeolite with one-dimensional 14-ring channel system. This zeolite shows good thermal stability. Previously it was prepared as pure silica or isomorphously substituted with boron, gallium and aluminium [17]. The CFI zeolite has slightly elliptic pores with diameter 7.2 × 7.5 Å. The synthesis of the CFI is more advantageous in comparison

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with Ti-DON requiring a quaternary ammonium salt as a template instead of a cobalt organometallic complex for DON zeolite [16].

In this contribution, we report the first synthesis of titanosilicate form of the zeolite CIT-5 (Ti-CFI) and a characterization of this material. High thermal stability of the CFI structure as well as easy incorporation of Ti into the framework enables its application as a catalyst for epoxidation of bulky olefins and terpenes. The results of catalytic testing in epoxidation with hydrogen peroxide are also presented as an additional characterization technique with the aim to demonstrate the usefulness of our approach.

2. Experimental

2.1. Synthesis of CFI

Titanium(IV) butoxide (Aldrich, 97%), lithium hydroxide hydrate (Fluka, 99%), Cab-O-Sil M-5 (Havel Composites, Czech Republic), (−)-spartein sulfate pentahydrate (SAFC, 99%), and methyl iodide (Fluka, 99%) were used as purchased.

The *N*(16)-methylsparteinium hydroxide, used as a structure directing agent (SDA), was prepared according to the procedure described in reference [18]. *N*(16)-Methylsparteinium iodide was prepared by a reaction of (−)-spartein and methyl iodide in acetonitrile at room temperature for 72 h. The resulting iodine salt was ion exchanged into hydroxide form using strongly basic anion exchange resin AG1-X8 (Biorad, OH^- form). Properly ion exchanged SDA solution exhibited pH 14.0 and no opacity after acidification with 1 M HNO_3 to pH 1 and addition of 1 volume of 0.06 M $AgNO_3$ solution.

The synthesis of the CFI was based on the procedure described in reference [18]. *N*(16)-Methylsparteinium hydroxide (0.3 M aqueous solution, *N*-MeSpa OH) was mixed with demineralised water and lithium hydroxide hydrate in a Teflon-lined autoclave. A solution of titanium(IV) butoxide in 1-butanol (25%, TBOTi) was added dropwise to the synthesis mixture under vigorous stirring for 2 min. The resulting mixture was homogenized at room temperature for 30 min. Finally, Cab-O-Sil M-5 was added and the mixture was stirred for another 30 min. In some cases the mixture was seeded with earlier prepared "as-synthetized" CFI crystals. The milky homogeneous mixture, with molar composition 0–2.0 TBOTi, 10 *N*-MeSpa OH, 5 LiOH, 50 SiO_2 and 2500 H_2O, was closed in an autoclave and heated under agitation to 155–170 °C for 6–17 days. Lithium hydroxide serves as an accelerator for the crystallization of the CFI phase. On the other hand Li^+ does not compete with *N*-methylsparteinium in templating the structure due to its small ionic radius [18].

The solid product was collected by filtration, washed out with demineralised water and dried overnight at 65 °C. Calcination of the samples was carried out in a stream of air at 570 °C for 8 h.

To remove extra-framework titanium species from the CFI samples, some samples were treated with nitric acid solution prior to the calcination. 30–90 ml (depending on Si/Ti ratio) of 2.0 M HNO_3 solution was used per 1 g of dry as-synthetized material. The mixture was heated at 100 °C for 16 h. After the given time, the solid material was filtered off, washed with water and calcined as described above.

In order to remove Li^+ anions, some samples were ion-exchanged with ammonium nitrate. Calcined samples were treated four-times with 1.0 M NH_4NO_3 solution (Lach-Ner, 99%) for 4 h at room temperature using 100 ml of the solution per 1 g of the sample. The samples were re-calcined at 540 °C for 6 h before use.

2.2. Synthesis of TS-1

Titanosilicate TS-1 was prepared from a gel with initial Si/Ti ratio 40 according to the procedure described in reference [19] using tetraethyl orthotitanate (Aldrich, technical grade), tetraethyl orthosilicate (Aldrich, 98%), and tetrapropylammonium hydroxide (Aldrich, 20% in water) as an SDA.

2.3. Characterization

X-ray powder diffraction patterns (XRD) were collected using a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator and a position sensitive detector Våntec-1 using CuKα radiation in Bragg–Brentano geometry. Data were collected in continuous mode over the 2θ range of 5–50° with scan speed of 0.0610°/s.

The size and shape of zeolite crystals were examined by scanning electron microscopy (SEM) on a JEOL, JSM-5500LV microscope. The images were collected with acceleration voltage of 20 kV. Energy dispersive X-ray spectroscopy (EDX) analyses were performed using Hitachi S-4800 field emission scanning electron microscope at 25 kV with Noran EDX system. Also some SEM images were collected using the Hitachi system at 5 kV.

Argon sorption isotherms were measured at liquid argon temperature (−186 °C) with Micromeritics ASAP 2020 volumetric instrument. To attain sufficient accuracy in the accumulation of the adsorption data, the ASAP 2020 was equipped with pressure transducers covering the 133 Pa, 1.33 kPa and 133 kPa ranges. Prior to the sorption measurements, individual zeolites were outgassed under turbomolecular pump vacuum at 300 °C for 6 h.

BET area was evaluated using adsorption data in the range of a relative pressure from $p/p_0 = 0.055$ to $p/p_0 = 0.22$. The *t*-plot method [20] was applied to determine the volume of micropores (V_{micro}). The adsorbed amount of argon at $p/p_0 = 0.99$ reflects the total adsorption capacity (V_{total}).

UV–vis absorption spectra were collected for calcined samples using a PerkinElmer Lambda 950 Spectrometer with a 5 mm or 2 mm quartz tube and a large 8 × 16 mm slit. The data were collected in the wavelength range of 190–500 nm.

Chemical composition of the Ti-CFI (60), (40) and (25) was determined also by X-ray fluorescence analysis (XRF) with a spectrometer Philips PW 1404 using an analytical program UniQuant. The samples were mixed with dentacryl as a binder and pressed on the surface of cellulose pellets.

2.4. Catalytic reactions

The catalytic activity of Ti-zeolites was tested in epoxidation of 1-octene (Aldrich, 98%), cyclooctene (Aldrich, 99%), α-pinene (Acros organics, 98%) and norbornene (Aldrich, 99%) with hydrogen peroxide (Aldrich, 35 wt.% aqueous solution) as oxidant in acetonitrile (Fisher chemical, HPLC grade). Mesitylene (Sigma–Aldrich, 99%) or 1,3-diisopropylbenzene (Fluka, 95%) were used as internal standards. The activity was compared with standard TS-1 zeolite. The reactions were carried out at 50 or 60 °C in a following way. The catalyst was activated by heating at 450 °C for 90 min and cooled down in a desiccator. The catalyst (50 mg) was added to 6 ml of acetonitrile followed by 300 mg of the alkene and 150 mg of the internal standard. The mixture was heated in a flask under Dimroth condenser to the reaction temperature and the reaction was started by addition of 0.5 mol equivalent of H_2O_2 (based on alkene). Samples of the reaction mixture were taken in regular intervals, centrifuged and analysed using an Agilent 6850 GC system with 20 m long DB-5 column, an autosampler and a FID or a MS detector. Helium was used as a carrier gas.

Table 1
Description of the synthesis of Ti-CFI samples.

Sample	Si/Ti (RM)	Temperature (°C)	Yield (%)	Crystal size (μm)	Si/Ti (EDX)	Time (day)	Structure[a]
Ti-CFI (100)	100	170	85	10–40	106	6	CFI + Am.
Ti-CFI (60)	60	155	79	10–20	63[c]	11	CFI
Ti-CFI (40)	40	155	79	10–20	36[c]	17	CFI
Ti-CFI (25)	25	160	98	10–20	23[c]	11[b]	CFI
Ti-CFI (10)	10	160	–	–	–	20[b]	Am.
Ti-AFI (a)	80	160	75	1–2.5	106	14	AFI
TS-1	40	175	85	0.2	38	6	MFI

[a] Am. stands for amorphous material.
[b] The synthesis was seeded with Ti-CFI (40).
[c] Si/Ti molar ratio determined by XRF.

In order to perform a leaching test, a reaction mixture was prepared as described above and it was left to react at 60 °C for 3 h. After the given time the catalyst was filtered off and the mixture was stirred on at 60 °C and samples were taken in 1 h intervals.

Epoxidation of norbonene in methanol was carried out using the same conditions as in [12] with 4-times smaller amount of reagents. 471 mg (5 mmol) of norbornene was dissolved in 7.6 ml (6.0 g) of methanol. 235 mg of mesitylene was added as an internal standard followed by 25 mg of activated catalyst. The mixture was heated to 60 °C and the reaction was started by addition of 2.5 mmol of H_2O_2.

3. Results and discussion

3.1. Synthesis

Results of syntheses of different Ti-CFI samples are summarized in Table 1. Well-crystalline CFI samples (Fig. 1) were obtained with Si/Ti ratios ranging from 106 to 23 in the product. Kubota et al. [18] reported synthesis of Al-CFI and pure silica CFI under static conditions with quartz tubes inside the autoclave but the attempts to use this method for Ti-CFI were not successful providing either amorphous material or cristobalite. After initial experiments represented by Ti-CFI (100) sample, the synthesis temperature was lowered from 170 °C to 155 °C in order to obtain more uniform crystal size distribution (see Fig. 2). As expected, this caused a prolongation of the synthesis time. However, comparing the syntheses Ti-CFI (60) and Ti-CFI (40) we conclude that also increasing amount of titanium in the synthesis mixture increases the synthesis time (from 11 days of Ti-CFI (60), to 17 days of Ti-CFI (40)). Both seeding of the reaction mixture or a slight increase in the synthesis temperature significantly shortened the synthesis time. As a result, Ti-CFI (25) sample crystallized in only 11 days.

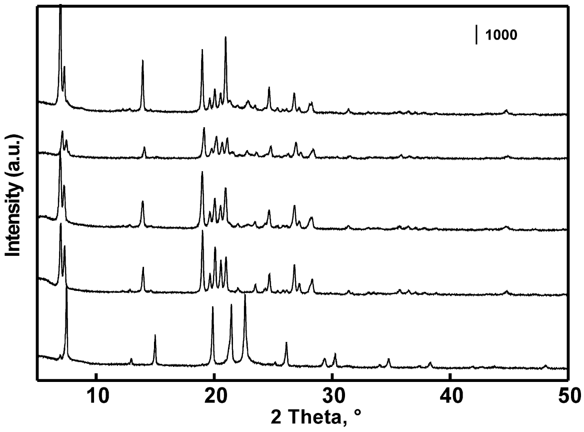

Fig. 1. XRD patterns of as-synthetized CFI and AFI samples. From the top: Ti-CFI (100), Ti-CFI (60), Ti-CFI (40), Ti-CFI (25), Ti-AFI (a).

N(16)-Methylsparteinium bromide can template also the synthesis of zeolite AFI [21]. Under certain crystallization conditions, AFI can crystallize together with CFI as observed by Barrett et al. [22]. The presence of particular anions (Br^- vs. OH^-) [21] or cations (Na^+, K^+ vs. Li^+) [17] seems to control the crystallization route and the purity of the final zeolite product. We observed the same effect in the case of Ti-CFI. When the SDA was used without ion-exchange only AFI phase was obtained after 14 days of the crystallization at 160 °C (sample Ti-AFI (a)). Lok et al. invented the synthesis of titanium containing aluminophosphate with AFI topology (TAPO-5) [23] but the synthesis of titanosilicate with AFI structure was not reported until now. Our results suggest that the preparation of AFI titanosilicate with higher Ti content should be also possible.

There are 3 characteristic diffraction lines of the CFI structure at low 2θ angles: 6.91°, 7.32° and 13.9° followed by a group of 5 peaks between 18° and 22° (Fig. 1).

The intensity of the first two diffraction lines depends on the presence of the structure-directing agent in the pores and on the orientation of the CFI crystals having the morphology of thin plates (Fig. 2). Kubota et al. reported that some diffraction lines may practically disappear if there is any preferred orientation of CFI crystals [18]. This may lead to more complex identification of the CFI phase. No preferential orientation was observed for Ti-CFI. The calcination of samples result always in a strong increase in the intensity of diffraction lines at $2\theta = 6.91°$ and 7.32° as well as an appearance of two additional weak diffraction lines at $2\theta = 12.2°$ and 12.9°. These two lines are also characteristic in the CFI pattern (Fig. 3).

A study of Si/Ti molar ratios in the reaction mixtures and in the crystalline products revealed that the Si/Ti ratio in the crystalline product practically follows that one in the reaction mixture. The lowest Si/Ti ratio achieved is 23, however not all the titanium is in the framework positions (see the discussion of UV/Vis results below). Syntheses with initial Si/Ti ratio 10 provided an amorphous material.

Scanning electron micrographs (SEM) show that the zeolite Ti-CFI crystallizes into thin plate crystals with the largest dimension up to approximately 20 μm (Fig. 2), sometimes forming aggregates. This morphology is the same as for aluminosilicate, pure siliceous, or borosilicate forms of the CFI [17,18]. The thickness of the crystals is about 0.2 μm, which is about 100 unit cells.

Textural properties of synthesized samples are summarized in Table 2. The data are consistent with those reported for CFI previously [17,18]. The micropore volume might be taken as a parameter

Table 2
Textural properties of CFI titanosilicates; the initial Si/Ti ratio is in brackets.

Sample	BET (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)
Ti-CFI (100)	272	0.068	0.524
Ti-CFI (60)	308	0.094	0.293
Ti-CFI (40)	339	0.098	0.256
Ti-CFI (25)	346	0.097	0.235
TS-1	445	0.127	0.375

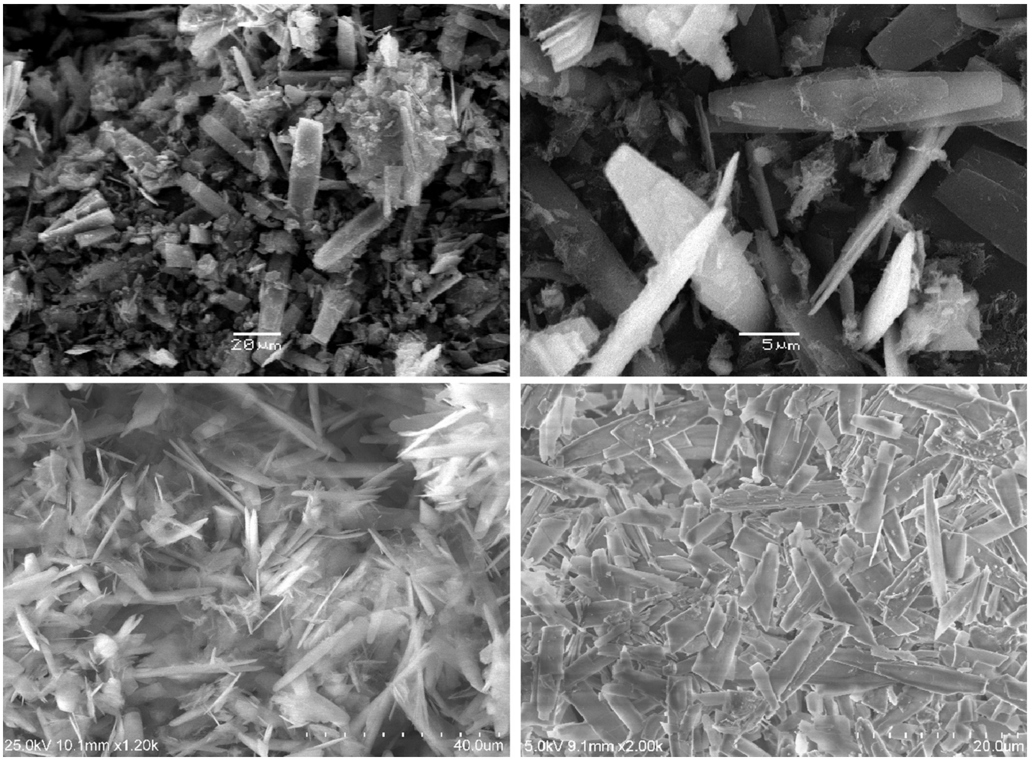

Fig. 2. SEM images of Ti-CFI (100) (top left), Ti–CFI (60) (top right), Ti-CFI (40) (bottom left) and Ti-CFI (25) (bottom right).

characterizing the quality of the sample. Well crystalline samples (Ti-CFI (60), (40) and (25)) exhibit micropore volume of 0.094, 0.098 and 0.097 cm^3/g respectively. CFI samples with $V_{micro} < 0.09\ cm^3/g$ contain some amorphous material (see Fig. 2, top left image). The uptake of argon at higher relative pressures is caused by interparticle condensation among individual flat crystals. Hysteresis loops result from the cavitation effect that manifest itself during desorption (Fig. 4).

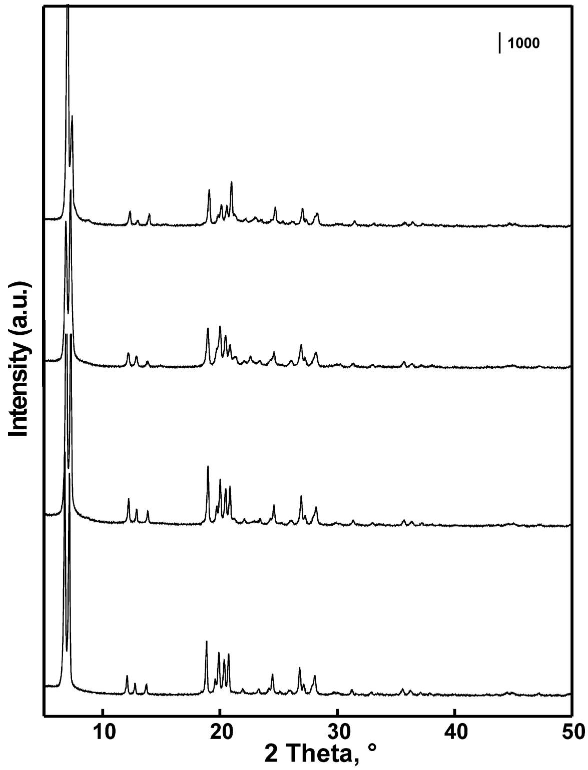

Fig. 3. XRD patterns of calcined CFI samples. From the top: Ti-CFI (100), Ti-CFI (60), Ti-CFI (40), Ti-CFI (25).

It is generally assumed that single framework "TiO_4" species are the active sites in epoxidation reactions [24]. On the other hand, extra-framework Ti species may direct the formation of stable dense TiO_2 phase after calcination, affecting negatively the selectivity for oxidation reactions [25]. The coordination state of Ti species was studied using UV-vis spectroscopy. As observed in Fig. 5, all 3 well crystalline samples (Ti-CFI (60), (40) and (25)) have similar spectra with 2 bands centred at 220 and 260 nm. Zecchina et al. ascribed these bands to tetrahedrally coordinated "TiO_4" species and hexacoordinated extra-framework "TiO_6" species respectively [26]. We conclude that part of titanium is in isolated extra-framework positions.

The extra-framework Ti species might be removed by treatment with boiling HNO_3 prior to the calcination of the sample [25]. We examined this procedure using 2 samples: Ti-CFI (60) and Ti-CFI (25). Fig. 5 shows that nearly all extra-framework Ti from Ti-CFI (60) sample was successfully removed. On the other hand, in the spectrum of Ti-CFI (25), a new band appeared centred at 330 nm. This band indicates the formation of dense TiO_2 (Fig. 5B) [26]. When the amount of HNO_3 used for the treatment of Ti-CFI (25) was increased to 60 g of 2 M HNO_3 per 1 g of the zeolite, the only band at 220 nm was observed as in case of Ti-CFI (60). We conclude that high excess of the acid is necessary to dissolve all extra-framework Ti. Another significant disadvantage of this HNO_3 treatment is the loss of some tetrahedral titanium indicated by the decrease in intensity of the band at 220 nm.

All the spectra of calcined samples were collected and the absence of adsorption bands above 300 nm shows that the formation of dense TiO_2 phase does not occur during calcination of untreated samples. Furthermore Guo et al. reported that not only framework "TiO_4" species but also isolated extra-framework "TiO_6"

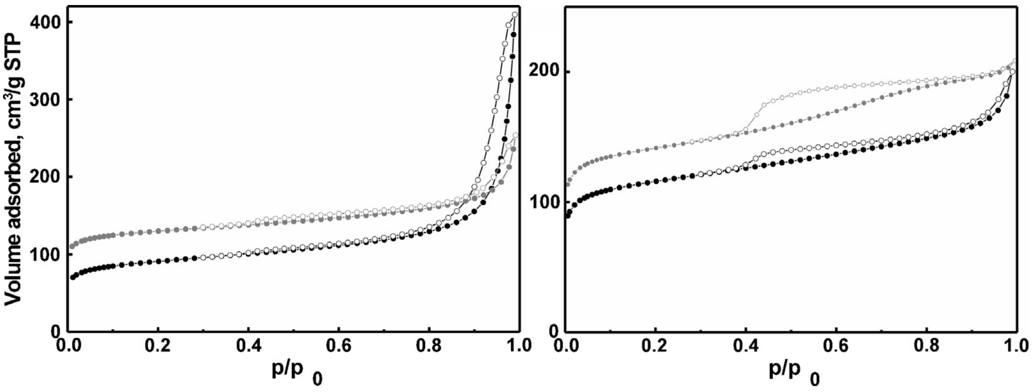

Fig. 4. Argon sorption isotherms of Ti CFI (100) (left black), Ti-CFI (60) (left gray), Ti-CFI (40) (right black) and Ti-CFI (25) (right gray); adsorption branch is in full dots, desorption is in empty dots; gray isotherms are moved +25 cm^3/g for clarity.

species (with absorption band at 270 nm) are active in the epoxidation reaction [27]. Taking into account these findings together with the loss of some framework titanium mentioned above, we used untreated samples in catalytic experiments.

3.2. Catalysis

The Ti-CFI catalysts were tested in the epoxidation of 1-octene, cyclooctene, α-pinene and norbornene and compared with TS-1 zeolite. Results of the catalytic tests are summarized in Table 3. In order to suppress possible intramolecular rearrangements of either substrates or products, the reactions were carried out in acetonitrile [12], which is weakly basic in contrast to alcoholic solvents. Several examples of reactions in methanol are also presented (Table 3, entries 8, 9, 14, 15); however, the solvent effect on the reaction was not systematically studied.

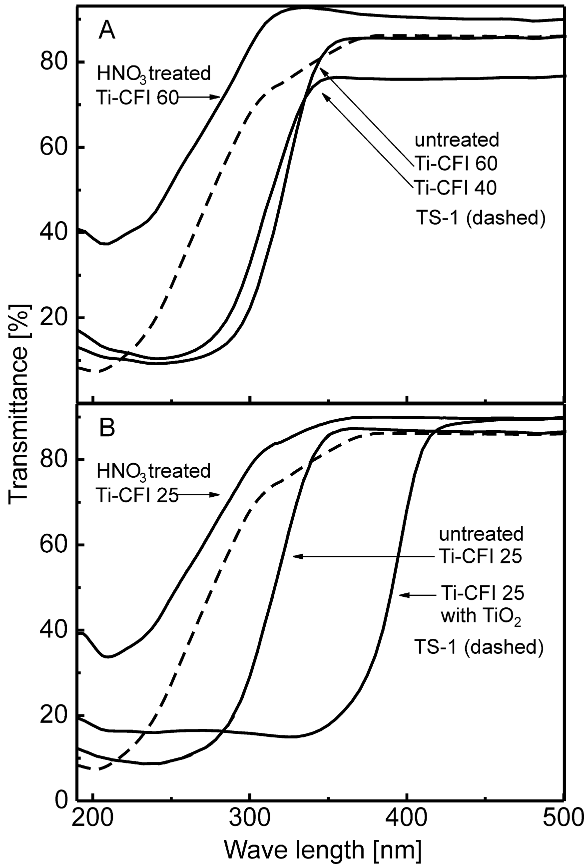

Fig. 5. UV-vis spectra of calcined and HNO$_3$ treated CFI samples and TS-1.

For 1-octene, the performance of the TS-1 is better (56% conversion, 91% selective to the epoxide after 3 h) compared with Ti-CFI (conversion 26%, 46% selective to the epoxide after 3 h) as the linear molecule can easily access TS-1 pores, which entrances are over the whole external surface of the crystal. In contrast to TS-1, only a small fraction of Ti-CFI external surface contains the entrances to the channel system (the channels of CFI are parallel to the longest dimension of the crystals [17]).

When using cyclooctene as a substrate, the Ti-CFI catalysts provided higher conversions (21%) than TS-1 (14%) after 3 h as well as higher yield of the epoxide (7.1%, 5.3% contra 1.0% for Ti-CFI (40), Ti-CFI (100) and TS-1 after 3 h, respectively). The active sites in Ti-CFI are more easily accessible for bulkier substrate than the catalytic centers in medium-pore TS-1. The selectivity to the epoxide (defined as amount of epoxide among all observed oxygenate products) increased from 77 up to 99% when Ti-CFI was ion-exchanged with ammonium nitrate (entry 6) probably due to the removal of residual Li$^+$ cations from the material [28]. Cyclooctenone and hydroxy-cyclooctene were observed as main oxidation byproducts in all the reactions. Our results indicate that the material should be ion-exchanged before catalytic tests. The effect of solvent was not studied systematically, however, in cyclooctene epoxidation we tested acetonitrile as well as methanol under otherwise the same reaction conditions over ion-exchanged catalysts Ti-CFI (40) and Ti-CFI (60). Conversion of cyclooctene in acetonitrile over ion-exchanged Ti-CFI (40) was 4.8% after 3 h while in methanol the conversion was only 3.2%. Selectivity to cyclooctene oxide was practically 100%. In the case of ion-exchanged catalyst Ti-CFI (60), the conversion of cyclooctene was 10.5% in acetonitrile and 2.4% in methanol after 3 h. Again, the selectivity to the epoxide was higher than 99%. It can be concluded that cyclooctene epoxidation in acetonitrile proceeds with a higher reaction rate than in methanol while the selectivity to the epoxide over both Ti-CFI catalysts is close to 100%.

α-Pinene underwent the epoxidation over Ti-CFI catalyst although the selectivity to epoxide was low (38% after 4 h) in comparison to cyclooctene and norbornene (selectivity to the epoxide 75–99%) at the conversion of 20–30%. It is in accordance with the results obtained by van der Waal et al. in epoxidation reactions of other terpenes like α-terpineol or limonene over Ti-BEA zeolite. Terpenes easily undergo intramolecular rearrangements [12]. It was evidenced in our case by observation of a variety of side products including carbonyl and hydroxyl compounds. In contrast, TS-1 completely failed to catalyze the epoxidation of α-pinene as expected. The α-pinene is a bulky rigid molecule, not able to enter the pores of TS-1.

Table 3
Oxidation of various alkenes with H_2O_2 over Ti-CFI and TS-1 catalysts.

Entry	Substrate	Catalyst	Si/Ti	*t* (°C)	Time (h)	$X_{(\text{alkene})}$ (%)[c]	Selectivity to oxygenates (%)[d]	Epoxide in products (%)[e]
1	1-Octene	Ti-CFI(40)	36	50	3	26	3	46
2	1-Octene	TS-1	38	50	3	56	29	91
3	Cyclooctene	Ti-CFI(40)	36	50	3	21	34	75
4	Cyclooctene	Ti-CFI(100)	106	50	3	21	25	77
5	Cyclooctene	TS-1	38	50	3	14	7.2	99
6	Cyclooctene	Ti-CFI(40)[b]	36	60	3	4.8	54	99
7	Cyclooctene	Ti-CFI(60)[b]	63	60	3	10.5	20	99
8	Cyclooctene[a]	Ti-CFI(40)[b]	36	60	3	3.2	66	99
9	Cyclooctene[a]	Ti-CFI(60)[b]	63	60	3	2.4	38	99
10	α-Pinene	Ti-CFI(60)	63	50	4	24	5.8	38
11	α-Pinene	TS-1	38	50	4		No epoxide	
12	Norbornene	Ti-CFI(60)[b]	63	60	4	29	21	95
13	norbornene	TS-1	38	60	4	56	8.6	90
14	Norbornene[f]	Ti-CFI(25)[b]	23	60	1	16	5.9	82
15	Norbornene[f]	Ti-CFI(40)	36	60	1	7	1.8	81

[a] Reaction performed in methanol.
[b] Ion-exchanged catalyst.
[c] Conversion of alkene is defined as overall amount of consumed alkene.
[d] Selectivity to oxygenates is defined as [oxygenate products]/[consumed alkene].
[e] Amount of the epoxide among all observed oxygenate products.
[f] Reaction performed in methanol under conditions used in [12].

Norbornene was oxidized to 2,3-epoxynorbornane with both Ti-CFI and TS-1 catalysts. The best result was obtained using ion-exchanged Ti-CFI (60) catalyst (29% conversion; 21% selective to oxygenates; selectivity to oxygenates oxidation is defined as [oxygenate products]/[consumed alkene]; 95% selective to the epoxide after 4 h). To compare the performance of the catalyst with previously published data for Ti-BEA and Ti-MCM-41, two reactions were carried out in methanol under the same conditions as in reference [12]. The conversions of norbornene in 1 h over ion-exchanged Ti-CFI (25) and Ti-CFI (40) were 16% and 7% respectively. Van der Waal et al. achieved conversion of 13.3% (Ti-BEA) and 6.7% (Ti-MCM-41). For both Ti-CFI (40) and ion-exchanged Ti-CFI (25) the selectivity to oxygenates in 1 h is lower than that reported in [12] (1.8% and 5.9%, respectively, contra 67% Ti-BEA; 65% Ti-MCM-41). However, the Ti-CFI catalysts are more selective to the epoxide than Ti-BEA (81–82% contra 56%). Main oxygenate byproduct was 3-hydroxy-norbornan-2-on.

The leaching test was done with ion exchanged Ti-CFI (60) catalyst. The reaction mixture containing cyclooctene as a substrate was left to react at 60 °C for 3 h. Then the catalyst was filtered off and the mixture was stirred at 60 °C and samples were taken in 1 h intervals. No further formation of cyclooctene oxide was observed for additional 4 h. This result evidences that the reaction does not proceed in the homogeneous phase.

The epoxides are stable under the reaction conditions while diols-products of epoxide hydrolysis–were not observed. The stability of the epoxides under the reaction conditions was studied in an experiment, where cyclooctene oxide and α-pinene oxide, respectively, were used instead of substrate at 60 °C under the same conditions (including the presence of hydrogen peroxide) as the catalytic experiments. No drop in concentration of the epoxides was observed during 5 h.

4. Conclusions

The first synthesis of titanosilicate with CFI topology is reported. The Ti-CFI was synthetized using *N*(16)-methylsparteinium hydroxide as the template and titanium(IV) butoxide and Cab-O-Sil M-5 as the source of titanium and silicon, respectively, in the presence of Li cations. The lowest Si/Ti ratio in product, obtained using our synthesis protocol, was 23.

The incorporation of titanium was confirmed by EDX and UV/Vis spectroscopy. The length of the hydrothermal synthesis increased while the Si/Ti molar ratio decreased in the reaction mixture. Textural properties of the samples determined from argon adsorption at −186 °C are consistent with those reported previously.

Prepared CFI titanosilicates are active catalysts for epoxidation of C═C double bond with hydrogen peroxide as an oxidant. For bulky substrates like cyclooctene, α-pinene, and norbornene, the performance exceeds conventional TS-1 zeolite demonstrating that the preparation of large pore titanosilicates is a useful approach.

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