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Titanosilicate beads as versatile catalysts for the conversion of trioses to lactates and for the epoxidation of alkenes

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ABSTRACT

Titanosilicate beads with hierarchical porosity (TiSil-HPB-60) were prepared from an anion-exchange resin and proved to be a versatile heterogeneous catalyst displaying activity both in the conversion of trioses to ethyl lactate and in the epoxidation of alkenes. In the former reaction, TiSil-HPB-60 showed higher catalytic activity compared to two well-known titanosilicate catalysts: the crystalline microporous TS-1 and the ordered mesoporous Ti-MCM-41. Notably, TiSil-HPB-60 displayed significantly high selectivity towards ethyl lactate due to the absence of strong Brønsted acid sites. In the epoxidation of alkenes with aqueous H_2O_2, TiSil-HPB-60 displayed improved epoxide yield compared to TS-1 and Ti-MCM-41 when the bulky cyclohexene was used as substrate, while TS-1 was the most active catalyst with the linear 1-octene. In both reactions, the separation of TiSil-HPB-60 from the reaction mixture is very straightforward, thanks to its bead format, and the catalyst can be reused in successive catalytic cycles without significant loss of activity.

1. Introduction

Porous titanosilicates (e.g. TS-1 and Ti-MCM-41) have long been known to possess remarkable activity in the selective oxidation of organic molecules at mild conditions using H_2O_2 as oxidant [1–14]. On the other hand, some studies opened up to their novel application in the reactions of transesterification, aldol condensation and aminolysis of epoxides, indicating that porous titanosilicates can be employed as Lewis-acid catalysts [15,16]. Recently, we synthesized titanosilicate beads with hierarchical porosity (TiSil-HPB-60) from a preformed titanosilicate solution using a porous anion-exchange resin as hard template [17]. TiSil-HPB-60 was used as a catalyst for the epoxidation of a wide range of bulky alkenes with *tert*-butyl hydroperoxide and aqueous H_2O_2 and showed improved catalytic performances compared to Ti-MCM-41 and TS-1. It is worth noting that the separation of TiSil-HPB-60 from the reaction solutions is very straightforward, which is relevant in the perspective of an industrial application. Here, we demonstrate the versatility of TiSil-HPB-60, by employing this material as heterogeneous catalyst both for epoxidation reactions and for the conversion of dihydroxyacetone to ethyl lactate. Lactic acid and alkyl lactates can be used as environmentally friendly solvents and play an important role in the production of biodegradable polymers such as polylactic acid (PLA) [18,19]. The conventional process to synthesize lactic acid is based on the microbial fermentation of glucose and sucrose [20]. However, such process is limited by low productivities and needs expensive and energy-inefficient separation and purification steps. An alternative and sustainable route to produce lactic acid or alkyl lactate is provided by the catalytic conversion of triose sugars, *i.e.* dihydroxyacetone (DHA) and glyceraldehyde (GLA). Considering that DHA and GLA can be obtained by the oxidation of glycerol, which is the main by-product of the production of biodiesel via transesterification, the catalytic conversion of trioses to lactates represents an important reaction in the field of renewable biomass conversion and green chemistry. Recently, various solid acid materials have been reported as heterogeneous catalysts for the conversion of trioses to lactic acid or alkyl lactate [21–25]. Systematic studies with zeolites with different types and number of acid sites showed that a combination of Lewis acidity and mild Brønsted acidity catalyzes the selective conversion of trioses to the desired lactate product. On the other hand, strong Brønsted acid sites catalyze the formation of the dialkyl acetal of pyruvic aldehyde side-product [23]. TiSil-HPB-60 is expected to have a suitable population of acid sites for catalyzing the selective synthesis of lactates from trioses.

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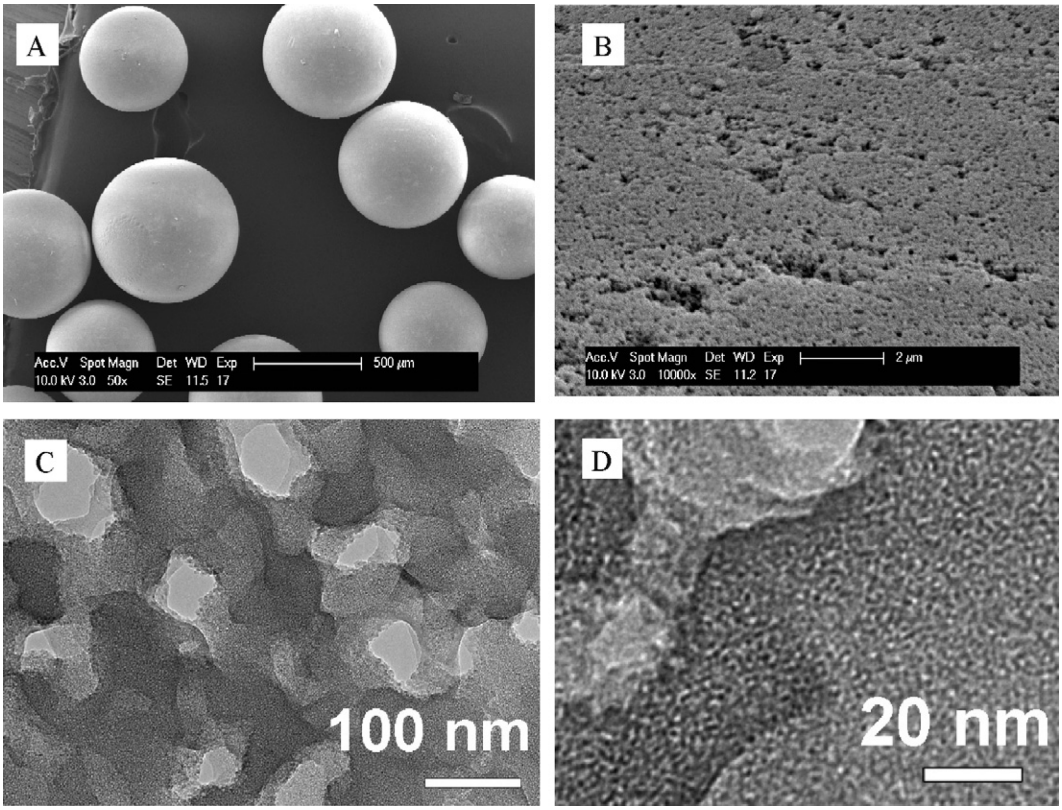

Fig. 1. SEM (A and B) and TEM (C and D) images of TiSil-HPB-60.

2. Experimental

2.1. Materials

The preparation of titanosilicate beads with hierarchical porosity (TiSil-HPB-60) was performed according to our recently reported procedure [17]. Briefly, Amberlite® IRA-900 resin was used as the hard template and a preformed titanosilicate solution (with Si/Ti = 31.8) was used as the inorganic source. TiSil-HPB-60 with Si/Ti = 36 was obtained after hydrothermal treatment at 60 °C for 24 h followed by calcination at 550 °C for 6 h. Titanosilicate beads with lower Ti content (Si/Ti = 54 and 76) were prepared via similar procedures, using a molar ratio of Si to Ti of 47.7 and 95.5 in the preformed titanosilicate solution.

Ti-MCM-41 (Si/Ti = 59) and TS-1 zeolite (Si/Ti = 35) with crystal size of *ca.* 190 ± 20 nm were synthesized according to literature methods [2,26]. Si-MCM-41 was prepared via similar procedure as that for Ti-MCM-41, except for no addition of Ti source. TiO_2 used in this work was purchased from Aldrich.

2.2. Characterization

X-ray diffraction (XRD) patterns were measured on a STOE STADI P instrument using Cu K_α radiation. The isotherms of nitrogen adsorption/desorption were measured at liquid nitrogen temperature using a Coulter Omnisorp and a Micromeritics TriStar 3000. The pore-size distribution was calculated using Horvath–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) models [27,28]. UV–visible spectra were measured with a Varian Cary 5 spectrophotometer in the 200–800 nm region. The samples were not treated before measurement and the UV–visible spectra were recorded in air. Scanning electron microscopy (SEM) images were taken on a Philips XL30 FEG apparatus. Si/Ti molar ratios were determined by means of EDX analysis on a Philips XL30 FEG: each sample was measured 5 times in five randomly selected areas and the average of the results was calculated. Transmission electron microscopy (TEM) investigation was made on special prepared plan-view sample, using a Philips CM20 electron transmission microscope operating at 200 kV [17]. NH_3 temperature-programmed desorption (NH_3-TPD) measurements were carried out to characterize the acidity of the samples. After pretreatment of the samples (70.1 mg) in He with a flow rate of 20 ml/min at 500 °C for 1 h, the samples were exposed to 5% ammonia in N_2 at 100 °C for 15 min and were then purged with He for 30 min. NH_3-TPD profiles were obtained between 100 and 750 °C with a heating ramp at 10 °C/min by monitoring the desorbed ammonia with a Pfeiffer Omnistar quadrupole mass spectrometer.

2.3. Catalytic tests

Conversion of dihydroxyacetone to ethyl lactate. All the catalysts were treated at 120 °C overnight prior to use. Typically, 5 ml of 0.4 M dihydroxyacetone in ethanol and decane (GC internal standard) were added to 0.2 g of catalysts. The reaction was performed in closed glass vials at the selected temperature for 6 h under magnetic stirring. The product yields were determined using an Interscience Trace GC Ultra equipped with a RTX-5 fused silica column (5 m, 0.1 mm). TiSil-HPB-60 deposited spontaneously at the bottom of the reaction vial a few seconds after the stirring was stopped. Before the recycling tests, the reaction solution was removed with a glass pipette. Next, ethanol was added and the sample was stirred for few minutes. After the stirring was stopped and the beads had deposited, the ethanol solution was removed with a pipette. The procedure was repeated for a total of four times, after which the beads were dried at 120 °C and reused.

Epoxidation of alkenes with aqueous H_2O_2. The epoxidation reactions were carried out in a glass vial under vigorous stirring. In a typical run, the alkene, the solvent (methanol or acetonitrile),

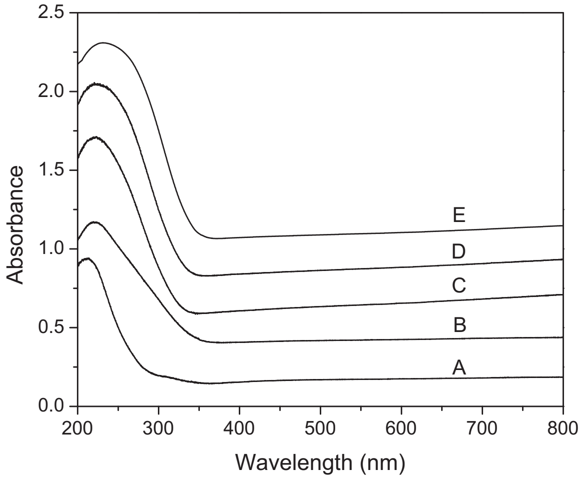

Fig. 2. UV–Vis spectra of TS-1 (A), Ti-MCM-41 (B), TiSil-HPB-60 (Si/Ti = 76) (C), TiSil-HPB-60 (Si/Ti = 54) (D) and TiSil-HPB-60 (Si/Ti = 36) (E). For the sake of clarity, spectra B-E are offset along the vertical axis.

aqueous H_2O_2 and the catalyst were mixed in the vial and heated to 60 °C. After reaction for 5 h, the products were analyzed on the same GC Ultra used for monitoring the synthesis of lactates.

3. Results and discussion

3.1. Characterization of the materials

TS-1 and Ti-MCM-41 were characterized by X-ray diffraction: the patterns correspond to the expected MFI-type zeolitic structure for TS-1 and to the typical hexagonal (P6mm) arrangement of mesoporous channels for Ti-MCM-41. TiSil-HPB-60 has been characterized in detail in previous work [17]: it can be described as amorphous titanosilicate beads (0.5–1.5 mm) with a hierarchical porosity including micropores (0.5 nm) and large mesopores with a diameter of *ca.* 40–50 nm (Fig. 1). The BET surface area of TS-1, Ti-MCM-41 and TiSil-HPB-60 (Si/Ti = 36) is 425, 916 and 618 m^2/g, respectively. The BJH pore-size distribution (from adsorption) of Ti-MCM-41 presents a maximum at 2.4 nm and the cumulative pore volume is 0.54 cm^3/g. It is worth mentioning that TiSil-HPB-60 contains TS-1 zeolite building units [17], which is an important difference compared to other conventional mesoporous titanosilicates such as Ti-MCM-41.

The coordination environment of Ti in TS-1, Ti-MCM-41 and TiSil-HPB-60 was investigated by UV–Vis spectroscopy. A main band centered at 210, 220 and 220–230 nm (Fig. 2A–E), respectively, indicates that most of the Ti species are located in the framework in tetrahedral coordination. The variety in band center position of the three titanosilicates is ascribed to the presence of different types of tetrahedral Ti-sites, such as $Ti(OSi)_4$ and $Ti(OH)(OSi)_3$. The latter would generate a broad band centered at 230 nm [29,30]. Moreover, a small amount of higher-coordinated Ti species coexist with the tetrahedral Ti sites both in Ti-MCM-41 and TiSil-HPB-60 materials, as indicated by the broad signal extending up to 290 nm. These higher-coordinated Ti species are assigned to species originating from the reversible interaction of tetrahedral Ti with moisture, and/or to polymerized octahedral species. The absence of the band characteristic of octahedral extra-framework titanium at about 330 nm indicates that no separated titania (anatase) phase was formed during the synthesis of any of the titanosilicates.

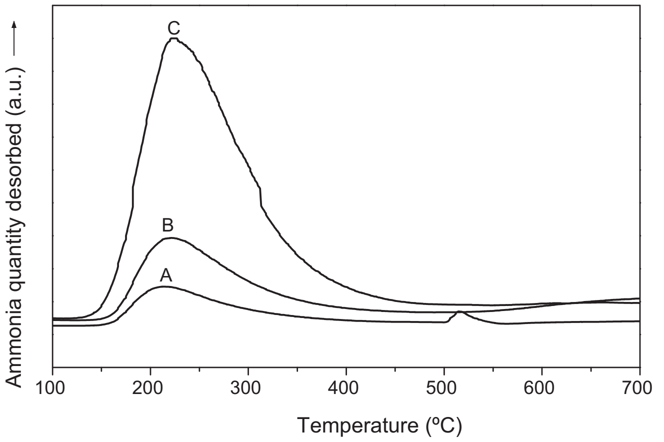

Fig. 3. Temperature programmed desorption of NH_3 (NH_3-TPD) profiles of TS-1 (A), Ti-MCM-41 (B), and TiSil-HPB-60 (Si/Ti = 36) (C).

To determine the population of acid sites, an NH_3-TPD study was performed on the titanosilicates: all the materials show a main desorption peak between 216 and 224 °C, corresponding to mild acid sites (Fig. 3). The different intensity of this peak indicates that the number of acid sites (per gram of material) increases in the order: TS-1 < Ti-MCM-41 < TiSil-HPB-60. Although it has been reported that Lewis acid sites in titanosilicates are the predominant species [15,16], it is likely that the observed NH_3-TPD peak also contains a contribution from mild Brønsted acid sites. Particularly, the presence of a large population of surface silanol groups in TiSil-HPB-60, which can act as weak Brønsted acid sites, was proved by ^{29}Si NMR results in our previous work [17].

3.2. Catalytic performances

TiSil-HPB-60 was studied as heterogeneous catalyst in two reactions for the sustainable production of valuable chemicals: the conversion of the triose sugar dihydroxyacetone to ethyl lactate and the epoxidation of alkenes with aqueous hydrogen peroxide. The catalytic performance of TiSil-HPB-60 in these reactions was compared to that of two well-known titanosilicate materials: TS-1 and Ti-MCM-41.

TiSil-HPB-60 displayed much higher epoxide yield than both Ti-MCM-41 and TS-1 in the epoxidation of cyclohexene with aqueous H_2O_2 (Table 1) [17]. The improved catalytic behavior of TiSil-HPB-60 is mainly ascribed to its large mesopores, which can promote higher activity than with TS-1 by improving the accessibility of active titanium sites to cyclohexene molecules, and higher selectivity than with Ti-MCM-41 thanks to a higher rate of diffusion of the products out of the larger pores of TiSil-HPB-60 [17]. The combined selectivity towards cyclohexene epoxide plus 1,2-cyclohexanediol (formed from the hydrolysis of the epoxide) on TiSil-HPB-60 is *ca.* 95%, indicating that the radical mechanism leading to allylic oxidation products does not take place in a significant amount [17]. Furthermore, TiSil-HPB-60 proved to be active in the epoxidation of

Table 1
Catalytic performances in the epoxidation of alkenes.[a]

Catalyst	Si/Ti[b]	X_{CH} (%)[c]	Y_{CHE} (%)[d]	X_{1O} (%)[e]	Y_{EO} (%)[f]
TiSil-HPB-60	36	20.2	8.2	12.6	1.1
Ti-MCM-41	59	28.8	2.6	4.9	0.4
TS-1	35	8.7	3.7	29.4	18.8

[a] Epoxidation of cyclohexene: 4.5 mmol of cyclohexene, 4.5 ml of acetonitrile, 2.25 mmol of aqueous H_2O_2 (50 wt.%), 60 mg of catalyst, 5 h at 60 °C. Epoxidation of 1-octene: 5 mmol of 1-octene, 7.6 ml of methanol, 2.5 mmol of aqueous H_2O_2 (35 wt.%), 30 mg of catalyst, 5 h at 60 °C.

[b] Molar ratios measured by EDX.

[c] X_{CH} = conversion of cyclohexene.

[d] Y_{CHE} = yield of cyclohexene epoxide.

[e] X_{1O} = conversion of 1-octene.

[f] Y_{EO} = yield of 1,2-epoxyoctane.

Table 2
Catalytic performances in the conversion of DHA to ethyl lactate.[a]

Catalyst	Si/Ti[b]	Y_{EL} (%)[c]	Y_{Ac} (%)[d]	Y_{He} (%)[e]	S_{EL} (%)[f]	TON[g]
TiSil-HPB-60	36	29.6	0.6	0	97.9	6.6
Si-MCM-41	–	0	0	0	–	–
Ti-MCM-41	59	11.7	0.9	1.4	83.7	4.2
TS-1	35	13.1	0	0.3	97.6	2.9
TiO_2	–	0.1	0	0	100	<0.1

[a] 5 ml of ethanol solution containing dihydroxyacetone (0.4 M) and 200 mg of catalyst, 90 °C, 6 h.

[b] Molar ratios measured by EDX.

[c] Y_{EL} = yield of ethyl lactate.

[d] Y_{Ac} = yield of diethyl acetal of pyruvic aldehyde.

[e] Y_{He} = yield of ethyl hemiacetal of pyruvic aldehyde.

[f] S_{EL} = selectivity towards ethyl lactate.

[g] Turnover number (TON) expressed as moles of ethyl lactate obtained per mole of Ti in the catalyst.

other bulky substrates, such as cyclooctene, cyclodecene, cyclododecene and cyclododecatriene [17]. However, TiSil-HPB-60 gave only poor epoxide yield in the epoxidation of the linear 1-octene with aqueous H_2O_2. With this substrate, TS-1 gave much higher epoxide yield, while Ti-MCM-41 was even less active than TiSil-HPB-60 (Table 1). The major side-products in the epoxidation of 1-octene are 1,2-octanediol and the corresponding methyl ether, generated from the epoxide by reaction with water and methanol, respectively. The lower activity in the epoxidation of 1-octene with TiSil-HPB-60 compared to TS-1 is ascribed to the higher surface hydrophobicity of TS-1 (see Refs. [17,31]), which favors the diffusion of the apolar, linear 1-octene through the pores of the catalyst, and to the higher ratio of active Ti centres in framework tetrahedral sites in TS-1 (see Section 3.1). These results demonstrate that TiSil-HPB-60 is the most favorable catalyst in the epoxidation of bulky substrates, while for linear alkenes TS-1 remains the catalyst of choice.

For the conversion of dihydroxyacetone to lactate in ethanol, the catalytic performance of TiSil-HPB-60 was compared to that of the other titanosilicates, TS-1 and Ti-MCM-41, and to that of all-silica MCM-41 (Si-MCM-41) and of titanium dioxide. All three titanosilicates were active in the conversion of dihydroxyacetone (Table 2). Three products were observed: ethyl lactate, the diethyl acetal of pyruvic aldehyde, and a small amount of the reaction intermediate ethyl hemiacetal of pyruvic aldehyde [32]. It has been proposed that the reaction starts with the formation of pyruvic aldehyde, from which it can proceed towards the lactate by rearrangement via a hydride-shift mechanism with incorporation of an ethanol molecule on Lewis acid sites, or towards the acetal by the reversible addition of ethanol on strong Brønsted acid sites [23,32]. While all tested titanosilicates were active in the reaction, negligible DHA conversion and ethyl lactate formation were observed when Si-MCM-41 and TiO_2 were used as catalysts (Table 2), indicating that Ti sites incorporated in the framework of silica, which act as Lewis acid sites, are playing an essential role as catalytic active sites. All active catalysts gave very high selectivity towards ethyl lactate, in agreement with the expected lack of strong Brønsted acid sites in these materials. Compared with TS-1 and Ti-MCM-41, TiSil-HPB-60 displayed much higher yield of ethyl lactate and TON based on ethyl lactate (Table 2): these results are ascribed to the larger number of acid sites in TiSil-HPB-60 (see Section 3.1) and to the presence of larger mesopores in these titanosilicate beads, which is helpful for faster diffusion of reactants and products.

Fig. 4 shows the dependence of catalytic activity and selectivity towards ethyl lactate on reaction time with TiSil-HPB-60. The activity gradually increased with reaction time and tended to reach a plateau after 5 h up to 24 h. Notably, the selectivity towards ethyl lactate remained higher than 90% and no significant change was observed as the reaction proceeds.

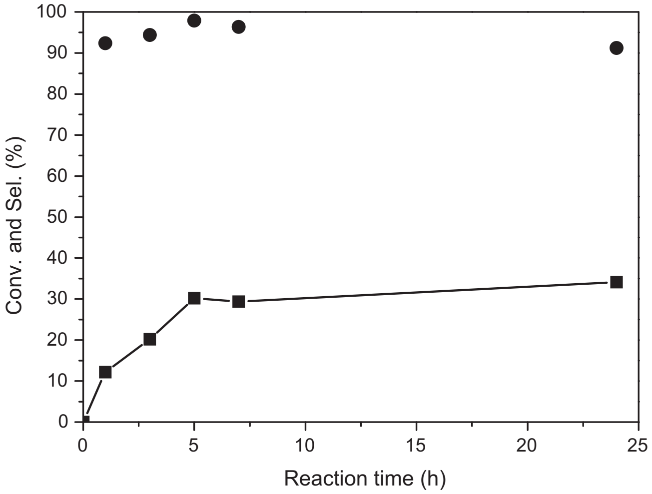

Fig. 4. Conversion of DHA (as sum of the yields of all reaction products) (■) and selectivity towards ethyl lactate (●) on TiSil-HPB-60 as a function of reaction time.

In order to evaluate whether all the Ti atoms in the titanosilicate beads contribute to the conversion of the triose to lactate, we synthesized and tested titanosilicate beads with different Ti content. Characterization of the titanosilicate beads by UV–Vis spectroscopy shows that all three TiSil-HPB-60 materials exhibit analogous absorption bands, indicating that the coordination environments of the titanium sites are similar among these materials (Fig. 2C–E). The titanosilicate beads displayed a linear increase in the activity in the conversion of DHA with increasing Ti content (Fig. 5), suggesting that most, if not all, of the Ti sites equally contribute to the catalytic activity of the material. This result also indicates that most of the Ti species in the titanosilicate beads are accessible for the reactants, implying that TiSil-HPB-60 with hierarchical porosity does not suffer from diffusion limitations in this reaction.

The effect of the catalyst amount on the activity was studied as well for TiSil-HPB-60 (Fig. 6): the linear increase in the activity observed with increasing amount of the catalyst employed (at least up to 0.4 g) is in agreement with the absence of mass diffusion limitations. When 0.1 g of catalyst were used in the reaction, the selectivity towards ethyl lactate was lower than that with a

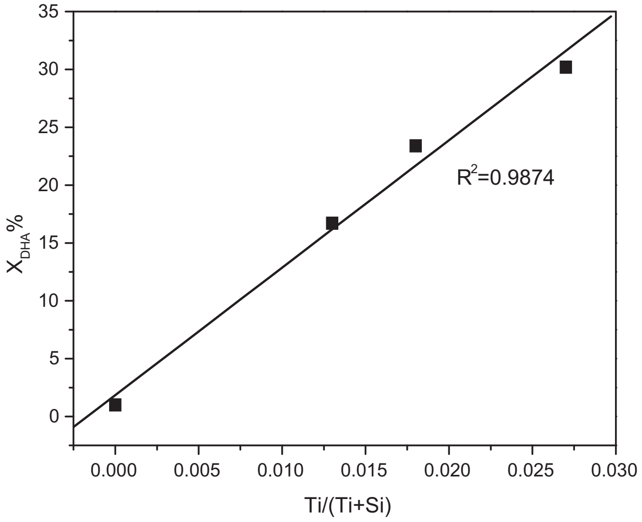

Fig. 5. Conversion of DHA (as sum of the yields of all reaction products) as a function of Ti content in TiSil-HPB-60 (as determined by EDX analysis). The conversions were measured after reaction for 6 h at 90 °C.

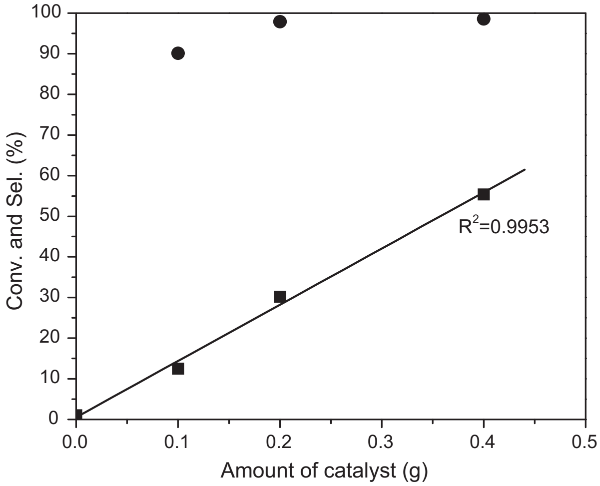

Fig. 6. Conversion of DHA (as sum of the yields of all reaction products) (■) and selectivity towards ethyl lactate (●) as a function of the amount of TiSil-HPB-60 employed in the reaction. The conversions and selectivities were measured after reaction for 6 h at 90 °C.

Table 3
Catalytic performances in the conversion of DHA with TiSil-HPB-60 at different temperatures (of the reaction block).[a]

T (°C)	Y_{EL} (%)	Y_{Ac} (%)	Y_{He} (%)	S_{EL} (%)
75	15.5	1.0	3.1	79.1
90	29.6	0.6	0	97.9
105	47.5	1.2	0.3	97.0

[a] For the reaction conditions, see Table 2.

higher amount of catalyst (0.2 and 0.4 g) and a higher amount of ethyl hemiacetal of pyruvic aldehyde (1% yield) was observed, in line with the role of hemiacetal as reaction intermediate and with the lower selectivity at lower conversion previously observed with other heterogeneous catalysts [23,32].

TiSil-HPB-60 showed higher lactate yield and selectivity at higher reaction temperature (Table 3), in accordance with previous results and with the hypothesis for which the lactate is the most thermodynamically favorable product of the conversion of trioses [23].

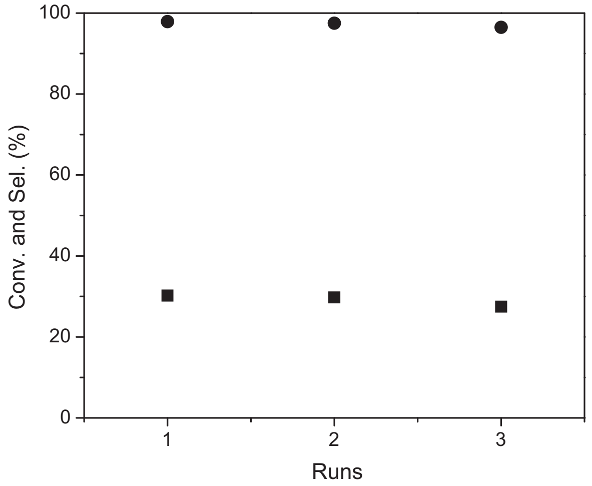

Fig. 7. Conversion of DHA (as sum of the yields of all reaction products) (■) and selectivity towards ethyl lactate (●) upon recycling of TiSil-HPB-60. The conversions and selectivities were measured after reaction for 6 h at 90 °C.

In view of a possible industrial application, it is important to evaluate the reusability of TiSil-HPB-60: for this purpose, the beads were tested in several catalytic cycles. The recycling procedure for TiSil-HPB-60 only implied four washings in ethanol at room temperature without any calcination. It is worth noting that the bead shape of TiSil-HPB-60 was unaffected by stirring during the catalytic tests. The beads deposited automatically on the bottom of the vial in a few seconds after stopping the stirring and, therefore, could be easily separated from the reaction solution without centrifugation or filtration, as observed in the epoxidations [17]. No significant loss of catalytic activity was observed and the selectivity towards ethyl lactate remained approximately constant when reusing TiSil-HPB-60 in three successive catalytic runs (Fig. 7), proving the stability of this material under the employed reaction and recycling conditions. This result also reveals that no deactivation due to adsorbed reaction residues occurs, probably thanks to the large non-ordered mesopores that favor a rapid mass transport of reaction residues away from the active titanium sites.

4. Conclusions

Titanosilicate beads with hierarchical porosity (TiSil-HPB-60) are active and highly selective catalysts for the formation of ethyl lactate from the triose sugar dihydroxyacetone. TiSil-HPB-60 is more active than TS-1 and Ti-MCM-41 and more selective than heterogeneous catalysts containing Brønsted acid sites under the same reaction conditions. The good activity and high selectivity towards ethyl lactate and the ease of reuse demonstrate the potential of TiSil-HPB-60 titanosilicate beads as catalyst in the conversion of these renewable compounds to desirable chemicals. This versatile catalyst is also superior to the other studied titanosilicates in the epoxidation of cycloalkenes, while it displays lower activity than TS-1 in the conversion of the linear 1-octene.

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