## Titanosilicate Beads with Hierarchical Porosity: Synthesis and Application as Epoxidation Catalysts

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**Abstract:** Porous titanosilicate beads with a diameter of 0.5–1.5 mm (TiSil-HPB-60) were synthesized from a preformed titanosilicate solution with a porous anion-exchange resin as template. The bead format of this material enables its straightforward separation from the reaction mixture in its application as a liquid-phase heterogeneous catalyst. The material displays hierarchical porosity (micro/mesopores) and incipient TS-1 structure building units. The titanium species are predominantly located in tetrahedral frame-

#### Introduction

Since the discovery of microporous TS-1<sup>[1]</sup> and mesoporous Ti-MCM-41,<sup>[2-4]</sup> many porous titanosilicates with tetrahedrally substituted Ti species have been widely studied in an attempt to promote heterogeneous oxidations of various organic substrates with hydrogen peroxide.<sup>[5–13]</sup> Numerous studies reveal that high specific surface areas and pore architectures in well-defined micro- and mesoporous structures are pivotal for the success of these titanosilicates as catalysts for heterogeneous oxidations.<sup>[14]</sup> It is generally accepted that particle size is another structural parameter of

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work positions. TiSil-HPB-60 is a highly active catalyst for the epoxidation of cyclohexene with *t*-butyl hydroperoxide (TBHP) and aqueous  $H_2O_2$ . With both oxidants, TiSil-HPB-60 gave higher epoxide yields than Ti-MCM-41 and TS-1. The improved catalytic performance of TiSil-HPB-60 is mainly as-

**Keywords:** epoxidation • green chemistry • heterogeneous catalysis • hierarchical porosity • titanosilicate beads cribed to the large mesopores favoring the diffusion of reagents and products to and from the titanium active sites. The epoxide yield and selectivity could be further improved by silylation of the titanosilicate beads. Importantly, TiSil-HPB-60 is a stable catalyst immune to titanium leaching, and can be easily recovered and reused in successive catalytic cycles without significant loss of activity. Moreover, TiSil-HPB-60 is active and selective in the epoxidation of a wide range of bulky alkenes.

these materials, which plays a very important role in heterogeneous oxidation.<sup>[15-18]</sup> For example, TS-1 nanoparticles showed much higher activity in phenol hydroxylation than large TS-1 crystals, as a consequence of the strong diffusion limitation experienced by the reactants on reaching the active sites in large crystals.<sup>[15]</sup> Ti-MCM-41 nanoparticles displayed higher conversions and initial reaction rates in the epoxidation of cyclohexene than Ti-MCM-41 with micrometric particle size, because the accessibility of the catalytic Ti species was enhanced in these Ti-MCM-41 nanoparticles.[17-19] These results indicate that porous titanosilicates in the form of nanoparticles have many benefits for catalytic applications in various selective oxidations over the corresponding large particles. An alternative way to improve the catalytic activity of TS-1 crystals in the epoxidation of large substrates is to increase the accessibility of the Ti sites by creating mesopores in the zeolitic structure.<sup>[20,21]</sup> However, a drawback of all these systems in heterogeneous oxidations is their awkward separation from the reaction solution during catalyst recycling, which normally requires high-speed centrifugation or special filtration. This hinders recovery of the products and recycling of the catalysts and, therefore, limits broad industrial application of these porous titanosilicates as heterogeneous catalysts in selective oxidations. Furthermore,

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some porous titanosilicates suffer from leaching of active titanium species in the presence of  $H_2O_2$ , which results in their gradual deactivation.<sup>[22,23]</sup> It is of great interest to develop novel porous titanosilicates with highly catalytic and stable Ti species that also have well-defined macroscopic morphologies, which can facilitate separation from reaction solutions.

Herein, we report the synthesis and catalytic application of such a material in the form of titanosilicate beads with hierarchical porosity and active and stable Ti species (TiSil-HPB-60). This material was prepared by using anion-exchange resin beads as a shape- and structure-directing agent. The obtained titanosilicate beads were used to catalyze the epoxidation of various alkenes with *t*-butyl hydroperoxide (TBHP) and aqueous  $H_2O_2$ , and proved to be active and selective catalysts with all substrates tested. Notably, the separation of the beads from the reaction solution was extremely straightforward and did not require any centrifugation or filtration.

#### **Results and Discussion**

**Characterization of the catalysts**: TiSil-HPB-60 can be described as titanosilicate beads with an amorphous structure with incipient TS-1 features, and a hierarchical porosity that includes disordered micro- and mesopores. This description stems from the full characterization of the material.

After synthesis and calcination, TiSil-HPB-60 consists of hard, white beads. The material retains the same bead-size distribution as that of the resin beads used as template; bead size ranges from 0.5 to 1.5 mm (see SEM images in Figure 1 A and C). The resin beads as well as TiSil-HPB-60



Figure 1. SEM images of A), B) Amberlite IRA-900, C), D) TiSil-HPB-60, and E), F) TiSil-Pow-60.

contain a large amount of mesopores as well as a small quantity of macropores (Figure 1B and D). In contrast, the material prepared without the resin template, TiSil-Pow-60, contains irregular bulky particles (Figure 1E) without meso-or macropores (Figure 1F).

TEM indicates that the mesopores of TiSil-HPB-60 are predominantly within the range of 20–50 nm (Figure 2A and B), with a lesser contribution of larger pores at 50–150 nm.



Figure 2. TEM images of a bead of TiSil-HPB-60 at different magnifications. Scale bars: Characteristic mesopores are indicated by the arrows.

The walls between these meso/macropores contain micropores with a diameter of about 0.5 nm (Figure 2 C). These micropores are generally disordered, in that they are not in the form of a zeolitic structure, although domains with short-range order are also observed (Figure 2 C, inset).

The characterization of the textural features of the materials was completed by measuring their nitrogen adsorption/desorption isotherms. The N<sub>2</sub> adsorption/desorption isotherm of TiSil-Pow-60 belongs to type I.<sup>[24]</sup> The predominant adsorption finishes below  $P/P_0=0.05$  (Figure 3 A), which is



Figure 3. Nitrogen adsorption/desorption isotherms of A) TiSil-Pow-60 and B) TiSil-HPB-60.

characteristic of microporous materials templated from tetrapropylammonium hydroxide (TPAOH). The N<sub>2</sub> adsorption/desorption isotherm of TiSil-HPB-60 has a hysteresis loop above  $P/P_0=0.9$  in addition to a steep uptake below  $P/P_0=0.05$  (Figure 3B), showing the presence of meso- and/or macropores connected through windows of smaller size leading to the so-called bottleneck effect.<sup>[25]</sup> Based on the Horvath–Kawazoe (HK) method, the size of the micropores in TiSil-HPB-60 and TiSil-Pow-60 is 0.5 nm (Figure 4A and



Figure 4. Pore-size distributions of A), B) TiSil-HPB-60, and C), D) TiSil-Pow-60.

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C), which is comparable to the diameter of micropores in TS-1 or ZSM-5 zeolites templated by TPAOH. Notably, the Barrett-Joyner-Halenda (BJH) poresize distribution curve of TiSil-HPB-60 from the adsorption branch indicates that meso- and macropores are present (Figure 4B). However, the poresize distribution curve cannot provide complete information on large meso- and macropores in TiSil-HPB-60 due to the limitations of N2 adsorption analysis. The absence of meso- and macropores in TiSil-Pow-60 is confirmed by its pore-size distribution curve (Figure 4D).

400 d V/dlogd (mm<sup>3</sup> g<sup>-</sup> Intruded volume (mm<sup>3</sup> g<sup>-1</sup>) 300 200 0.01 0.1 10 100 0.001 1 Pore diameter (um) 100 0 . . . . . . . . . . . . . . . . . 1 1 1 1 1 1 1 1 0.01 0.1 1 10 100 1000 Pressure (MPa)

Figure 5. Mercury intrusion curve obtained over TiSil-HPB-60 and the related pore-size distribution curve (inset).

To get a more defined and quantitative description of the porosity in the range of large meso- and macropores, a mercury intrusion porosimetry (MIP) measurement was performed on TiSil-HPB-60 (Figure 5). Only a narrow range of pressures is required to fill most of the porous structure, which indicates a narrow distribution of pore sizes. Indeed, the pore-size distribution (inset, Figure 5) displays a narrow range of pores centered at 40-50 nm. A small fraction of smaller pores (4-20 nm) also appears to be present, while the contribution of the macropores with diameter > 50 nm observed by SEM and TEM is negligible. Combining the results of N<sub>2</sub> adsorption and MIP, the porosity of TiSil-HPB-60 can be described as a bimodal system, with a rather narrow size distribution of micropores (0.5 nm) and of large mesopores (40-50 nm). The pore sizes and volumes and the specific surface areas

The pore sizes and volumes and the specific surface areas of TiSil-HPB-60, TiSil-Pow-60, and the two reference materials Ti-MCM-41 and TS-1 are summarized in Table 1. The

Table 1. Textural properties and specific surface areas.

	Pore size [nm] <sup>[a]</sup>	Micropore $V [cm^3g^{-1}]^{[a]}$	Mesopore V [cm <sup>3</sup> g <sup>-1</sup> ]	Surface area [m <sup>2</sup> g <sup>-1</sup> ] <sup>[a]</sup>
TiSil-HPB-60	0.5; 40–50 <sup>[b]</sup>	0.27	0.47 <sup>[b]</sup>	618
TiSil-Pow-60	0.5	0.21	_	464
Ti-MCM-41	2.4	-	$0.54^{[a]}$	916
TS-1	0.5	0.17	-	425

[a] Determined from N<sub>2</sub> adsorption isotherms at 77 K. [b] Determined by MIP and, thus, based on analysis of pores with diameter  $\ge 4$  nm.

micropore volumes of TiSil-HPB-60 and TiSil-Pow-60 are higher than those of TS-1 zeolite although their micropore sizes are equal; this is possibly due to the disordered micropore structure in the former materials.

**)**. (inset).

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Neither TiSil-HPB-60 nor TiSil-Pow-60 displays any XRD peaks in the  $2\theta$  range between 1 and 60° (not shown here). This indicates that there is no short- or long-range order in the materials, which is consistent with TEM characterization results (Figure 2). The absence of a crystalline structure in TiSil-HPB-60 and TiSil-Pow-60 is ascribed to incomplete crystallization due to the low temperature (60°C) and short synthesis time (24 h).

The FTIR spectrum of TS-1 zeolite exhibits a characteristic band at around 560 cm<sup>-1</sup>, which is assigned to a 5-membered ring of Si–O–T (T=Si or Ti) (see Figure 6A).<sup>[26]</sup> A



Figure 6. IR spectra of A) TS-1, B) TiSil-Pow-60, and C) TiSil-HPB-60 in the region of 400-1000 cm<sup>-1</sup>.

similar but weaker band is present in the FTIR spectra of TiSil-Pow-60 and TiSil-HPB-60 (Figure 6B and C), which indicates that both materials contain TS-1 building units as a consequence of using a preformed titanosilicate solution containing TPAOH in their synthesis.

UV/Vis spectroscopy is generally recognized as one of the most suitable methods to characterize the coordination of Ti species in zeolites and mesoporous titanosilicates. The UV/ Vis spectra of both TiSil-HPB-60 and TiSil-Pow-60 exhibit a band centered at 230 nm with similar intensity (Figure 7), which can be attributed to tetrahedral Ti species in amorphous titanosilicates.<sup>[27,28]</sup> This indicates that the use of the resin beads as shape- and structure-directing agents does not have an influence on the incorporation of Ti species into the silica framework. Note that, although TiSil-HPB-60 contains a certain amount of TS-1 building units, the UV/Vis spectrum is different from that of well-manufactured TS-1. This is ascribed to the presence of various types of tetrahedral Ti sites, such as Ti(OSi)<sub>4</sub> and Ti(OH)(OSi)<sub>3</sub>, which generate the broad band centered at 230 nm.<sup>[29,30]</sup> Moreover, a small amount of higher-coordinated Ti species coexist with the tetrahedral Ti sites in both materials, as indicated by the shoulder between 270 and 290 nm, which is assigned to reversible penta-coordinated Ti species that form from the in-



Figure 7. UV/Vis spectra of A) TiSil-HPB-60 and B) TiSil-Pow-60.

teraction of Ti species with moisture and/or to polymerized hexa-coordinated Ti species.<sup>[28]</sup> The lack of the absorption band characteristic of octahedral extra-framework titanium at about 300–330 nm in both materials shows that no separate titania (anatase) phase is formed during the synthesis.

The fraction of Si atoms in the form of SiOH groups in TiSil-HPB-60, TiSil-Pow-60, and Ti-MCM-41 was determined by <sup>29</sup>Si MAS NMR spectroscopy (Table 2). Each of

Table 2. Silanol content and water adsorption capacity.

	SiOH content [%] <sup>[a]</sup>	Water adsorption capacity [mg g <sup>-1</sup> ] <sup>[b]</sup>
TiSil-HPB-60	50.4	154.6
TiSil-Pow-60	37.6	153.4
Ti-MCM-41	37.6	54.7
S-TiSil-HPB-60	31.6	28.3

[a] Calculated from <sup>29</sup>Si MAS NMR as SiOH(%) =  $\frac{100(2Q^2+Q^3)}{\sum Q^3}$ %. [b] Calculated from TGA by the weight loss of the samples below 150 °C.

the three materials exhibits three peaks at  $\delta = -110$ , -100, and -90 ppm (Figure 8A–C), which are attributed to Si(OSi)<sub>4</sub> ( $Q^4$ ), HOSi(OSi)<sub>3</sub> ( $Q^3$ ), and (HO)<sub>2</sub>Si(OSi)<sub>2</sub> ( $Q^2$ ), respectively.<sup>[12,31]</sup> TiSil-HPB-60 has a higher SiOH content than TiSil-Pow-60 and Ti-MCM-41, which can be attributed to the higher amount of structural defects (disordered meso-



Figure 8. <sup>29</sup>Si MAS NMR spectra of A) Ti-MCM-41, B) TiSil-Pow-60, C) TiSil-HPB-60, and D) S-TiSil-HPB-60.

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pores) in TiSil-HPB-60 than TiSil-Pow-60, and to the lower condensation degree of SiOH groups (due to the low synthesis temperature) than in Ti-MCM-41. To increase the hydrophobicity of the catalyst, TiSil-HPB-60 was treated with trimethylchlorosilane (TMCS) to silylate the surface silanol groups. The successful functionalization of TiSil-HPB-60 is demonstrated by the appearance of a peak at  $\delta = 14$  ppm assigned to (CH<sub>3</sub>)<sub>3</sub>Si–(OSi) groups<sup>[32]</sup> and by the concomitant decrease in the intensity of the peaks due to silanol groups (S-TiSil-HPB-60, Figure 8D and Table 2).

The hydrophilicity of TiSil-HPB-60 (with and without silulation), TiSil-Pow-60, and Ti-MCM-41 were evaluated by thermogravimetric analysis (TGA) from the water adsorption capacity, which was calculated from the weight loss of the samples below 150 °C (Figure 9 and Table 2). TiSil-HPB-



Figure 9. Thermogravimetric analysis of A) TiSil-HPB-60, B) TiSil-Pow-60, C) Ti-MCM-41, and D) S-TiSil-HPB-60.

60 and TiSil-Pow-60 show markedly higher water adsorption capacities than Ti-MCM-41, which suggests that the hydrophilicity estimated by TGA cannot be directly correlated with the SiOH content determined by <sup>29</sup>Si NMR spectroscopy when comparing materials with different structural and textural properties. On the other hand, both the TGA and <sup>29</sup>Si NMR spectroscopy data clearly indicate that the silylation of TiSil-HPB-60 leads to an increase in the hydrophobicity of the material.

On the basis of the characterization results, it is possible to propose a path for the formation of TiSil-HPB-60 by the means of templating with anion-exchange resin beads. The negatively charged titanosilicate species in the preformed alkaline titanosilicate solution can exchange with anions in the resin beads. The resin-titanosilicate composites evolve through condensation of the titanosilicate species, which takes place during the hydrothermal treatment. The material, at this stage, consists of two interconnected 3D networks: an organic part originating from the resin, and an inorganic part consisting of the condensed titanosilicate matter (as shown by energy dispersive X-ray (EDX) analysis). In the next step, the resin and TPAOH are removed by calcination, generating a self-bonded solid with hierarchical porosity (TiSil-HPB-60). This procedure is similar to that reported for the preparation of Silicalite-1 microspheres composed of primary nanoparticles (ca. 100 nm) by using shape-directing macro-templates.<sup>[33]</sup>

Catalytic performance: The epoxidation activity of TiSil-HPB-60 and TiSil-Pow-60 was compared with that of two well-known titanosilicate catalysts: the crystalline microporous TS-1, and the ordered mesoporous Ti-MCM-41. Aqueous H2O2 and TBHP were employed as oxidants. The epoxidation of cyclohexene was chosen as a test reaction because this substrate is too large to diffuse into the pores of TS-1,<sup>[32]</sup> but may be converted on the Ti sites in the hierarchical porous structure of TiSil-HPB-60. In the epoxidation of cyclohexene with TBHP (ca. 5.5 m in decane), cyclohexene epoxide (CHE) was the main product with each catalyst tested (Table 3). TS-1 showed the expected low conversion of cyclohexene due to the hindered accessibility of the small micropores of TS-1 to the bulky reactants (cyclohexene and TBHP);<sup>[34]</sup> the activity displayed is mainly ascribed to the conversion on the external surface of TS-1.

Table 3. Catalytic performance in the epoxidation of cyclohexene with  ${\rm TBHP}^{[{\rm a}]}$ 

	Si/Ti <sup>[b]</sup>	Conversion [%] <sup>[c]</sup>	Yield of CHE [%]	$\begin{array}{c} TOF \\ [h^{-1}]^{[d]} \end{array}$	CHE [%]
TiSil-HPB-60	36.1	25.6	23.1	8.6	90.3
TiSil-Pow-60	37.8	6.2	4.2	2.2	67.0
Ti-MCM-41	59.3	29.1	21.9	15.8	75.4
TS-1	34.8	8.7	5.6	2.8	64.0

[a] Reaction conditions: 60 mg catalyst, 4.5 mmol cyclohexene, and 2.25 mmol TBHP (ca. 5.5 m in decane), 5 h at 60 °C. [b] Molar ratios measured by EDX. [c] Based on cyclohexene; the theoretical maximum conversion achievable under the employed reaction conditions is 50 %. [d] TOF=moles of cyclohexene converted per mole Ti of the catalyst per hour.

The catalytic behavior of TiSil-Pow-60 is slightly inferior to that of TS-1, which suggests that the disordered micropores (ca. 0.5 nm) in the material are inaccessible to the reactants, as are the pores of TS-1. Notably, the conversion of cyclohexene on TiSil-HPB-60 was much higher than on TS-1 and TiSil-Pow-60, and was comparable to that on Ti-MCM-41, which indicates the good accessibility of the active Ti sites in TiSil-HPB-60 to the reactants, similarly to what occurs in Ti-MCM-41. It has been revealed that the accessibility and molecular transport to the active sites in zeolitic micropores could be increased by the interconnection of secondary mesopores created in the crystals.<sup>[35]</sup> We propose that, in TiSil-HPB-60, a similar role is played by the disordered mesopores, which favor the accessibility of the active titanium sites to bulky reactants. Another contribution to the higher conversion of TiSil-HPB-60 compared with that of TS-1 is provided by the higher micropore volume of the former, which implies that a large fraction of titanium sites

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are located near the pore mouths, where the reaction of bulky compounds can be catalyzed, notwithstanding the small pore size (0.5 nm). However, TiSil-HPB-60 showed a lower turnover frequency (TOF) than Ti-MCM-41, presumably due to its higher hydrophilicity and lower specific surface area relative to Ti-MCM-41 (Tables 1 and 2). Still, the highest yield and selectivity towards cyclohexene epoxide, the target product of the epoxidation, were observed with TiSil-HPB-60.

When aqueous  $H_2O_2$  was used as the oxidant, four different products were obtained from the oxidation of cyclohexene: CHE, ALLYLIC (2-cyclohexene-1-ol + 2-cyclohexene-1-one), and CHD (1,2-cyclohexanediol) (Table 4). It has

Table 4. Catalytic performance in the epoxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub>.<sup>[a]</sup>

Catalyst	Si/Ti <sup>[b]</sup>	Conversion [%] <sup>[c]</sup>	Yield	$\begin{array}{c} {\rm TOF} \\ [h^{-1}]^{[d]} \end{array}$	Product selectivity [%]		
			CHE [%]		CHE	ALLYLIC	CHD
TiSil-HPB-60	36.1	20.2	8.2	6.9	40.7	5.3	54.0
TiSil-Pow-60	37.8	8.8	1.3	3.4	14.2	10.5	75.3
Ti-MCM-41	59.3	28.8	2.6	15.5	8.9	11.4	79.7
TS-1	34.8	8.7	3.7	2.8	42.7	5.2	52.1
S-TiSil-HPB-60	39.8 <sup>[e]</sup>	20.8	12.4	8.3	59.4	5.3	35.3

[a] Reaction conditions: 4.5 mL of CH<sub>3</sub>CN, 4.5 mmol of cyclohexene, 2.25 mmol of  $H_2O_2$  (50 wt %), 60 mg of catalyst, 60 °C, 5 h. [b] Molar ratios measured by EDX. [c] Based on cyclohexene; the theoretical maximum conversion achievable under the employed reaction conditions is 50%. [d] TOF=moles of cyclohexene converted per mole Ti of the catalyst per hour. [e] Calculated on the basis of the molar ratio of Si/Ti in TiSil-HPB-60 and of the degree of silylation in S-TiSil-HPB-60 (from <sup>29</sup>Si MAS NMR).

been shown that the O-O bond of Ti-oxo species (Tiperoxo, Ti-hydroperoxo, or Ti-superoxo) generated on titanosilicate molecular sieves by contact with H<sub>2</sub>O<sub>2</sub> cleaves either hetero- or homolytically. Heterolytic cleavage leads to the epoxide product (CHE), while homolytic cleavage leads to the allylic oxidation products 2-cyclohexene-1-ol (CH-OH) and 2-cyclohexene-1-one (CH-ONE).  $^{\left[ 11,36\right] }$  CHD is formed by the hydrolysis of the epoxide ring of cyclohexene oxide, which is catalyzed by acid sites. Similarly to the trend observed with TBHP, Ti-MCM-41 and TiSil-HPB-60 displayed higher conversions of cyclohexene and TOFs than TS-1 and TiSil-Pow-60, which confirms the advantage of the presence of mesopores in the epoxidation of the bulky cyclohexene. Although TiSil-HPB-60 has a lower TOF than Ti-MCM-41, as in the epoxidation with TBHP, the epoxide yield with TiSil-HPB-60 is more than double that with any other catalysts tested. Interestingly, TiSil-HPB-60 showed much higher selectivity towards CHE and lower selectivity towards CHD than Ti-MCM-41, which suggests that the hydrolysis of CHE with H<sub>2</sub>O was less favorable on TiSil-HPB-60. It has been reported that lower silanol content and higher surface hydrophobicity in titanosilicate catalysts result in a lower number of surface acid sites and lower adsorption of water on the surface and, thus, in higher selectivity towards CHE.<sup>[30, 37, 38]</sup> However, in our case, TiSil-HPB-60 has a higher silanol content and lower hydrophobicity than Ti-MCM-41 (Table 2), which indicates that these features cannot account for the observed selectivity trend. Not only the number but also the strength of the acid sites influences their selectivity towards epoxides. To compare the acid strengths of the titanosilicates, a NH<sub>3</sub> temperature-programmed desorption (TPD) study was performed; all of the materials show an analogous desorption band between 216 and 224 °C (not shown here), which indicates a similar, weak acid strength. The intensity of this signal demonstrates that the number of these acid sites (per gram of material) is higher in TiSil-HPB-60 than in Ti-MCM-41, which is opposite to the observed trend for selectivity towards the epoxide. It is clear that the selectivity trend should be described by taking into account other parameters. An explanation for the higher CHE selectivity with TiSil-HPB-60 can be found

> in the expected improved diffusion rate of the products through the large mesopores of TiSil-HPB-60, which would imply a shorter residence time of the formed epoxide in the vicinity of the active sites, with a consequently lower chance of further reaction. An additional reason for the observed selectivity trend may be the nature of the acid sites that are formed in the presence of H<sub>2</sub>O<sub>2</sub> by silanol groups adjacent to Ti sites. It has been reported that addition of H<sub>2</sub>O<sub>2</sub> to the system of

three nontitanosilicates (H-ZSM-5, silicalite-1, and deboronated B-Beta) produced no enhancement of the solvolysis of CHE. In contrast, the coexistence of H<sub>2</sub>O<sub>2</sub> with calcined [Ti,Al]-Beta catalyst promoted the solvolysis of CHE.<sup>[37]</sup> Therefore, it has been proposed that silanol groups hydrogen bonding to titanium hydroperoxide species in the presence of  $H_2O_2$  behave as stronger acid sites, and catalyze the hydrolysis of epoxides to diols.[37] Based on these observations, we propose that less of this types of acid sites are formed during the epoxidation on TiSil-HPB-60 than on Ti-MCM-41, presumably because a large portion of the silanol groups of TiSil-HPB-60 are not adjacent to titanium hydroperoxide species. To acquire a deeper insight into the role of the silanols, we prepared a silvlated TiSil-HPB-60 (S-TiSil-HPB-60). <sup>29</sup>Si NMR spectroscopy results show that S-TiSil-HPB-60 has a lower silanol content than TiSil-HPB-60 (Table 2) and (CH<sub>3</sub>)<sub>3</sub>Si- groups are successfully attached on the surface (Figure 8D): as a result, S-TiSil-HPB-60 has higher hydrophobicity than TiSil-HPB-60 (as shown by TGA, Table 2). It has been reported that the silvlation of Ti-MCM-41 brings about an increase in the catalytic conversion of cyclohexene and selectivity towards the epoxide when H<sub>2</sub>O<sub>2</sub> is used as oxidant. This effect is ascribed to the improved hydrophobicity of the catalyst surface.<sup>[30,38]</sup> Similarly, S-TiSil-HPB-60 showed a higher selectivity towards CHE (59.4%, Table 4), which resulted in an epoxide yield of 12.4%, compared with 8.2% for untreated TiSil-HPB-60. However, S-TiSil-HPB-60 showed only a slight increase in the conversion (20.8%, Table 4). The small influence of the silylation on the catalytic conversion fits the hypothesis that a large fraction of the silanols in TiSil-HPB-60 are not adjacent to the Ti sites. In such case, the silylation would have a minor influence on the environment of the active titanium sites and, thus, on the catalytic conversion. On the other hand, the lower silanol population and the higher hydrophobicity of S-TiSil-HPB-60 decrease the chance of hydrolysis of the formed epoxide, which leads to the observed increase in selectivity.

Leaching of titanium species under catalytic reaction conditions is a major drawback of some mesoporous titanosilicates, especially in the presence of hydrogen peroxide, which has strong complexing properties.<sup>[22]</sup> Since small amounts of leached Ti species can have a significant effect on the catalytic activity, a test for Ti leaching was carried out as follows:<sup>[39]</sup> The catalyst TiSil-HPB-60 was filtered from the reaction media after 20 min at the reaction temperature to avoid readsorption of the leached titanium, and the filtrate was divided into two parts: one was immediately analyzed by GC and the other was allowed to react for a further 5 h. The conversion of cyclohexene in the two parts of the filtrate was 6.3 and 7.4%, respectively, which reveals that after removal of the catalyst negligible cyclohexene epoxidation took place (taking into account self-oxidation of cyclohexene with  $H_2O_2$ ). This result shows that there was no Ti leaching from TiSil-HPB-60 during the epoxidation with H<sub>2</sub>O<sub>2</sub>. Considering the structure of TiSil-HPB-60, the high stability of titanium species in the presence of  $H_2O_2$  may be ascribed to the TS-1 building units present in TiSil-HPB-60, which stabilize the titanium species in the zeolite-like structure.

In view of potential industrial applications, recyclability is an important parameter in evaluating a catalyst. It has been reported that the deactivation of some mesoporous titanosilicates occurs during oxidation with TBHP and aqueous H<sub>2</sub>O<sub>2</sub> due to adsorbed reaction residues that hinder the accessibility of the active centers and/or due to Ti leaching. A calcination step is often necessary to regenerate the catalysts by eliminating adsorbed reaction residues around the active sites.<sup>[40]</sup> To complete the evaluation of our novel catalyst TiSil-HPB-60, the material was recovered from the reaction mixture and reused in several cycles. The straightforward recycling procedure for TiSil-HPB-60 only required four washings in ethanol at room temperature without any calcination. Note that the bead shape of TiSil-HPB-60 was unaffected by stirring during the catalytic tests (Figure 10A). The beads were deposited automatically on the bottom of the vial a few seconds after stirring was stopped (Figure 10B). Therefore, the beads could be easily separated from the reaction solution without centrifugation or filtration. No significant loss of catalytic activity was observed when reusing TiSil-HPB-60 in three successive catalytic runs with either TBHP or aqueous  $H_2O_2$  (Figure 11). This result reveals that there is no deactivation from adsorbed reaction residues, probably because the disordered mesopores favor rapid mass transport of reaction residues away from the active titanium sites.

# **FULL PAPER**



Figure 10. TiSil-HPB-60 under stirring (A) and in static conditions (a few seconds after stopping the stirring) (B).



Figure 11. Catalytic activity ( $\blacktriangle$  and  $\blacksquare$ ) and selectivity towards CHE ( $\blacktriangledown$  and  $\bullet$ ) with repeated use of TiSil-HPB-60 in the epoxidation of cyclohexene with TBHP (top) (ca. 5.5 M in decane) and H<sub>2</sub>O<sub>2</sub> (bottom).

Upon recycling, the selectivity towards CHE with TiSil-HPB-60 remained approximately constant in the case of TBHP, whereas it slightly and gradually decreased in the case of aqueous  $H_2O_2$ , which suggests that repeated use of TiSil-HPB-60 in the presence of  $H_2O_2$  may affect the acid sites.

One of the assets of TiSil-HPB-60 is constituted by its large mesopores, which enable the epoxidation of bulky alkenes. To show that this effect is not limited to cyclohexene, TiSil-HPB-60 was tested for the epoxidation of other bulky alkenes with molecular sizes beyond the range of TS-1 micropores, in the presence of  $H_2O_2$  (Table 5). TiSil-HPB-60

form spherical beads with a diameter of 0.5–1.5 mm. TS-1 structure-building units are detected in TiSil-HPB-60, and the predominant titanium species are in tetrahedral framework sites.

In the epoxidation of cyclohexene with *t*-butyl hydroperoxide, the yield of cyclohexene epoxide on TiSil-HPB-60 was much higher than on TS-1, and slightly higher than on Ti-MCM-41. In the case of aqueous  $H_2O_2$ , TiSil-HPB-60

Table 5. Catalytic performance of TiSil-HPB-60 in the epoxidation of various alkenes with  $H_2O_2$ .<sup>[a]</sup>

5 1	1			
Substrate	Conversion [%] <sup>[b]</sup>	Yield of epoxide [%]	Epoxide selec- tivity [%]	${\mathop{\rm TOF}}{[{{{\rm{h}}^{-1}}}]^{[c]}}$
<i>cis</i> -cyclooctene	29.0	29.0	99.9	9.7
trans-cyclodecene	41.9	40.6	96.7	14.1
cyclododecene <sup>[d]</sup>	9.3	9.2 <sup>[d]</sup>	99.1	3.1
trans,trans,cis-1,5,9-cyclododecatriene	11.3	10.8	95.6	3.8
(R)-(+)-limonene	4.4	4.3 <sup>[e]</sup>	96.8	1.5

[a] Reaction conditions: 4.5 mL CH<sub>3</sub>CN, 4.5 mmol alkene, 2.25 mmol  $H_2O_2$  (50 wt%), 60 mg catalyst, 60 °C, 5 h. [b] Based on the alkene: the theoretical maximum conversion achievable under the employed reaction conditions is 50%. [c] TOF=moles of alkene converted per mole Ti of the catalyst per hour. [d] Mixture of *cis* and *trans*. [e] Ring 1.7%; side chain 2.0%; diepoxide 0.5%.

proved to be active in all test reactions, which indicates that the Ti-sites in the bead material are also accessible to reactants bulkier than cyclohexene, and thus confirmed the advantage of its special pore architecture (micro/mesopores). Notably, the selectivity towards the epoxide is very high with all substrates, which is in line with the trend in selectivity reported and discussed above for the epoxidation of cyclohexene. The higher epoxide selectivities for the reactions with the alkenes in Table 5 compared with the selectivity for the epoxidation of cyclohexene is attributed to the higher structural stability of these epoxides relative to the more strained cyclohexene epoxide.<sup>[41]</sup> The activity and selectivity of TiSil-HPB-60 in the epoxidation of this series of alkenes are very promising when compared with the results obtained with other large-pore titanosilicates such as Ti-MCM-41 and Ti-Beta, although a thorough comparison is hindered by the use of different reaction conditions with the various catalysts.<sup>[41,42]</sup> It is remarkable that the alkene conversion with TiSil-HPB-60 increases with the size of the substrate going from cyclohexene to cyclodecene, while for Ti-Beta the alkene conversion was reported to decrease going from cyclohexene to larger cyclic alkenes.<sup>[34]</sup> This trend confirms the better accessibility of the Ti sites in the mesoporous TiSil-HPB-60 catalyst compared with those in microporous Ti-Beta.

#### Conclusion

Hierarchically porous titanosilicate beads were prepared by mixing a preformed titanosilicate solution with an anion-exchange resin as a template. TiSil-HPB-60 displays domains that contain disordered micropores of a similar size to those of TS-1. The domains are connected through mesopores to gave much higher epoxide yields than both Ti-MCM-41 and TS-1. The improved catalytic behavior of TiSil-HPB-60 is mainly ascribed to its mesoporosity, which promotes higher activity than that of TS-1 by improving the accessibility of active titanium sites to bulky substrates. Its mesoporosity also promotes higher selectivity relative to titanosilicates with smaller pores by allowing the products to readily diffuse out of the pores. Silylation of TiSil-

HPB-60 with TMCS brings about an increased TOF and an increased epoxide selectivity. The good catalytic activity of these titanosilicate beads in the epoxidation of cyclohexene with  $H_2O_2$  is highly relevant in the context of a sustainable process because  $H_2O_2$  is considered a clean and environmentally friendly oxidant.<sup>[43–46]</sup> TiSil-HPB-60 is also a stable catalyst that can be used in repeated cycles with both TBHP and  $H_2O_2$  without significant loss of activity. No titanium leaching was observed during the epoxidation. The catalyst can be easily recycled by straightforward washing without centrifugation or filtration, due to its bead format. This feature is very attractive for possible industrial applications. Furthermore, TiSil-HPB-60 is an active and selective catalyst for epoxidations of other bulky substrates, such as cyclooctene, cyclodecene, cyclododecene, and cyclododecatriene.

### **Experimental Section**

Preparation of the titanosilicate beads: Amberlite IRA-900 resin in the chloride form with bead size of 16-50 mesh and anion-exchange capacity of 4.2 meqg<sup>-1</sup> (Aldrich) was used as templating agent. Amberlite IRA-900 is a strongly basic, macroreticular resin with moderately high porosity and with benzyltrialkylammonium functionalities. In a typical synthesis of the titanosilicate beads, a preformed titanosilicate solution was prepared by mixing TPAOH (aqueous, 40%, 2.5 mL), H<sub>2</sub>O (7.5 mL), titanium isopropoxide (0.2 g), and tetraethyl orthosilicate (5 mL) under stirring at room temperature, followed by aging at 140 °C for 3 h in an autoclave. Next, Amberlite IRA-900 resin beads were added to the titanosilicate solution with a solution/resin weight ratio of 15:1. The mixture was stirred at room temperature for 24 h, transferred into an autoclave, and heated at 60°C for 24 h. Then, the liquid was decanted, the beads were washed several times with distilled water, and were finally dried at 60 °C. The resin beads used as templating agent and other organic materials were removed by calcination at 550 °C for 6 h, which led to the formation of the porous titanosilicate beads denoted as TiSil-HPB-60. For comparison, a titanosilicate (TiSil-Pow-60) was prepared by the same procedure

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used for TiSil-HPB-60, but without using the resin beads. Ti-MCM-41 and TS-1 zeolite (with crystal size of ca.  $(190\pm20)$  nm) were synthesized according to literature procedures  $^{[3,15]}$ 

Preparation of the trimethylsilylated titanosilicate beads: Trimethylsilylated TiSil-HPB-60 (S-TiSil-HPB-60) was obtained by silylation of TiSil-HPB-60 with TMCS. TiSil-HPB-60 (1 g) was degassed under vacuum at 120 °C for 7 h, and was then subsequently soaked in a TMCS solution in toluene (10 wt %, solid/liquid=1 g:50 mL) at 70 °C under stirring for 17 h. The solid sample was washed with toluene and acetone to remove any residual chemicals, and dried at 60 °C.

Characterization: Powder XRD patterns were measured on a STOE STADI P instrument with  $Cu_{K\alpha}$  radiation. FTIR spectra were recorded on a Nicolet 6700 spectrometer. UV/Vis 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/Vis spectra were recorded in air. The isotherms of nitrogen adsorption/desorption were measured at liquid-nitrogen temperature with a Coulter Omnisorp. The poresize distribution was calculated by using HK<sup>[47]</sup> and BJH<sup>[48]</sup> models. SEM images were taken on a Philips XL30 FEG apparatus. Si/Ti molar ratios were determined by EDX analysis on a Philips XL30 FEG: each sample was measured five times in five randomly selected areas, and the average of the results was calculated. TEM investigations were made on specially prepared plan-view samples by using a Philips CM20 electron transmission microscope operating at 200 kV. The plan-view samples were prepared as follows: Beads of the sample were mixed with epoxy glue, pressed into a tablet, and dried. The tablet underwent mechanical polishing followed by ion milling at low voltage and low angle by using a BALTEC RES 101 GVN ion milling machine. To minimize electron-beam damage of the structure during TEM measurements, a low-intensity electron beam at medium magnification was used. <sup>29</sup>Si MAS NMR spectra were recorded on a Bruker AMX300 spectrometer (7.0 T). The spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. TGA was carried out under N<sub>2</sub> with a ramp of 10 °Cmin<sup>-1</sup> on a TGA Q500 (from TA Instruments) equipped with a high-throughput sampling platform designed for 16 samples. The hydrophobicity of the samples was evaluated from TGA measurements of adsorbed water. NH<sub>3</sub> 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 mLmin  $^{-1}$  at 500 °C for 1 h, the samples were exposed to 5 % ammonia in N2 at 100 °C for 15 min, and were then purged with He for 30 min. NH<sub>3</sub> TPD spectra were obtained between 100 and 750 °C with a heating ramp of 10°Cmin<sup>-1</sup> by monitoring the desorbed ammonia with a Pfeiffer Omnistar quadrupole mass spectrometer. MIP measurements were carried out at Delft Solids Solutions (The Netherlands) on a CE Instruments Pascal 140 (evacuation, filling, and low pressure analysis) and Pascal 440 (high-pressure measurement). The samples were pretreated under vacuum at 225°C for 6 h before being transferred to the sample holder and weighed. The dry sample weight was used in the calculations. Catalytic tests: The epoxidation of cyclohexene was carried out in capped glass vials for 5 h at 60 °C under magnetic stirring (500 rpm). For the epoxidation with TBHP, the reaction mixture consisted of cyclohexene (4.5 mmol), TBHP (ca. 5.5 M in decane, 2.25 mmol), and catalyst (60 mg). After reaction, THF (4.5 mL) was added to the reaction to ensure the complete dissolution of the products. For the epoxidation with aqueous  $H_2O_2$ , the catalyst (60 mg) was mixed with  $H_2O_2$  (50%, 2.25 mmol), cyclohexene (4.5 mmol), and acetonitrile (4.5 mL). TiSil-HPB-60 was deposited spontaneously at the bottom of the vial a few seconds after stirring was stopped. It was therefore easily separated from the reaction solution by removal of the liquid with a pipette. The other catalysts were separated from the reaction solution by centrifugation at 3500 rpm. All the tested samples were fleshly calcined. The products were analyzed on an Interscience Finnigan Trace GC Ultra equipped with a RTX-5 fused silica column (5 m, 0.1 mm). Octane was used as internal standard.

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