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Easily recoverable titanosilicate zeolite beads with hierarchical porosity: Preparation and application as oxidation catalysts

Wenjing Cheng^{a,1}, Yanqiu Jiang^{a,1}, Xianzhu Xu^a, Yan Wang^a, Kaifeng Lin^{a,*}, Paolo P. Pescarmona^{b,*}

^aAcademy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, 150080 Harbin, China

^bChemical Engineering Department, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT

Titanosilicate zeolite beads with hierarchical porosity and 0.2–0.5 mm diameter (HPB-TS-1) have been synthesized from a titanosilicate solution, employing a porous anion-exchange resin as shape- and structure-directing template. The characterization results showed the existence of crystalline TS-1 nanoparticles and of a network of connected large meso/macropores in the interior of the beads. These bead materials are active and selective heterogeneous catalysts for two classes of industrially relevant oxidation reactions: the hydroxylation of phenol and the epoxidation of alkenes. In both cases, a green oxidant such as hydrogen peroxide was utilized. HPB-TS-1 beads displayed high activity in the hydroxylation of phenol, due to their crystalline TS-1 structure with isolated tetrahedral Ti species. In the epoxidation of cyclohexene, HPB-TS-1 gave conversion comparable to that over a benchmark catalyst such as Ti-MCM-41, but more than double yield and selectivity of the target product, cyclohexene oxide. HPB-TS-1 was also active and selective in the epoxidation of other bulky alkenes, i.e., *cis*-cyclooctene and *trans*, *trans*, *cis*-1,5,9-cyclododecatriene. The catalytic performance of HPB-TS-1 stems from the presence of crystalline TS-1 nanodomains, which are accessible through a network of meso/macropores within the beads. Notably, the bead format of these catalysts causes their spontaneous settling upon cessation of the agitation, thus enabling their straightforward separation from the reaction mixture. The HPB-TS-1 catalysts could be efficiently recycled in the hydroxylation of phenol with aqueous H₂O₂ via a calcination approach.

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1. Introduction

Since the groundbreaking discovery of zeolite TS-1 (MFI framework type), titanium-substituted zeolites have been attracting much attention for their remarkable catalytic performance in the selective oxidation of alkenes, alkanes, aromatics, alcohols, and other substrates, using aqueous H₂O₂ as a clean and environmentally friendly oxidant [1,2]. Besides their high surface area, tunable pore size, and high thermal stability, the excellent catalytic activity of such titanosilicate zeolites stems from the isolated, tetrahedrally coordinated Ti species [3–11]. However, these titanosilicate zeolites cannot effectively catalyze the conversion of bulky molecules, which are too large to access the active titanium sites located inside the micropores (<1 nm). The diffusion limitation imposed by the pores of zeolites can be mitigated by decreasing the particle

size to the nanometer scale [12–15], which leads to an increase in the external surface area. However, the preparation and catalytic application of these zeolite nanocrystals is hampered by their awkward separation from the reaction mixture, normally requiring high-speed centrifugation or special filtration. This hinders the recovery of the products and the recycling of the catalysts and therefore limits broad industrial application of these zeolite nanocrystals as heterogeneous catalysts in liquid-phase oxidation.

An alternative way to overcome the diffusion limitation of bulky molecules in zeolites is the creation of mesopores or macropores in the zeolitic structure [16]. Well-defined meso- or macroporous arrays could show optimal fluxes, thus minimizing issues related to diffusion. In recent years, there has been growing interest in the improved transport properties of such hierarchically porous zeolites with microporous crystalline domains and meso- or macropores [16,17]. The strategies used to generate this secondary porosity in zeolites up to now can be classified as non-templated or templated routes [13,18–20]. The former include approaches such as dealumination by acid leaching or steaming at high temperature, and selective desilication of zeolites in basic media [21].

* Corresponding authors. Fax: +31 50 3636521 (P.P. Pescarmona).

E-mail addresses: linkaifeng@hit.edu.cn (K. Lin), p.p.pescarmona@rug.nl (P.P. Pescarmona).

¹ These authors have contributed equally to this study.

Though these routes are effective in creating secondary mesopores in the crystalline structure, they do not allow controlling the volume and diameter of the mesopores [20,22]. Alternatively, routes employing soft or hard templates with well-defined morphology and structure have been widely used, as they allow tailoring the size and geometry of the hierarchical pores. With this approach, mesoporous zeolites can be prepared using carbonaceous template materials such as carbon nanotubes, carbon black, carbon aerogels and ordered mesoporous carbon, but the preparation of these carbon templates is complicated and high temperatures and inert gases are needed during carbonization [12,18,23]. For soft templating methods, the most commonly used templates include traditional surfactants for mesopore creation, organosilane agents, sugars, and cationic polymers [22,24–26]. Such hierarchically porous zeolites display very promising catalytic performances in heterogeneous reactions with both small and bulky substrates. However, most of the attention has been devoted to the preparation of hierarchical aluminosilicate zeolites (ZSM-5 and Beta), whereas the synthesis of hierarchical titanasilicate zeolites is less explored. This might be due to the difficulty of incorporating isolated, tetrahedral Ti species into the zeolite framework when a template for the generation of mesopores is applied in the process. Another challenge in the synthesis of these materials is to achieve a good connection between the created mesopores, which is considered to be vital to maximize the benefits of hierarchical porosity in catalysis [27]. Recently, the synthesis of a hierarchical TS-1 with a well connected network of meso/macropores inside the zeolite crystal using caramel as template was reported [28]. This hierarchical TS-1 showed improved catalytic performance compared with conventional TS-1 in the selective oxidation of cyclohexene, thiophene, benzothiophene, and 4,6-dimethyl dibenzothiophene using H_2O_2 as the oxidant. These results underline the relevance of developing novel hierarchically porous titanasilicate zeolites with highly active Ti species and connected networks of mesopores.

In a previous paper of some of us, a novel method for the preparation of hierarchically porous titanasilicate beads based on the use of anion-exchange resin beads as shape- and structure-directing agents was reported [29]. The bead-shaped catalysts displayed high catalytic activity, due to their large mesopores, and were easily separated and recycled without requiring centrifugation or filtration, owing to their bead format. However, based on the preparation conditions applied, the microstructure of titanasilicate beads was mainly amorphous, whereas a crystalline TS-1 structure would be expected to lead to enhanced catalytic activity in oxidation reactions. In the present work, hierarchical TS-1 beads with a connected network of meso/macropores were successfully synthesized using anion-exchange resin beads as a hard template. The obtained beads were used to catalyze the hydroxylation of aromatics and the epoxidation of various alkenes with aqueous H_2O_2 as a green oxidant, and proved to display high activity and selectivity with all substrates tested.

2. Experimental

2.1. Synthesis of the catalytic materials

Amberlite IRA-900 resin beads in the chloride form with a bead size of 16–50 mesh and an anion-exchange capacity of 4.2 meq/g (Alfa Aesar) was used as a templating agent. Amberlite IRA-900 is a macroreticular resin with high porosity and with benzyltrialkylammonium functionalities.

In a typical synthesis of hierarchically porous TS-1 zeolite beads (HPB-TS-1), a titanasilicate solution was prepared by mixing aqueous tetrapropylammonium hydroxide (TPAOH, 50%, 2.0 mL), H_2O (8.0 mL), titanium isopropoxide (0.2 g), and tetraethyl orthosilicate (5 mL) under stirring at 40 °C. Next, IRA-900 resin beads were added

to the titanasilicate solution with a solution-to-resin mass ratio of 20:1. The mixture was stirred at 40 °C for 24 h, transferred into an autoclave, and hydrothermally treated with the following temperature programming: 60 °C for 24 h, from 60 to 100 °C at 10 °C/h, 100 °C for 19 h, from 100 to 165 °C at 16 °C/h, 165 °C for 24 h. After cooling to room temperature, the aqueous slurry was decanted and the beads were washed several times with distilled water and finally dried at 60 °C. Meanwhile, a powder sample was obtained from the slurry via centrifugation. The beads obtained in this step were then subjected to acid treatment (2 M nitric acid at 120 °C for 24 h) with the purpose of removing possible extraframework Ti species [5,8]. The resin beads used as templating agents and other organic residues were removed by calcination in air at 550 °C for 6 h, which led to the formation of the hierarchically porous TS-1 zeolite beads denoted as HPB-TS-1. The as-synthesized hierarchical porous TS-1 zeolite beads calcined without prior treatment by nitric acid were denoted as HPB-TS-1_{AS}. The calcined powder obtained from the slurry was denoted as Pow-TS-1. Based on the amount of tetraethyl orthosilicate employed in the synthesis, the typical yield of HPB-TS-1 was 20–25% and that of Pow-TS-1 was 50–55%. Moreover, hierarchically porous titanasilicate beads were also prepared with different solution-to-resin mass ratios (6.8:1 and 10:1), while all other conditions were as described above. These materials were named HPB-TS-1(6.8) and HPB-TS-1(10), where the value in parentheses indicates the solution-to-resin mass ratio. Another set of reference titanasilicate bead samples (HPB-TiSil-60, HPB-TiSil-100, HPB-TiSil-170) was prepared according to the general procedure described above, with the difference that the hydrothermal treatment was carried out at a given fixed temperature (60, 100, or 170 °C) for 72 h instead of using the programmed temperature profile (vide supra). All the methods used in the preparation of the materials presented in this work are summarized in [Scheme S1](#) (see the Supplementary Information).

2.2. Characterization

Powder XRD patterns were measured on a Bruker D8 instrument using Cu K α radiation. FT-IR spectra were recorded on a Perkin Elmer 100 spectrometer. UV–vis spectra were measured with a Perkin Elmer Lambda 750 spectrophotometer in the region 200–800 nm. The samples were not treated before measurement and the UV–vis spectra were recorded in air. Prior to analysis by XRD, FT-IR, and UV–vis measurements, the beads were ground to a powder. The isotherms of nitrogen adsorption–desorption were measured at liquid nitrogen temperature using a Micromeritics ASAP 2020 system. The micropore size distribution was calculated using the Horvath–Kawazoe (HK) model [30] and the mesopore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) model [31] applied to the desorption branch. Scanning electron microscopy (SEM) images were taken on a Hitachi SU8010 apparatus. SEM analysis of the as-synthesized bead-shaped samples provided the average bead size and the surface morphology, whereas the inner structure was investigated by SEM analysis after the beads were ground into powder. Transmission electron microscopy (TEM) images were taken on an FEI-T12 electron microscope. For the preparation of the samples for TEM analysis, the beads were ground into powder, which was then dispersed in ethanol, followed by sonication of the suspension for 10 min. One drop of the suspension was placed on a TEM grid and allowed to dry overnight. Si/Ti molar ratios were determined by elemental analysis using an Agilent ICP-MS 7500c inductively coupled plasma mass spectrometer.

2.3. Catalytic tests

The liquid-phase hydroxylation of phenol was carried out under shaking at 120 rpm, in glass vials soaked in a water bath at 80 °C.

Shaking was chosen as the agitation method because the beads tend to deteriorate upon stirring with a magnetic bar. Typically, the reaction mixture consisted of 470 mg of phenol (5 mmol), 15 mL of distilled water, and 50 mg of catalyst. When the temperature was increased to 80 °C, aqueous H₂O₂ (35 wt.%) at a phenol-to-H₂O₂ molar ratio of 3 was added in one dose. At the end of the test, the bead-shaped catalysts deposited spontaneously at the bottom of the vial within a few seconds after the agitation was stopped. Therefore, the beads were easily separated from the reaction solution by removal of the liquid with a pipette. The catalysts in powder form (Pow-TS-1, TS-1) were separated from the reaction solution by centrifugation. After reaction for 4 h, the products were determined using a gas chromatograph (GC) SP-6800A equipped with an SE-54 capillary column (30 m, 0.32 mm) and an FID detector. The reusability of the bead-shaped catalysts in consecutive runs was evaluated following two different recycling approaches: the first involving washing with ethanol, and the second including calcination at 550 °C for 4 h in air after the washing step.

For the epoxidation of cyclohexene with aqueous H₂O₂, 4.5 mmol of cyclohexene, 4.5 mL of acetonitrile, 2.25 mmol of aqueous H₂O₂ (35 wt.%), and the catalyst (60 mg) were mixed in the vial under shaking and heated to 60 °C. After reaction for 5 h, the products were analyzed using an Agilent 7890A GC system equipped with an HP-5 column (30 m, 0.32 mm).

The assignment of the products was confirmed by gas chromatography–mass spectrometry analysis (GC–MS) on an Agilent 7890A gas chromatograph (HP-5MS column, 30 m, 0.25 mm) coupled to an Agilent 5975 MSD mass spectrometer.

The amount of H₂O₂ decomposed in H₂O and O₂ during the catalytic test was determined by means of the titration of the reaction solution (after 4 h at 80 °C for phenol hydroxylation or after 5 h at 60 °C for cyclohexene epoxidation) with a 0.1 M solution of Ce(SO₄)₂, obtained by dissolving Ce(SO₄)₂·4H₂O (50.0 mmol) in H₂SO₄ (28 mL) and bidistilled H₂O (28 mL), and diluted to a total volume of 500 mL with H₂O. The obtained colorless solution was titrated with the 0.1 M Ce^{IV} solution until it turned yellow ($2\text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Ce}^{3+} + 2\text{H}^+ + \text{O}_2$).

3. Results and discussion

In this work, a titanosilicate with a macroscopic bead format containing TS-1 nanocrystals surrounded by a network of meso- and macropores (HPB-TS-1) was prepared and tested as a heterogeneous catalyst for oxidation reactions with hydrogen peroxide as oxidant. The TS-1 nanocrystals are expected to contain highly active tetrahedral Ti sites and to display a relatively high external surface area, while the hierarchical porous structure will grant accessibility to the TS-1 domains. Moreover, the bead format will allow straightforward separation of the catalyst from the reaction mixture. The successful synthesis of a catalytic material with these highly desirable features was demonstrated by full characterization of HPB-TS-1 and of selected reference materials with a combination of techniques.

3.1. Synthesis and characterization of the catalysts

The HPB-TS-1 material was prepared employing Amberlite IRA-900 resin beads as shape- and structure-directing agent. These resin beads display irregular pores in the mesoporous range and, to a lesser extent, in the macroporous range (Fig. 1A–C). The choice of these resin beads was inspired by previous reports [29,32,33], but the synthesis method was carefully tuned in this work to achieve the formation of TS-1 nanocrystals within the porous beads. This was a challenging yet rewarding task, as demonstrated by the less attractive features of the other bead materials that were

prepared in this work (vide infra). A crucial feature of the method used to prepare HPB-TS-1 was the accurate control of the temperature profile during the hydrothermal step of the synthesis. The HPB-TS-1 samples obtained after synthesis and calcination consist of white beads with diameter ranging from 0.2 to 0.5 mm (Fig. 1D and I), which is slightly smaller than that of the starting resin beads, as observed in other amorphous titanosilicate beads [32]. In contrast, the centrifugate from the decanted aqueous slurry, denoted as Pow-TS-1, is a fine powder consisting of TS-1 nanoparticles (vide infra for the XRD analysis) with a size of 300–400 nm (Fig. 1H). Pow-TS-1 has morphology and particle size similar to those of a reference TS-1 sample that was prepared by an analogous procedure but without the resin beads (Fig. 1N). This indicates that a fraction of conventional TS-1 grew outside the beads of HPB-TS-1 during the applied synthesis procedure. The surface of the as-synthesized beads (HPB-TS-1_{AS}) is partially covered with a layer of well-defined, discrete particles with the typical shape of MFI zeolite crystals (Fig. 1E and F), but with different morphology compared to the particles in Pow-TS-1. This layer of particles was removed from the surface of the beads by the acid treatment used in the preparation of the final catalyst (HPB-TS-1, Fig. 1I and J). The layer of particles can also be washed away from the surface of HPB-TS-1_{AS} by water treatment at 80 °C for 4 h (see Fig. S1), suggesting that the interaction between the discrete particles and the bead body is rather weak. As anticipated, HPB-TS-1 contains a large number of irregular mesopores as well as a small number of macropores (Fig. 1J and K). This porosity reflects the related features of the surface of the resin beads used as template (Fig. 1B). The meso- and macropores in HPB-TS-1 are expected to be connected because they are created by removal of the continuous resin structure upon calcination.

High-magnification SEM images of the interiors of HPB-TS-1_{AS} and HPB-TS-1 indicate that the beads are composed of particles with the typical morphology of MFI-type crystals, with a rather uniform size of ca. 150–200 nm (Fig. 1G and K). The formation of these nanocrystals with uniform size is attributed to their competitive growth in the confined space within the resin beads. Note that the zeolitic particles are interconnected, so that they build a robust bead. Therefore, the mesopores originating from the interstices between the zeolite nanocrystals should be considered structural (and thus different from the interparticle mesopores that can be observed in the case of discrete nanoparticles).

Transmission electron microscopy (TEM) images of HPB-TS-1 confirm the presence of large mesopores and macropores in the interior of the beads (Fig. 2A and B). TEM images with higher magnification (Fig. 2C and D) show the well-defined crystalline domains of the microporous MFI zeolite, located in the meso/macroporous structure of HPB-TS-1. The combination of SEM and TEM analyses showed that the ordered micropores of the TS-1 crystals in HPB-TS-1 are partially open onto the meso/macropores, leading to the formation of the desired interconnected hierarchical pore system.

Characterization of HPB-TS-1 by powder X-ray diffraction (XRD) evidences a well-resolved MFI pattern (Fig. 3), thus confirming the presence of the TS-1 crystals observed by SEM and TEM. Notably, the crystallinity of the acid-treated HPB-TS-1 is superior to that of the as-synthesized HPB-TS-1_{AS}, as indicated by the disappearance of the broad band at 23° assigned to amorphous (titano)silicate (Fig. 3A and B). This implies that amorphous species could be mostly removed via acid treatment. It is worth noting that the acid treatment procedure (reflux at 120 °C for 24 h) is similar to the procedure employed for evaluating the hydrothermal stability of porous materials (treatment in boiling water) [34]. Importantly, the crystallinity level of the TS-1 particles within the beads in HPB-TS-1 is analogous to that of the TS-1 sample prepared in the absence of the bead template (Fig. 3D) and to the powder sample

Fig. 1. SEM images of IRA-900 (A: the whole beads; B: the surface; C: the interior); HPB-TS-1_{AS} (D: the whole beads, E: the surface and interior of a fractured bead; F: the discrete crystals covering the surface; G: the interior); Pow-TS-1 (H); HPB-TS-1 (I: the whole beads; J: the surface; K: the interior of a fractured bead); regenerated HPB-TS-1 (L: the whole beads; M: the interior of a fractured bead); TS-1 crystals (N).

Fig. 2. TEM images of fragments of the HPB-TS-1 beads. Characteristic meso- and macropores are indicated by the arrows.

Fig. 3. XRD patterns of HPB-TS-1_{AS} (A), HPB-TS-1 (B), Pow-TS-1 (C), and TS-1 (D) samples.

(Pow-TS-1) that was obtained together with the beads (Fig. 3C). In agreement with the XRD data, the FT-IR spectra of the beads (Fig. S2) display the characteristic peaks of TS-1 [35,36]. The spectra of the bead materials also show a large and intense band at 3450–3300 cm^{-1} , attributed to silanol groups interacting with water adsorbed in the pores of the bead [37]. The presence of adsorbed water is confirmed by the water bending mode at about 1640 cm^{-1} . These bands are significantly less intense in the FT-IR spectrum of Pow-TS-1 (Fig. S2), indicating higher hydrophilicity of the bead materials. This feature can be explained by the smaller size of the TS-1 crystals in the bead materials, which implies a relatively higher external surface and thus a higher population of

silanol groups. Moreover, the porous structure within the beads can favor trapping of water within the material.

The importance of the programmed temperature profile employed in the hydrothermal synthesis of HPB-TS-1 is demonstrated by comparison with titanosilicate bead samples prepared at a given, fixed temperature (HPB-TiSil-60, HPB-TiSil-100, HPB-TiSil-170, where the number indicates the temperature in $^{\circ}\text{C}$). The XRD patterns of HPB-TiSil-60 and HPB-TiSil-100 only display the broad band centered at 23° due to amorphous (titano)silicate, indicating that these temperatures are too low to achieve crystallization into a TS-1 structure (Fig. S3). On the other hand, the XRD pattern of HPB-TiSil-170 shows the characteristic peaks for MFI zeolites, though the signal is noisier than in HPB-TS-1_{AS} (Fig. S3). These results clearly reveal that temperature plays an important role in the formation of TS-1 crystals, regardless of the presence of resin beads, and that crystallization occurs both inside and outside the beads at higher temperature, confirming the free mass transport of titanosilicate species from the starting solution into the beads via ion exchange. In the attempt to minimize the observed formation of powder TS-1 material outside the beads, the titanosilicate beads were prepared with a larger amount of resin relative to the titanosilicate solution (solution-to-resin mass ratios of 10 and 6.8). However, the crystallinity of the obtained materials is inferior to that of HPB-TS-1_{AS}, as shown by the higher relative intensity of the broad band at 23° assigned to amorphous species (Fig. S3). This implies that the chemistry of the resin itself, such as active groups and counterions, influences the crystallization process. These results underline the importance of careful tuning of the synthesis parameters to obtain the desired bead materials consisting of TS-1 nanocrystals.

The textural properties of the prepared materials were investigated by N_2 physisorption (Fig. 4). The adsorption-desorption

Fig. 4. Nitrogen adsorption–desorption isotherms of HPB-TS-1_{AS} (A) and HPB-TS-1 (B). The isotherm of A is offset by 150 cm³/g along the vertical axis to facilitate its visualization.

isotherms of the hierarchically porous titanasilicate beads with and without acid treatment show a steep uptake of N₂ below $p/p^0 = 0.05$, which is characteristic of microporous materials prepared using tetrapropylammonium hydroxide (TPAOH) as template [28]. In addition to this uptake, the two samples display a defined hysteresis loop above $p/p^0 = 0.7$, showing the presence of meso- and/or macropores connected through windows of smaller size, leading to the so-called bottleneck effect [38].

Based on the Horvath–Kawazoe (HK) method, the sizes of the micropores in HPB-TS-1_{AS} and HPB-TS-1 are about 0.54 and 0.55 nm (Fig. 5), which correspond well with the diameter of micropores in TS-1 or in other MFI zeolites templated by TPAOH [28]. The BJH pore size distribution indicates that very large mesopores and macropores are present in the beads (Fig. 5), mainly in the range 20–100 nm. Although this information is only qualitative due to the limitations of N₂ physisorption analysis in the large mesopore range, it is in agreement with the porosity observed by SEM (vide supra) and with previous reports on titanasilicate beads [29]. The pore volumes were calculated to be 0.56 and 0.55 cm³/g for HPB-TS-1_{AS} and HPB-TS-1, respectively. The specific surface area of HPB-TS-1 (227 m²/g) is lower than that of HPB-TS-1_{AS} (387 m²/g), probably due to the removal of the layer of TS-1 crystals on the external surface of the beads via acid treatment (vide supra).

The coordination of titanium species in zeolites and mesoporous titanasilicates can be monitored based on the position of the UV–vis absorption of the material [39]. Ideally, the titanium species are incorporated into the framework of crystalline zeolite TS-1 in tetrahedral coordination sites, and this is regarded as the key factor in their catalytic activity and stability [40]. The UV–vis spectrum of HPB-TS-1_{AS} shows a broad band in the range 215–320 nm (Fig. 6), ascribed to the coexistence of various types of tetrahedral Ti sites, such as Ti(OSi)₄ and Ti(OH)(OSi)₃, and a certain amount of higher-coordination Ti species, such as reversible pentacoordinated Ti species generated by the interaction of Ti species with moisture and polymerized hexacoordinated Ti species [39]. On the other hand, the UV–vis spectrum of the powder material obtained together with HPB-TS-1_{AS}, i.e., Pow-TS-1, exhibits a narrow band centered at ca. 215–220 nm, which corresponds to the characteristic signal of isolated tetrahedral Ti sites in TS-1 zeolites [10], with a shoulder extending to higher wavelengths (Fig. 6). These results indicate that the use of the resin beads as shape- and structure-directing agents partially hinders the formation of the crystalline TS-1 framework, possibly due to the pore space

Fig. 5. Pore-size distributions of HPB-TS-1 (A and B) and HPB-TS-1_{AS} (C and D).

Fig. 6. UV–vis spectra of HPB-TS-1_{AS} (A), HPB-TS-1 (B), and Pow-TS-1 (C).

restrictions within the resin bead template and/or to the types of functional groups and counterions present in the resin. Although HPB-TS-1_{AS} contains extraframework Ti sites with higher coordination (penta, hexa), these are effectively removed by the treatment with nitric acid [8], as shown by the narrow band at 210 nm in the UV–vis spectrum of HPB-TS-1, with only a narrow shoulder at higher wavelengths (Fig. 6). This result is fully in agreement with the XRD data (vide supra), and confirms that the acid treatment allows removing the amorphous species and generating a material in which titanium is mainly in isolated tetrahedral sites, the desired active sites for catalytic application.

Based on the discussion of the synthesis and characterization results, we propose a path for the formation of HPB-TS-1 by means of templating with anion-exchange resin beads (Scheme 1). In the alkaline synthesis medium, negatively charged titanasilicate oligomers can be formed in solution and, once the beads are added, can exchange with the anions of the resin beads. Subsequently, the condensation and crystallization of the titanasilicate species occurs in the resin–titanosilicate composites during the hydrothermal treatment. These composites consist of two interconnected 3D networks: an organic part originating from the resin, and an inorganic part consisting of the condensed titanosilicate matter [29]. If the temperature of the hydrothermal step is low, the condensed titanosilicate matter is amorphous, whereas the titanosilicate domains gradually grow into TS-1 zeolite crystals if the hydrothermal treatment takes place at $T \geq 165^\circ\text{C}$. The crystallization becomes more efficient if the temperature profile is carefully controlled. Upon calcination, the organic resin bead is removed, thus generating titanosilicate beads with a unique inner structure in which aggregates of TS-1 zeolite crystals are interconnected by a three-dimensional network of meso- and macropores, as proven by SEM, TEM, N_2 physisorption, and XRD. Compared with conventional ordered mesoporous materials, the meso/macropore size of the HPB-TS-1 sample is much larger and the size distribution is relatively broad, which is potentially favorable for mass transport of reactants and products during catalytic reactions.

The temperature program used in the synthesis of HPB-TS-1 proved to be vital for the formation of robust beads. This was demonstrated by the tendency of the sample prepared under direct hydrothermal treatment at 170°C (HPB-TiSil-170) to disintegrate upon calcination (Fig. S4).

3.2. Catalytic activity

The titanosilicate material HPB-TS-1 was studied as a heterogeneous catalyst for two types of oxidation reactions: the hydroxylation of phenol and the epoxidation of alkenes. In both cases, aqueous hydrogen peroxide was employed as the oxidant. This is considered a very sustainable oxidant, being relatively inexpensive, safer than molecular oxygen, and environmentally friendly, as it generates H_2O as by-product [41,42].

The first reaction in which HPB-TS-1 was tested as a heterogeneous catalyst is the hydroxylation of phenol (Table 1 and Fig. S5), which is an important industrial reaction for the production of dihydroxybenzenes and their derivatives [43]. This reaction is widely employed in the evaluation of porous titanosilicate catalysts because it is very sensitive to the features of the catalyst [44,45]. For example, the well-known ordered mesoporous Ti-MCM-41 is almost inactive for the hydroxylation of phenol. This has been attributed to the lower oxidation ability of titanium species in the amorphous mesoporous walls of Ti-MCM-41, compared with the Ti sites in the crystalline framework of TS-1 [46]. In this work, HPB-TS-1 beads displayed high catalytic turnover frequency ($\text{TOF} = 49.7 \text{ h}^{-1}$), which is comparable to that obtained on TS-1 nanocrystals ($\text{TOF} = 52.5 \text{ h}^{-1}$), as summarized in Table 1. The minor difference in activity can be ascribed to the relatively low surface area of the HPB-TS-1 material. Also the selectivity of HPB-TS-1 is very similar to that of TS-1, with catechol and hydroquinone being the major products (Table 1). These results clearly indicate that the Ti species in the beads have analogous catalytic properties to those in TS-1 nanocrystals, as expected based on the presence of TS-1 crystals with tetrahedral Ti sites within HPB-TS-1, which were evidenced by XRD and UV–vis characterization (vide supra). In contrast, HPB-TS-1_{AS} displayed significantly lower conversion than HPB-TS-1 (Table 1). This is ascribed to the presence of weakly active or inactive extraframework Ti-species with higher coordination in HPB-TS-1_{AS}, as proved by UV–vis spectroscopy. Pow-TS-1 gave phenol conversion and product selectivity analogous to those for the TS-1 sample (Table 1). This confirms the similarity between these two materials evidenced by the physicochemical characterization.

These catalytic results indicate that the connected meso/macropore system in HPB-TS-1 allows efficient mass transport of the reactants to the TS-1 domains containing the titanium active sites. This was confirmed by means of the Weisz–Prater criterion [47] using the measured catalytic data. This analysis indicates that the HPB-TS-1 catalyst does not suffer from diffusion limitations in the meso/macroporous network present inside the beads (see the Supplementary Information). It is concluded that our catalyst combines the high activity of TS-1 nanocrystals with the straightforward separation endowed by its bead format. Indeed,

Scheme 1. Proposed steps leading to the formation of the hierarchically porous beads consisting of TS-1 zeolite crystals, via templating with anion-exchange resin beads.

Table 1Catalytic performance of the titanasilicate materials in the hydroxylation of phenol with aqueous H₂O₂:^a

Catalyst	Si/Ti ^b	TOF (h ⁻¹) ^c	Conv. (%) ^d	Product selectivity (%) ^e		
				CAT	HQ	BQ
HPB-TS-1	41	49.7	17.6	51.0	42.2	6.8
HPB-TS-1 _{AS}	33	8.6	4.0	46.9	7.4	45.7
Pow-TS-1	41	50.9	17.8	47.2	45.0	7.8
TS-1	35	52.5	21.3	50.8	43.7	5.5

^a Reaction conditions: 15 mL of water, 0.47 g of phenol, H₂O₂ (35 wt.%) in molar ratio H₂O₂:phenol = 1:3, 50 mg of catalyst, 80 °C, 4 h.^b Determined by ICP-MS.^c Turnover frequency is defined as mol of phenol converted per mol of Ti atoms of the catalyst per hour, calculated based on the conversion after 30 min of reaction (see Fig. S5 and Table S1).^d Based on phenol; the maximum theoretical conversion achievable under the employed reaction conditions is 33%.^e CAT = catechol, HQ = hydroquinone, and BQ = para-benzoquinone. The tar product is not included, and the product selectivity is calculated as CAT (or HQ or BQ)/(CAT + HQ + BQ). **Fig. 7.** Recycling tests of HPB-TS-1 as catalyst for the hydroxylation of phenol with aqueous H₂O₂. Recycling approach: washing (▲) or calcination (▼).

the beads deposited automatically at the bottom of the reaction vial few seconds after the agitation was stopped. This allowed separation from the reaction solution without centrifugation or filtration, which is a very attractive feature for any practical application of these catalysts. Importantly, SEM images of the used catalyst show that neither the bead shape nor the TS-1 crystals within HPB-TS-1 were affected during the catalytic test (Fig. 1L and M). The reusability of the catalyst in consecutive runs was evaluated following two different recycling approaches. If the protocol only involved washing with ethanol, the phenol conversion decreased in subsequent runs (Fig. 7), probably due to the deposition of reaction residues (e.g., tar) in the micropores of the TS-1 domains. In line with this hypothesis, when the regeneration of HPB-TS-1 was carried out via calcination at 550 °C for 4 h in air, most of the original activity of the catalyst was recovered (Fig. 7).

The second class of reactions that was selected for testing HPB-TS-1 was the epoxidation of alkenes with aqueous hydrogen peroxide. This is an attractive reaction, because the obtained epoxides are highly useful intermediates for the manufacture of a range of

important commercial products [48]. In our strategy, efficient mass transport through the connected meso/macroporous network in the beads in combination with the small size of the TS-1 domains (implying a larger fraction of active sites at the micropore mouth and on the external surface of the crystallites) should lead to enhanced epoxidation activity with substrates that suffer from diffusion limitation in the micropores of TS-1 [16,49]. To evaluate this, the epoxidation of cyclohexene was chosen as a test reaction. Cyclohexene is frequently employed as a test substrate to evaluate titanasilicate catalysts, because its bulkiness limits its diffusion in the micropores of TS-1 [49]. Indeed, the TS-1 sample showed the expected low conversion of cyclohexene (Table 2), with the activity being mainly ascribed to the conversion on the external surface of the TS-1 particles. Coherently, the catalytic behavior of Pow-TS-1 is very similar to that of the TS-1 sample (Table 2). Notably, the conversion of cyclohexene, the TOF value, and the epoxide yield over HPB-TS-1 beads were much higher than those over TS-1 (Table 2 and Fig. S6), proving the anticipated accessibility of the active Ti sites exposed on the meso/macropores in our catalyst (i.e., the Ti sites at the micropore mouth or on the external surfaces of the TS-1 nanocrystals).

The catalytic performance of HPB-TS-1 was also compared with that of Ti-MCM-41 [29], which is known to display high activity in the epoxidation of cyclohexene due to the sufficiently large size of its ordered mesoporous channels [50]. Although HPB-TS-1 showed relatively lower conversion than Ti-MCM-41, presumably due to its lower specific surface area, the yield of cyclohexene oxide, i.e., the target product of the epoxidation, was more than double with HPB-TS-1 compared to Ti-MCM-41 (Table 2). This result stems from the much higher selectivity toward the epoxide and lower selectivity toward 1,2-cyclohexanediol over HPB-TS-1, which suggests that the hydrolysis of the epoxide product with H₂O was less favorable on HPB-TS-1. Ti-MCM-41 is characterized by amorphous walls that are intrinsically rich of surface silanols, which favor the adsorption of water on the surface, thus promoting the hydrolysis of the epoxide to the diol [29,51]. Although the FT-IR spectra showed that the bead materials also contain silanol groups that tend to adsorb water (vide supra), the much larger meso/macropores of HPB-TS-1 compared with the narrow mesopores characteristic of Ti-MCM-41 are expected to allow easier diffusion of water (formed during the reaction) from the active sites, thus decreasing the chances of hydrolysis of the formed epoxide.

Table 2Catalytic performance of the titanasilicate materials in the epoxidation of cyclohexene with aqueous H₂O₂:^a

Catalyst	Si/Ti ^b	TOF (h ⁻¹) ^c	Conv. (%) ^d	Yield (%) ^e	H ₂ O ₂ decomp. (%)	Product selectivity (%) ^f		
						CHO	CHD	ALLYLIC
HPB-TS-1	41	23.3	15.9	4.7	8.0	29.3	37.5	33.2
HPB-TS-1 _{AS}	33	23.4	22.5	5.4	30.7	24.1	48.6	27.3
Pow-TS-1	41	7.7	4.4	1.3	6.2	30.3	59.2	10.5
TS-1	35	8.0	4.5	1.7	3.1	37.9	54.8	7.3
Ti-MCM-41 ^g	59	n.d. ^h	28.8	2.6	n.d. ^h	8.9	79.7	11.4

^a Reaction conditions: 4.5 mL of MeCN, 4.5 mmol of cyclohexene, 2.25 mmol of H₂O₂ (35 wt.%), 60 mg of catalyst, 60 °C, 5 h.^b Determined by ICP-MS.^c Turnover frequency is defined as mol of cyclohexene converted per mol of Ti atoms of the catalyst per hour, calculated based on the conversion after 30 min of reaction (see Fig. S6 and Table S1).^d Based on cyclohexene; the maximum theoretical conversion achievable under the employed reaction conditions is 50%.^e Yield of cyclohexene oxide.^f CHO = cyclohexene oxide, CHD = 1,2-cyclohexanediol, ALLYLIC = products of the allylic oxidation, i.e., 2-cyclohexene-1-ol and 2-cyclohexene-1-one.^g Results from Ref. [29]. Reaction conditions: 4.5 mL of MeCN, 4.5 mmol of cyclohexene, 2.25 mmol of H₂O₂ (50 wt.%), 60 mg of catalyst, 60 °C, 5 h.^h Not determined.**Table 3**Catalytic performance of HPB-TS-1 in the epoxidation of various alkenes with aqueous H₂O₂:^a

Substrate	Conv. (%) ^b	Epoxide selectivity (%)
cis-Cyclooctene	15.0	91.0
Cyclododecene ^c	3.3	98.5
trans, trans, cis-1,5,9-Cyclododecatriene	15.6	97.0

^a Reaction conditions: 4.5 mL of CH₃CN, 4.5 mmol of alkene, 2.25 mmol of H₂O₂ (35 wt.%), 60 mg of catalyst, 60 °C, 5 h.^b Based on the alkene; the maximum theoretical conversion achievable under the employed reaction conditions is 50%.^c Mixture of cis and trans.

The higher conversion of cyclohexene, though with lower epoxide selectivity, observed on HPB-TS-1_{AS} compared to HPB-TS-1 (Table 2) is ascribed to the higher surface area of the former. This result and its comparison with the opposite trend between the two catalysts observed in the hydroxylation of phenol (vide supra) suggest that some of the Ti species with higher coordination present in HPB-TS-1_{AS} contribute to the epoxidation activity [52], whereas the activity in the hydroxylation of phenol stems virtually only from isolated tetrahedral Ti sites in a crystalline framework.

The undesired decomposition of hydrogen peroxide (2H₂O₂ → 2H₂O + O₂) is often observed as a side reaction in oxidations catalyzed by titanasilicates. It has been generally accepted that this disproportionation reaction occurs more readily on extra-framework Ti sites [53]. Accordingly, a much higher degree of decomposition was observed over HPB-TS-1_{AS} (Table 2), which is the only material among those presented here that displays a significant population of Ti sites with higher coordination (vide supra). It has been proposed that molecular oxygen is involved in the homolytic radical pathways through which allylic oxidation products are formed in the oxidation of cyclohexene [54,55]. Therefore, the occurrence of the disproportionation of H₂O₂ can also be correlated to the higher selectivity toward allylic oxidation products observed over the bead catalysts (Table 2). However, other factors play a role in the observed formation of these products over the bead catalysts, because the selectivity is similar over HPB-TS-1 and HPB-TS-1_{AS}, but much less decomposition of

hydrogen peroxide occurs on the former. This suggests that the bead format of the catalysts may influence the selectivity in the oxidation of cyclohexene.

Finally, the potential of HPB-TS-1 in the epoxidation of bulky substrates was further tested using other alkenes with larger molecular size (Table 3). Although the catalyst gave lower conversion than with cyclohexene, it is still active with these much bulkier alkenes, indicating that a fraction of the titanium species are accessible through the meso/macropores of HPB-TS-1. Because the large alkenes cannot enter the micropores of TS-1, their conversion most likely occurs on the external surface of the TS-1 nanocrystals. The selectivity toward the epoxide was very high with all substrates (>90%), which is attributed to the higher structural stability of these epoxides relative to the more strained cyclohexene oxide [29].

4. Conclusions

Hierarchically porous TS-1 beads with a diameter of 0.2–0.5 mm (HPB-TS-1), built with TS-1 nanocrystals connected through meso/macropores, were prepared by using anion-exchange resin beads as a hard template. These titanasilicate beads proved to be active and versatile heterogeneous catalysts for oxidation reactions of both small and bulky substrates using the green oxidant hydrogen peroxide. The catalytic performance stems from the combination of the advantages of zeolitic nanodomains with those of a meso/macroporous structure within the beads. In the hydroxylation of phenol, HPB-TS-1 displayed comparable conversion and TOF value to those over TS-1, indicating the presence of highly active Ti sites. In the epoxidation of a bulkier substrate as cyclohexene, the catalytic conversion, TOF and epoxide yield over HPB-TS-1 are much superior to those over TS-1, thus underlining the importance of the small size of the TS-1 nanocrystals, which are accessible through the meso/macropores network. Finally, an important asset of HPB-TS-1 is its straightforward separation due to the bead format, which allows recovering the catalyst without centrifugation or filtration. This feature is very attractive for possible industrial applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2015.09.017>.

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