



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



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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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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].

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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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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),  $\text{H}_2\text{O}$  (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<sub>AS</sub>. 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 $\alpha$  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.

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