

Turning TS-1 zeolite into a highly active catalyst for olefin epoxidation with organic hydroperoxides†

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A new synthesis route, based on the silanization of zeolitic seeds, has been applied to prepare nanocrystalline TS-1 zeolite with hierarchical porosity, leading to materials exhibiting high catalytic activity in 1-octene epoxidation with organic hydroperoxides as oxidizing agents.

Titanium silicalite-1 (TS-1) is a highly versatile molecular sieve with MFI structure,¹ specially designed for selective oxidation reactions under mild conditions using hydrogen peroxide as oxidant. However, like most of the conventional zeolites, TS-1 zeolite suffers from intracrystalline diffusion limitations due to the small size of its micropores. Thus, when bulky substrates or oxidants (*i.e.* organic hydroperoxides) are used, the impossibility to access the active centers located inside the micropores leads to very low catalytic activity. To overcome this limitation, over the last few years intensive research has been carried out, focused on the synthesis of titanium-containing materials with enhanced accessibility to the reactive sites. In this way, Ti-zeolites with large pores,² Ti-MCM-41 mesoporous materials,³ Ti-delaminated zeolites,⁴ nanocrystalline TS-1,⁵ mesoporous TS-1⁶ and the synthesis of hybrid mesoporous Ti-containing materials with zeolitic pore walls⁷ have been explored and attempted.

In this work, we report a novel strategy for the synthesis of hierarchical nanocrystalline TS-1 zeolite characterized by having a bimodal pore architecture. The first pore system corresponds to the typical zeolitic microporosity. The second porosity comprises supermicro/mesopores, which provides an enhanced external surface area and leads to a faster transfer of both reactants and products, these facts being particularly interesting for the processing of bulky molecules.⁸

The synthesis method is based on the functionalization of zeolitic seeds by reaction with a silanization agent, thus hindering their growth and agglomeration during the crystallization step. This strategy has been previously applied with satisfactory results to the synthesis of ZSM-5, ZSM-11 and Al-Beta zeolites.⁹ In a typical synthesis, zeolitic seeds were firstly formed by a precrystallization step of the precursor gel at low temperature. Thereafter, the zeolitic seeds were functionalized by adding a silanization agent, in particular

phenylaminopropyltrimethoxysilane (PHAPTMS). The functionalized seeds were subsequently crystallized by microwave heating (see ESI† for detailed synthesis procedure). Two different samples were so obtained and identified as TS-1(5%) and TS-1(8%), where the number in brackets indicates the molar percentage of PHAPTMS added, in regard to the total silica amount present in the silica source. For comparison purposes, a reference TS-1 material, denoted as TS-1(0%), was also prepared using the same synthesis procedure but omitting the precrystallization and silanization steps.

Fig. 1 shows the XRD patterns of the TS-1 samples prepared from silanized seeds as well as that of the reference sample. Diffraction peaks corresponding to the MFI structure can be observed and denote that the three samples are highly crystalline. Nevertheless, reflections of the materials obtained from silanized seeds exhibit lower intensities than those of the reference material. This result is attributed to a reduction in the size of the crystalline domains, due to their hindered growth caused by the silanization agent. Moreover, this effect was more pronounced when the amount of silanizing agent used during the synthesis was increased.

Fig. 2 shows TEM micrographs corresponding to TS-1 (0%) and TS-1(8%) samples. The reference material comprises crystals with mean dimensions around 200 nm and having well defined edges. However, the silanized-seed zeolite consists of large and irregular aggregates with sizes in the range 100–150 nm and with a sponge-like aspect. These aggregates consist of small primary units with sizes below 20–30 nm, corroborating the size reduction of the crystalline domains detected by XRD. The crystalline nature of these units is evidenced by the diffraction fringes visible in the TEM images. Moreover, the presence of voids between the nanocrystallites

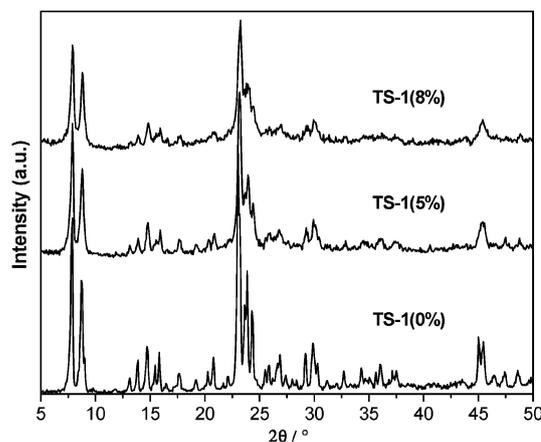


Fig. 1 XRD pattern of calcined samples.

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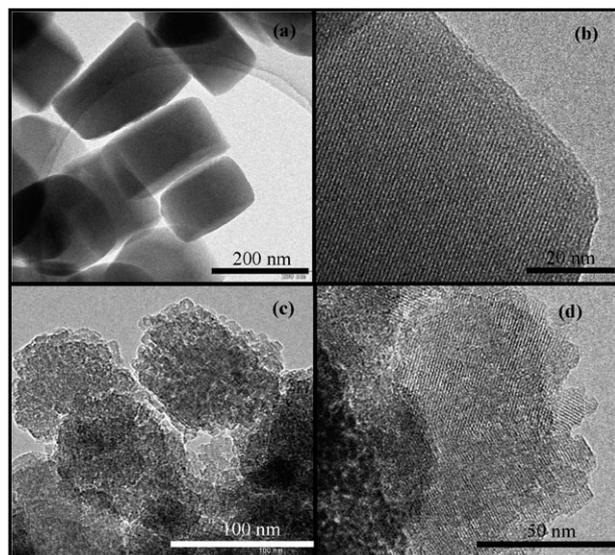


Fig. 2 TEM images: (a), (b) TS-1(0%) and (c), (d) TS-1(8%).

is clearly appreciated in the micrographs corresponding to sample TS-1(8%), which denotes the existence of a secondary porosity in the materials prepared from silanized seeds.

Through DR UV-Vis analyses of both the reference and silanized-seed zeolites (Fig. 3) the effective incorporation of titanium into the zeolite framework was confirmed. The absence of absorption at about 330 nm indicates that all the samples are free of non-desired extraframework TiO_2 phases. On the other hand, the presence of a band centered at 220 nm shows that the Ti atoms exhibit mainly tetrahedral coordination in the three samples. However, a shift is observed in the edge of this band towards higher wavelengths for the TS-1 samples prepared by seed-silanization. This fact suggests that some of the Ti atoms are penta- or hexacoordinated in these materials, which probably affects those Ti sites located on the outer surface of the nanocrystallites.

Table 1 summarizes both the titanium content of the samples determined by ICP-AES analyses and the synthesis solid yield. It can be observed that the silanized-seed samples presented Ti amounts close to that of the reference material.

However, the solid yield corresponding to the TS-1 samples prepared from seed-silanization was somewhat higher than that of the reference TS-1 material. This fact could be due to

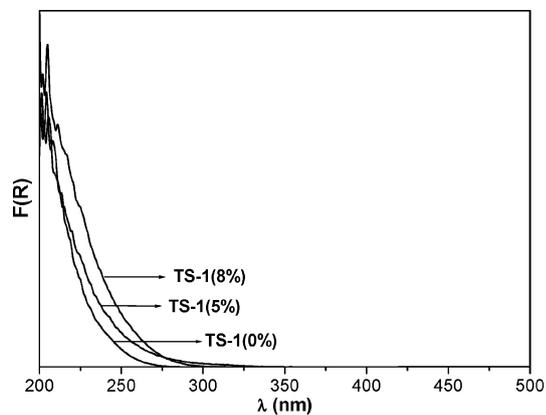


Fig. 3 DR UV-Vis spectra of calcined TS-1 samples.

the longer synthesis times used to obtain the silanized-seed samples, since both precrystallization and silanization stages were carried out prior to the final hydrothermal crystallization step. Furthermore, it must be taken into account that the raw gel in the silanized samples contained a higher silica amount than the reference TS-1 zeolite due to the presence of one silicon atom per mole of silanization agent.

The effective incorporation of the organosilane compound into the as-synthesized zeolites was confirmed by elemental CHN analyses, which provided proportions of PHAPTMS close to that theoretically introduced into the synthesis gel.

Fig. 4 illustrates the pore size distributions of the TS-1 samples calculated by applying the NLDFT model to the adsorption branch of the Ar isotherms at 87.4 K (inset of Fig. 4). The application of the NLDFT model allows a complete pore size distribution to be obtained within the micropore and mesopore ranges. A maximum is observed for the three samples around 5.2–5.4 Å, which corresponds to the mean pore size of MFI-type zeolites. However, in the pore size distribution curves corresponding to the silanized-seed TS-1 samples, additional peaks are observed within the range 10–50 Å. This result confirms the presence of a secondary porosity in the supermicro/mesopore region in these materials, which is originated from the voids existing between the nanocrystallites observed in the TEM images. Moreover, the contribution of this secondary porosity clearly increases with the amount of silanization agent.

The textural properties obtained from the Ar adsorption-desorption isotherms are shown in Table 1. The NLDFT model is also useful for estimating the contribution of both types of porosities to the pore volume and surface area of the materials. TS-1 samples prepared from organo-functionalized seeds possess lower micropore volume and micropore surface area but higher BET and external surface areas than the reference zeolite. Thus, while for the reference TS-1 sample the latter parameters were $415 \text{ m}^2 \text{ g}^{-1}$ and $50 \text{ m}^2 \text{ g}^{-1}$, respectively, such values increased up to $649 \text{ m}^2 \text{ g}^{-1}$ and $428 \text{ m}^2 \text{ g}^{-1}$, respectively, for TS-1(8%). This enhancement of the BET surface area, which is exceptionally high when compared to the conventional MFI zeolites, has been previously observed for nanozeolites formed by extremely small crystallites. Likewise, the large external surface area present in the seed-silanized samples corresponds to the surface area of the secondary porosity. A clear relationship is observed between the amount of seed-silanization agent introduced into the synthesis gel and the modification degree of the TS-1 textural properties.

The catalytic activity of the TS-1 samples for alkene epoxidation with bulky oxidants has been tested using 1-octene and tertbutylhydroperoxide (TBHP) as substrate and oxidizing agent, respectively. The conversion and selectivity values, together with the TBHP efficiency so obtained, are presented in Table 2. It is noteworthy that the activity of the hierarchical TS-1 zeolites prepared from silanized seeds was several times higher than the one obtained with the reference zeolite. On the other hand, both selectivity and TBHP efficiency were very high and not affected by the modification of the TS-1 zeolite properties caused by the seed-silanization treatment. These results cannot be explained by a higher hydrophobicity of the modified samples caused by the silanization agent as the latter is

Table 1 Physicochemical and textural properties of TS-1 samples

Sample	Si-Ti	Yield (%)	$S_{\text{BET}}/m^2 g^{-1}$	$S_{\text{MIC}}/m^2 g^{-1}$	$S_{\text{EXT}}/m^2 g^{-1}$	$V_{\text{MIC}}/cm^3 g^{-1}$
TS-1(0%)	81	52	415	365	50	0.195
TS-1(5%)	79	63	556	296	260	0.177
TS-1(8%)	72	65	649	220	428	0.132

^a Determined by applying the NLDFT method.

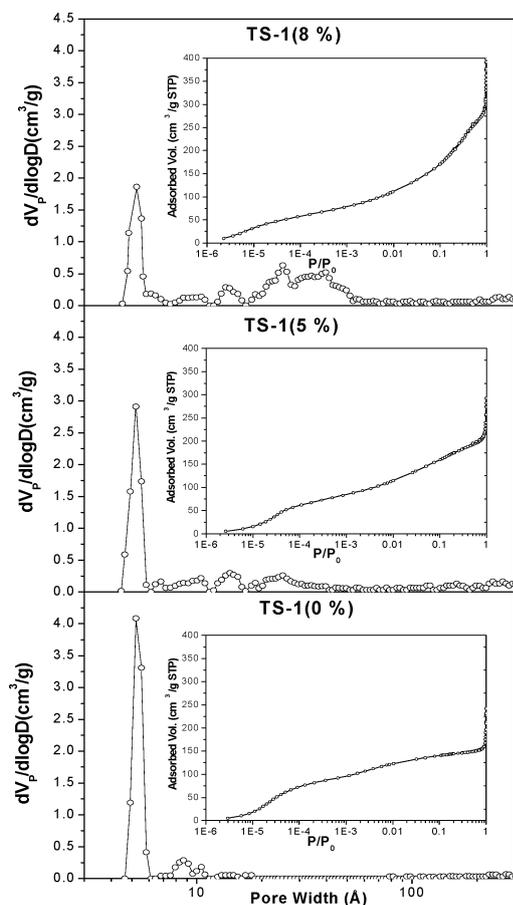


Fig. 4 Ar adsorption-desorption isotherms at 87.4 K and NLDFT pore size distributions calculated using cylindrical model.

Table 2 Catalytic activity of TS-1 samples in 1-octene epoxidation reaction with TBHP

Sample	1-Octene conversion (%)	Epoxide selectivity (%)	TBHP efficiency (%)
TS-1(0%)	5.6	100	94
TS-1(5%)	14.8	100	93
TS-1(8%)	42.1	100	97

^a Reaction conditions: 100 °C, 3 hours, (1-octene-TBHP)_{MOLAR} = 1.25, 0.2 g catalyst.

completely destroyed by calcination treatment before the catalytic runs.

The low activity observed for the reference TS-1 was an expected result due to the limited space existing within the TS-1 zeolitic micropores, which prevents the formation of bulky Ti-alkylperoxo complexes and their subsequent interaction with 1-octene molecules, as it has been widely reported in the literature.¹⁰

However, these drawbacks can be overcome by the use of TS-1 materials obtained from silanized seeds thanks to the presence of a hierarchical porosity, which provides a high external surface area and improved accessibility of both substrate and oxidizing agent to the Ti active sites. As a consequence, this approach allows TS-1 zeolite to be turned into a highly active and selective catalyst for alkene epoxidation with organic hydroperoxides.

In conclusion, we report a relatively simple and effective method for synthesizing hierarchical TS-1 zeolite based on the crystallization of silanized seeds. The materials so obtained are formed by the aggregation and intergrowth of very small nanocrystallites, showing a secondary porosity in the range of supermicro- and mesopores, additionally to the microporosity typical of MFI-type materials. Moreover, these TS-1 samples exhibit very high BET and external surface areas. All these features influence quite positively their catalytic properties for olefin epoxidation with organic hydroperoxides. Thus, hierarchical TS-1 zeolites have led to much higher conversions in the 1-octene epoxidation with TBHP than conventional TS-1 zeolite, while maintaining 100% epoxide selectivity and very high oxidant efficiencies.

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Supporting Information

Turning TS-1 zeolite into a highly active catalyst for olefin epoxidation with organic hydroperoxides

Experimental

Materials and chemical preparation

TS-1 samples with hierarchical porosity were obtained by adapting the method initially developed by Taramasso et al.¹. Tetraethylortosilicate (TEOS, from Alfa Aesar) and tetraethylortotitanate (TEOT, from Alfa Aesar) were used as silicon and titanium sources, respectively. Both chemicals were used as received. Firstly, both TEOS and TEOT were mixed at 30 °C into a round bottom flask. Subsequently, the previous solution was cooled down to 0 °C and a TPAOH aqueous solution (20% wt) was added dropwise. TPAOH not only acts as structure directing agent but also gives the basic pH necessary for the hydrolysis reactions. This reagent was alkali-free synthesized by reaction of tetrapropylammonium bromide (TPABr, from Aldrich) with Ag₂O (Alfa). After TPAOH addition, the TS-1 precursor solution was heated at 80°C in order to evaporate the alcohol molecules formed during the hydrolysis reactions. The final molar composition of the gel so obtained was SiO₂: 0.0163TiO₂: 0.44TPAOH: 28.5H₂O. This gel was precrystallized in a refluxing system under stirring conditions at 90°C for 24 hours. Thereafter, the silanization agent, phenylaminopropyl-trimethoxysilane (PHAPTMS, from Aldrich) was added to the gel in different quantities (5 and 8 mol%, referred to the silica source, TEOS) and the silanization reaction was performed under refluxing at 90°C for 6 hours. The final crystallization treatment was carried out by microwave heating of the silanized gel at 170 °C for 8 hours. The solid products so obtained were separated by centrifugation, washed several times with distilled water, dried overnight at 110 °C and, finally, calcined in air atmosphere at 550°C for 5 hours.

A reference TS-1 zeolitic material was prepared following the synthesis procedure previously described but omitting the precrystallization and silanization steps.

Characterization

X-Ray diffraction (XRD) patterns were collected using a Philips X'PERT MPD diffractometer operating with Cu K α radiation and a step size and time per step of 0.02° and 10 s, respectively. TEM images were obtained in a PHILIPS TECHNAI 20 electron microscope operating at 200 kV. Titanium content of the synthesized samples was determined by means of atomic emission spectroscopy with induced coupled plasma (ICP-AES) analyses performed in a Varian Vista AX spectrophotometer. Previously to the analyses, samples were dissolved by an acid digestion treatment. Diffuse Reflectance UV-Vis spectroscopy analyses (DR UV-VIS) were collected under room conditions using a CARY-500 spectrophotometer equipped with a diffuse reflectance accessory. Argon isotherms at 87 K were measured using a Micromeritics ASAP 2010 instrument. The total surface area was estimated according to the BET method whereas the pore size distribution was calculated by applying the NLDFT model with cylindrical pore geometry. The organic content of the samples was determined by elemental analyses making use of an Elementar Vario EL III analyzer equipped with a thermal conductivity detector.

Reaction tests

1-Octene epoxidations with TBHP were carried out in a magnetically stirred round bottom flask at 100°C for three hours where 2.4 g of 1-octene, 4 g TBHP (Fluka) and 0.2 g of catalyst were put in contact. The reaction products were determined by standard iodometric titration and by gas chromatography (capillary column 60 m x 0.25 mm, VARIAN FFAP, FID detector) using toluene (Sharlau) as internal standard.