

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.