

SUPPLEMENTARY MATERIAL

Synthesis of framework Ti-substituted, 3-D hexagonal, mesoporous Ti-SBA-12 for selective catalytic oxidation

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S1: X-ray diffraction and N₂ adsorption-desorption profiles

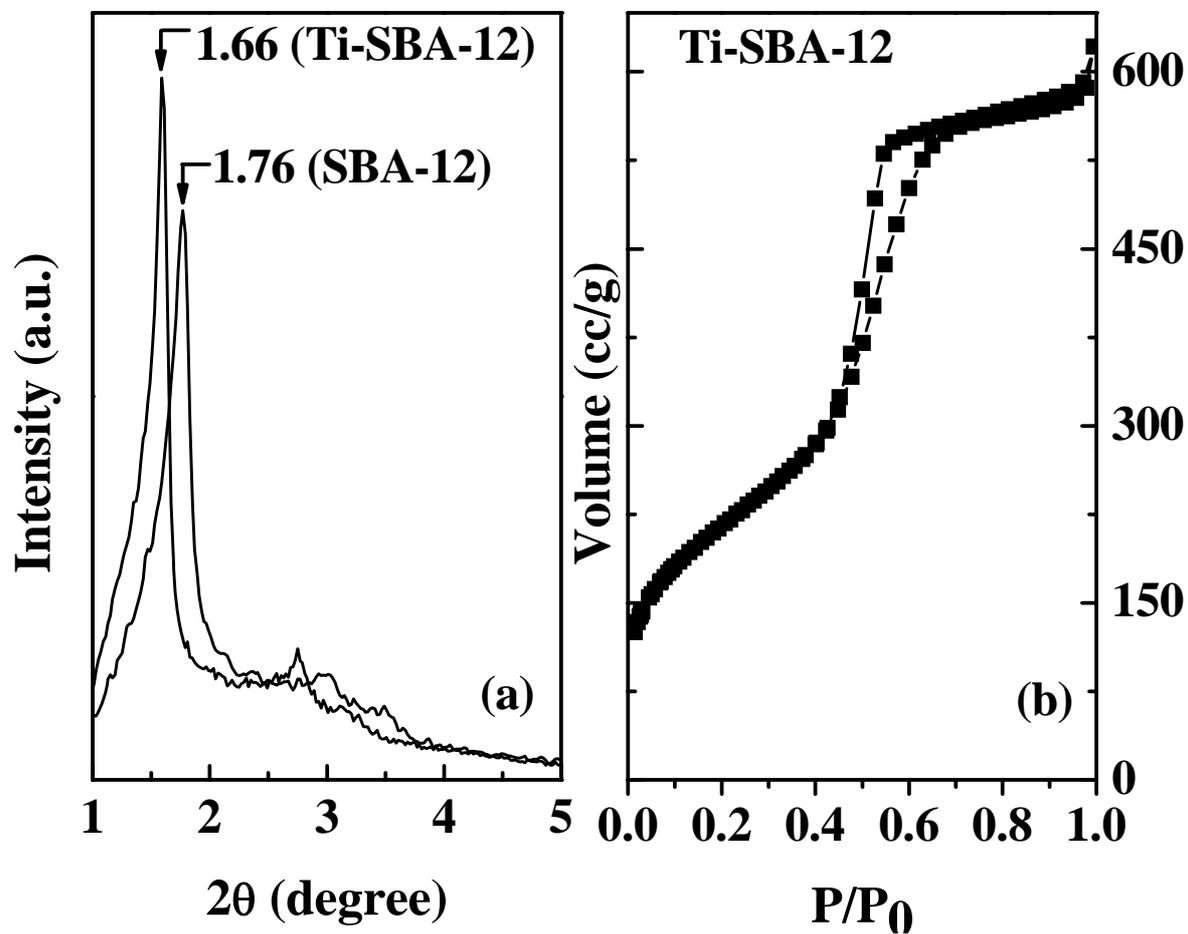
S2: Relationship between tetrahedral Ti content and molar ratio of Ti in Ti-SBA-12

S3: Oxidation products of cyclohexene

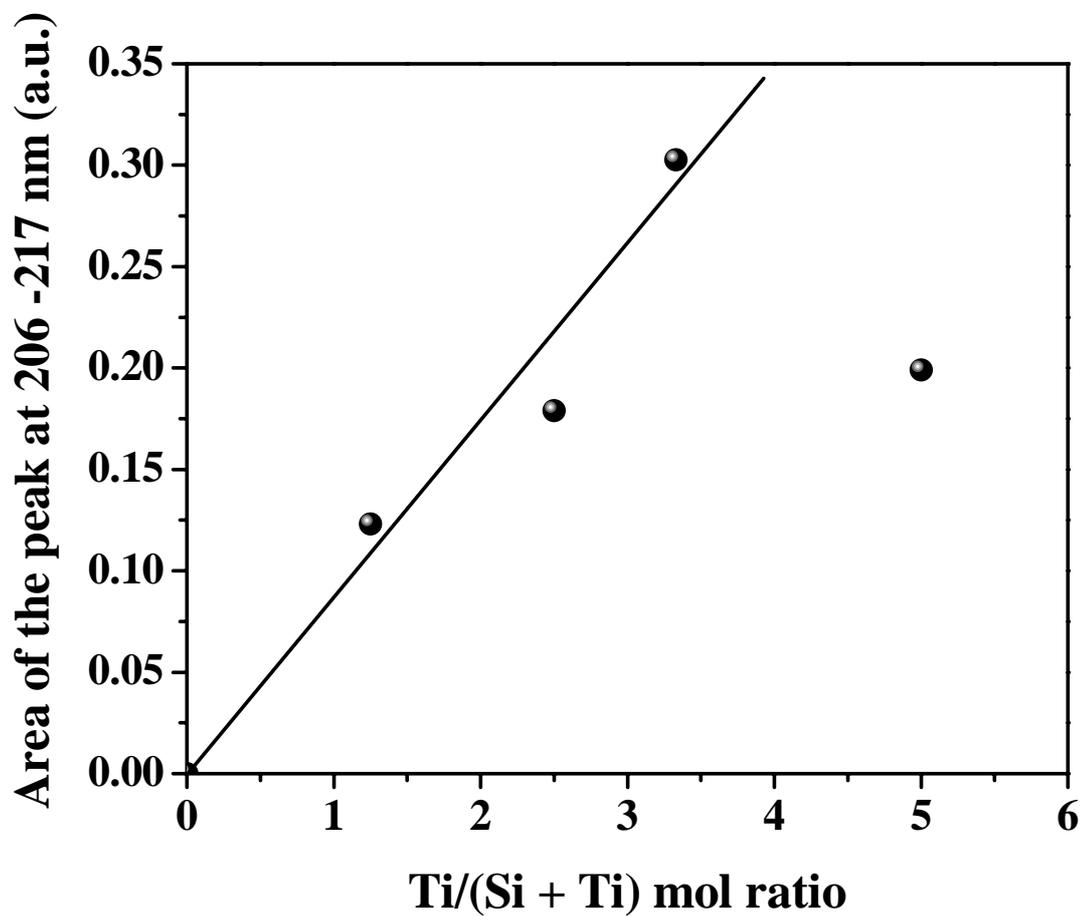
S4: Correlation between epoxide selectivity and tetrahedral Ti-content in Ti-SBA-12

S5: Experimental procedure for carrying out the catalytic reactions

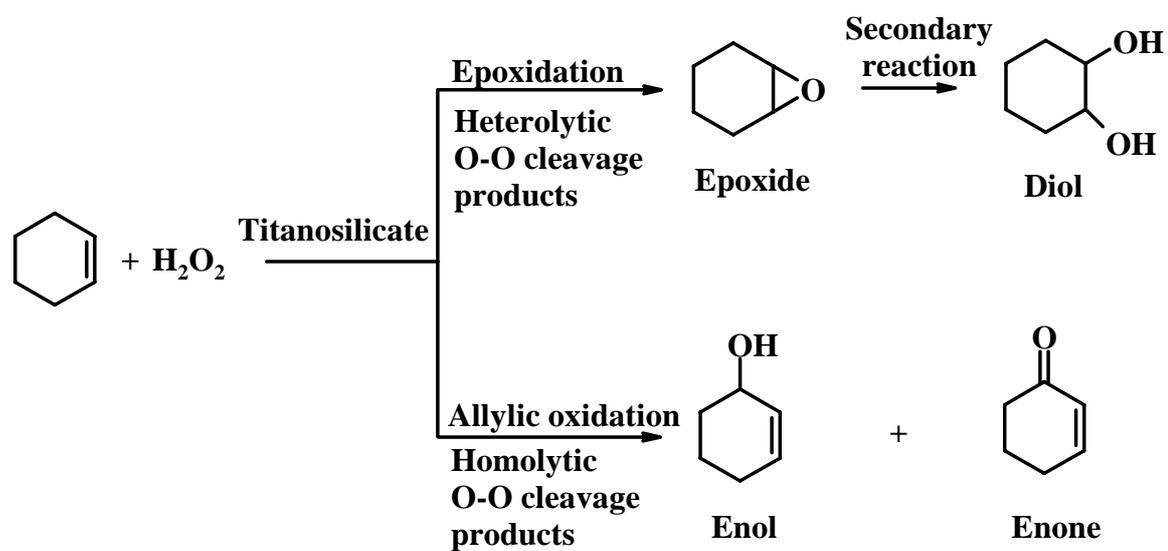
S6: Catalyst characterization procedures



S1: (a) Low-angle X-ray diffraction profiles of SBA-12 and Ti-SBA-12 prepared at 313 K using 0.2 M HCl. (b) N_2 adsorption-desorption isotherms of Ti-SBA-12 (Si/Ti = 80) prepared at 298 K using 2 M HCl.

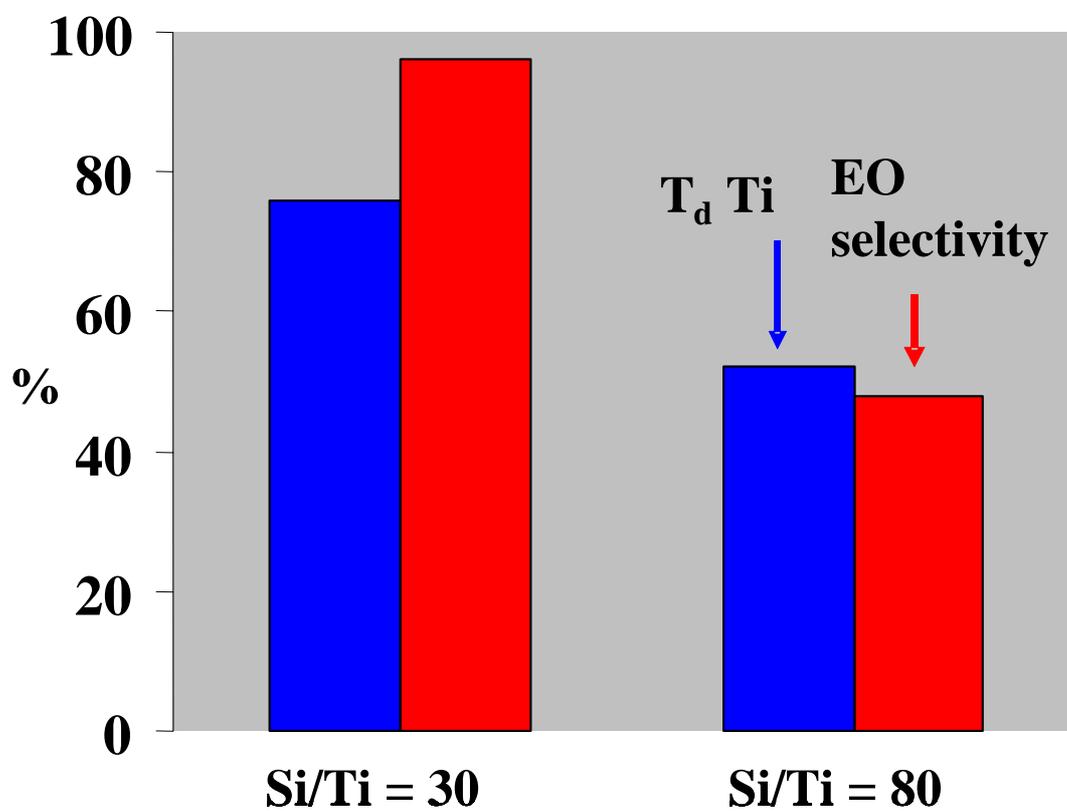


S2: Relation between tetrahedral Ti content (area of UV-visible bands at 206 – 217 nm) and molar ratio of Ti in Ti-SBA-12 prepared at 298 K using 2 M HCl.



S3: Reaction products of oxidation of cyclohexene.

Ti-SBA-12



S4: Epoxide selectivity changes with the concentration of tetrahedral Ti (from the UV band at 206 nm).

S5: Experimental procedure for carrying out the oxidation of cyclohexene

The reactions were conducted in a glass, double-necked, round-bottomed flask fitted with a water-cooled condenser and a rubber septum to inject the oxidant. In a typical reaction, 0.1 g of the catalyst, 0.82 g of cyclohexene and oxidant (0.567 g of 30% aq. H₂O₂ or 0.9 g of 5.5 M TBHP in decane; substrate to oxidant molar ratio being 2 : 1.2) and 5 ml of solvent (acetone, acetonitrile or dichloromethane) were taken in the round-bottomed flask. The reaction was conducted at 333 K for 12 h. The products were analyzed by gas chromatography (Varian 3400; CP-SIL8CB column; with a 30 m-long, and 0.53 mm-i.d.) and identified by GC-MS (Shimadzu QP-5000; with a 30 m-long, 0.25 mm-i.d., and 0.25 μ m-thick capillary column DB-1).

S6: Catalyst characterization procedures

X-ray diffractograms were recorded with a X'Pert Pro (Philips) diffractometer using Cu K α radiation and a proportional counter as detector. The XRD patterns were recorded in the 2 θ range of 0.5 – 5° at a scan rate of 1°/min. High resolution transmission electron micrographs of the samples were recorded on a FEI Technai-F30 instrument with a 300 kV field emission gun. The calcined sample was dispersed in isopropyl alcohol, deposited on a Cu grid and dried. Scanning electron micrographs were taken on a Leica STEREOSCAN 440, LEO Microscopy, Cambridge, UK instrument. The specific surface area of the samples was determined by the B.E.T. method using a NOVA 1200 Quanta Chrome equipment. The micropore volume was determined from the t-plot. The reference alumina sample supplied by Quanta Chrome was used for calibrating the instrument. The pore diameter was estimated using the Barret-Joyner-Halenda (BJH) model. FT-IR spectra were recorded on a Shimadzu 8300 spectrophotometer in the region

400 - 4000 cm^{-1} . Diffuse reflectance UV-visible (DRUV-vis) spectroscopic measurements for powder samples were conducted with a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere attachment (ISR 2200). Spectral grade BaSO_4 was used as the reference material. FT-Raman spectra were recorded with a Horiba JY LabRaman HR 800 MicroRaman spectrometer using wavelength 630 nm by (He-Ne) laser operating at 20 mW power. Electron paramagnetic resonance (EPR) spectra of the samples were recorded on a Bruker EMX X-band spectrometer operating at 100 kHz field modulation. The microwave frequency was calibrated using a frequency counter fitted in a microwave bridge ER 041 XG-D. The EPR spectra were recorded taking the samples in suprasil quartz tubes. Prior to the EPR measurements, the samples were activated at 373 K, in air. In the experiments with H_2O_2 , 0.1 ml of aqueous H_2O_2 (30%) was added to 45 mg of the titanosilicate sample; it was ensured that the whole sample was completely soaked in the oxidant medium. The catalyst changed its color from white to yellow, an indication of the formation of reactive oxo-titanium species.