Supporting Information

Simple Surfactant CTAB-Assisted Hierarchical Lamellar MWW Titanosilicate: A High-Performance Catalyst for Selective Oxidations Involving Bulky Substrates

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Experimental section:
For control experiments, the conventional titanosilicates, including microporous Ti-MWW, TS-1 and Ti-Beta, as well as mesoporous Ti-MCM-41 were synthesized according to the procedures described in the literatures. Typically, the layered precursor Ti-MWW-P was prepared in a boric system with piperidine (PI, Sinopharm) as OSDA. The molar composition of the starting gel was 1.0 SiO2 : (0.0067 - 0.05) TiO2 : 1.4 PI : 0.67 B2O3 : 19 H2O. After crystallization at 443 K for 7 days, the product was recovered by filtration and acid treated with 2.0 M HNO3 aqueous solution at a liquid-to-solid weight ratio of 30 to remove the extraframework Ti species under reflux conditions. After calcination at 823 K for 5 h, the Ti-MWW catalyst with 3D crystalline structure was obtained. The Si/Ti molar ratios in other titanosilicates were around 40. For the synthesis of microporous titanosilicate TS-1, the molar composition of the starting gel was 1.0 SiO2 : 0.025 TiO2 : 0.18 TPAOH : 20 H2O. The gel was transferred into autoclave and crystallized under 443 K for 48 h. After filtration and drying, the product was also treated with HCl aqueous solution at a liquid-to-solid weight ratio of 50. The conventional TS-1 with Si/Ti molar ratio around 40 was obtained after calcination in air at 823 K for 5 h to remove the OSDA. Another typical microporous titanosilicate Ti-Beta was synthesised by hydrothermal synthesis method under OH- condition with the existing of dealuminated Beta seeds. A gel with the molar composition 40 SiO2 (seed/SiO2 = 0.029) : 0.025 TiO2 : 22 TEAOH : 13.5 H2O : 265 H2O was reacted under 413 K for 14 days. The Ti-Beta with Si/Ti ratio around 40 was obtained after the calcination at 823 K for 5 h. The typical mesoporous titanosilicate Ti-MCM-41 synthesised by using amorphous silica as silica source, TBOT as titanium source, TMAOH aqueous (25 wt.%) and CTAB. The mixture with molar composition 1.0 SiO2 : 0.025 TiO2 : 0.26 TPAOH : 24 H2O : 0.4 CTAB was reacted at 408 K for 14 h under static conditions. After filtering and drying, Ti-MCM-41 with Si/Ti around 40 was obtained.

Characterization:
The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-Kα radiation (λ = 1.5405 Å). SEM images were captured with a Hitachi S4800 microscope. High resolution TEM images were collected with an FEI G2F30 with an accelerating voltage of 300 kV. Rotation electron diffraction (RED) were collected on a JEOL JEM2100 TEM by the RED program from a randomly selected crystal (beam tilt: -1.0° to 1.0°, goniometer tilt: -15.35° to 44.71°, exposure time: 1 s). 341 ED frames were recorded with a beam tilt step of 0.2° and goniometer tilt step of 2°. The reciprocal space reconstruction and data extraction were carried out by the RED data processing. N2 adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 adsorption instrument. Solid-state NMR spectra were collected on a Varian Model VNMRS-400 MB spectrometer. The amounts of Si, Ti and B were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. Infrared spectra were obtained on a Nicolet Nexus 670 FT-IR spectrometer at a spectral resolution of 2 cm⁻¹. The spectra in the region of framework vibrations (500 - 1100 cm⁻¹) were recorded using KBr pellet technique. The samples were pressed into the wafers (Ø 1.5 cm, 3 wt.% diluted in KBr). The UV-visible diffuse reflectance spectra were recorded on a PerkinElmer UV/vis Lambda25 spectrometer using BaSO4 as a reference. XPS spectra were recorded with an AXIS Supra/Ultra instrument (Kratos Analytical Ltd.) by
using monochromatic Al Kα radiation. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. The spectra were quantified by Kratos Analytical. Samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to C 1s peak of (C-C, C-H) bond, which was set to 284.4 eV. The data were analyzed with commercially available software CasaXPS.