

Supporting Information for

A low-deactivation-rate Lewis acid zeolite prepared in an alkali metal ion-containing system for alkene epoxidation

Kai-Rui Fu,^{†a} Ji-Kang Yao,^{†a} Qiang Xiao,^b Hai-Xia Liu,^a Tian-Duo Li,^{*a} Takashi Tatsumi^c and Jin-Gui Wang^{*a}

- ^a Shandong Provincial Key Laboratory of Fine Chemicals, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353 P.R. China. E-mail: JGWang@qlu.edu.cn; litianduo@163.com
- ^b Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, 321004, Jinhua, P.R. China
- ^c Catalytic Chemistry Division, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 2268503, Japan

Detailed experimental procedures

Chemicals and materials

Titanium tetra-n-butoxide and tetraethylorthosilicate were purchased from Aldrich. Tetrapropylammonium hydroxide (TPAOH) and Ethylenediaminetetraacetic acid (EDTA) were from Sigma-Aldrich. Reagents of 1-hexene and 1,2-epoxyhexane were purchased from TCI. Hydrogen peroxide (H₂O₂, 30 wt. % in water) and 0.1 M Ce(SO₄)₂ were from Macklin. All the chemical agents were used without further purification.

Synthesis of TS-1 zeolite catalysts

TS-1(EDTA) was synthesized as followed: firstly, titanium tetra-n-butoxide was added to H₂O₂ aqueous solution to form a stable Ti source of Ti-peroxo complex. Then, an aqueous solution of tetrapropylammonium hydroxide that contains approximately ~10 000 ppm K⁺ and ~600 ppm Na⁺ was added into above Ti solution followed by the addition of tetraethylorthosilicate under stirring. After 0.5 h, the resultant solution was heated to 353 K for 4 hours to evaporate alcohol generated during the hydrolysis of the Ti and Si precursors. And then EDTA was added. The molar composition of the final mixture was 100 SiO₂/ 2.5 TiO₂ /36 TPAOH /10 KOH /1 NaOH /130 EDTA /3500 H₂O. The final mixture was transferred into an autoclave and treated at 443 K for 2 days under static condition. The suspended TS-1 crystal was centrifuged, washed with distilled water, and dried at 373 K. The obtained product was treated under calcination at 823 K for 6 h to remove the organic templates.

TS-1-alkali was prepared by using the same procedures and gel composition except no EDTA added.

TS-1-con was prepared via conventional method in the absence of alkali metal ions and EDTA. The preparation processes were similar to synthesis of TS-1(EDTA).

Zeolite characterization

Powder X-ray diffraction pattern (PXRD) measurements were performed on a Bruker Powder D8 Advance diffractometer at 40 kV and 40 mA using $\text{CuK}\alpha$ radiation ($\lambda=1.5418$ Angstrom). Diffuse reflectance ultraviolet-visible (DRUV/Vis) spectrum were recorded on a SHIMADZU UV-2450 spectrophotometer at 298 K using BaSO_4 as a reference. IR spectrum were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer. Raman spectra were obtained using a Thermo SCIENTIFIC DXR Raman microscope with an excitation wavelength at 532 nm. Nitrogen adsorption-desorption isotherms were measured on a TriStar II 3020 sorption analyzer at 77 K. Elemental analyses (Si, Ti, Na and K) were performed on an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer ICP Optima 2000DV). X-ray Photoelectron Spectra (XPS) were recorded on a Thermo Fisher Scientific ESCALAB 250Xi X-ray Photoelectron spectrometer using Al X-ray source. ^{29}Si MAS NMR spectra were recorded on a Varian Infinity plus 400 instrument with 8 kHz spin rate. Thermogravimetry (TG) was performed with a TA SDT Q600 apparatus. Field-emission SEM images were obtained on a JEOL JSM-7600F microscope operated at 5 kV. TEM observations were performed on a JEOL JEM-1400 TEM microscope, working at 100 kV. Sample subjected to TEM measurements was dispersed in ethanol ultrasonically and was dropped on copper grids.

Catalytic reactions

Oxidation reactions were performed in a sealed 20 mL glass reactor immersed in a 60 °C oil bath. In a typical run, the reactions were carried out with catalyst (25 mg), 1-hexene (5.0 mmol) and H_2O_2 (5.0 mmol) in methanol (5.0 mL) with vigorous stirring for different time. After the reaction, certain amount of cyclohexanone was added as internal standard. The mixture was analyzed by gas chromatography with SE-30 capillary column. The amount of unconverted H_2O_2 was determined by titrating with $\text{Ce}(\text{SO}_4)_2$ aqueous solution (0.1 M). The products were verified using authentic chemicals commercially available.

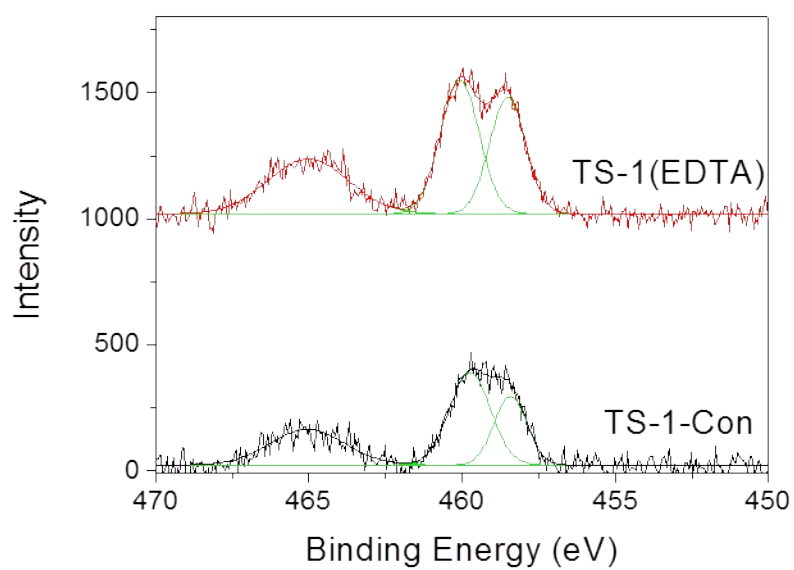


Fig. S1 XPS spectra at the Ti 2p region for TS-1 zeolite of (a) TS-1-Con and (b) TS-1(EDTA).

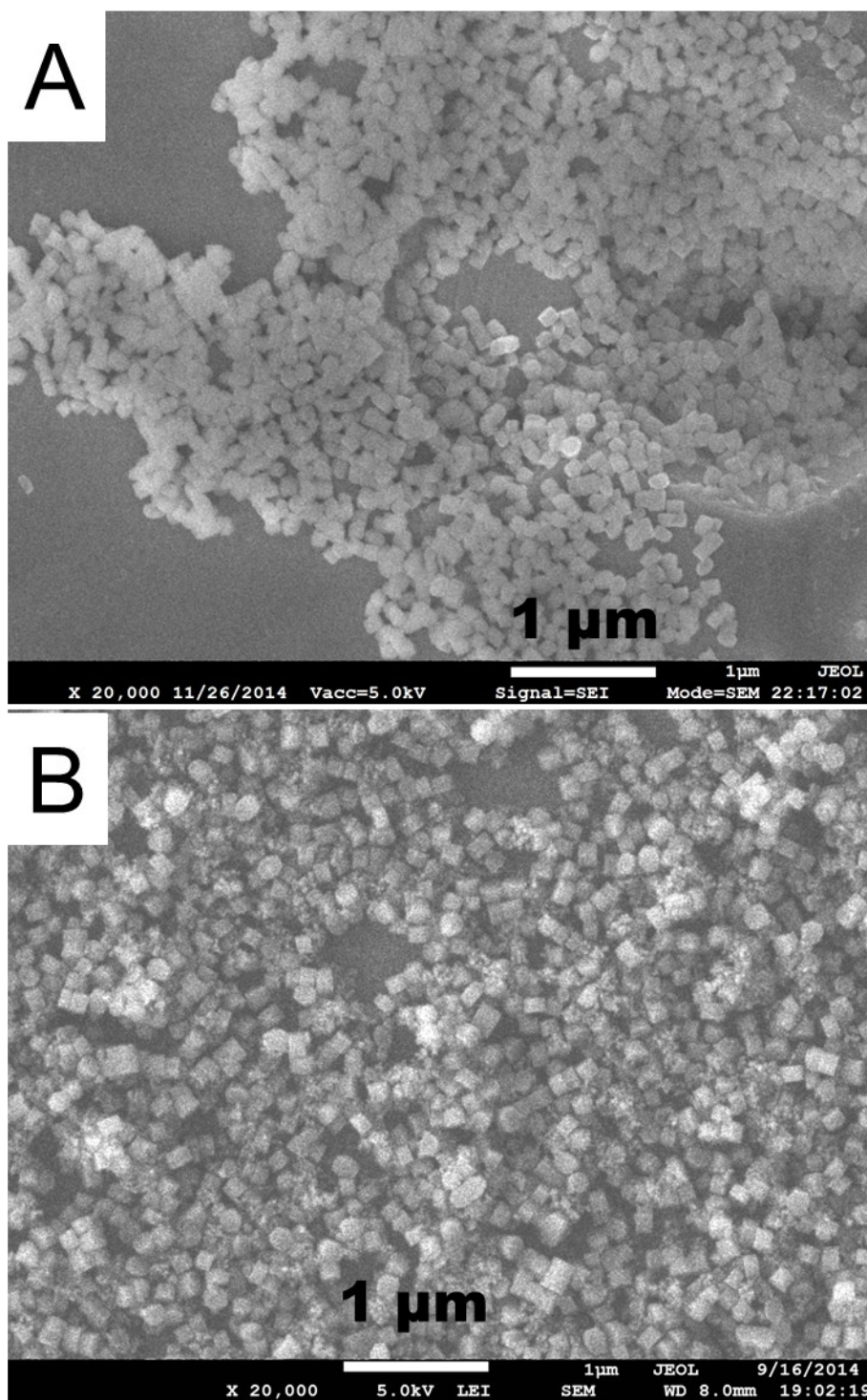


Fig. S2 SEM images of (A) TS-1-Con and (B) TS-1-Alkali.

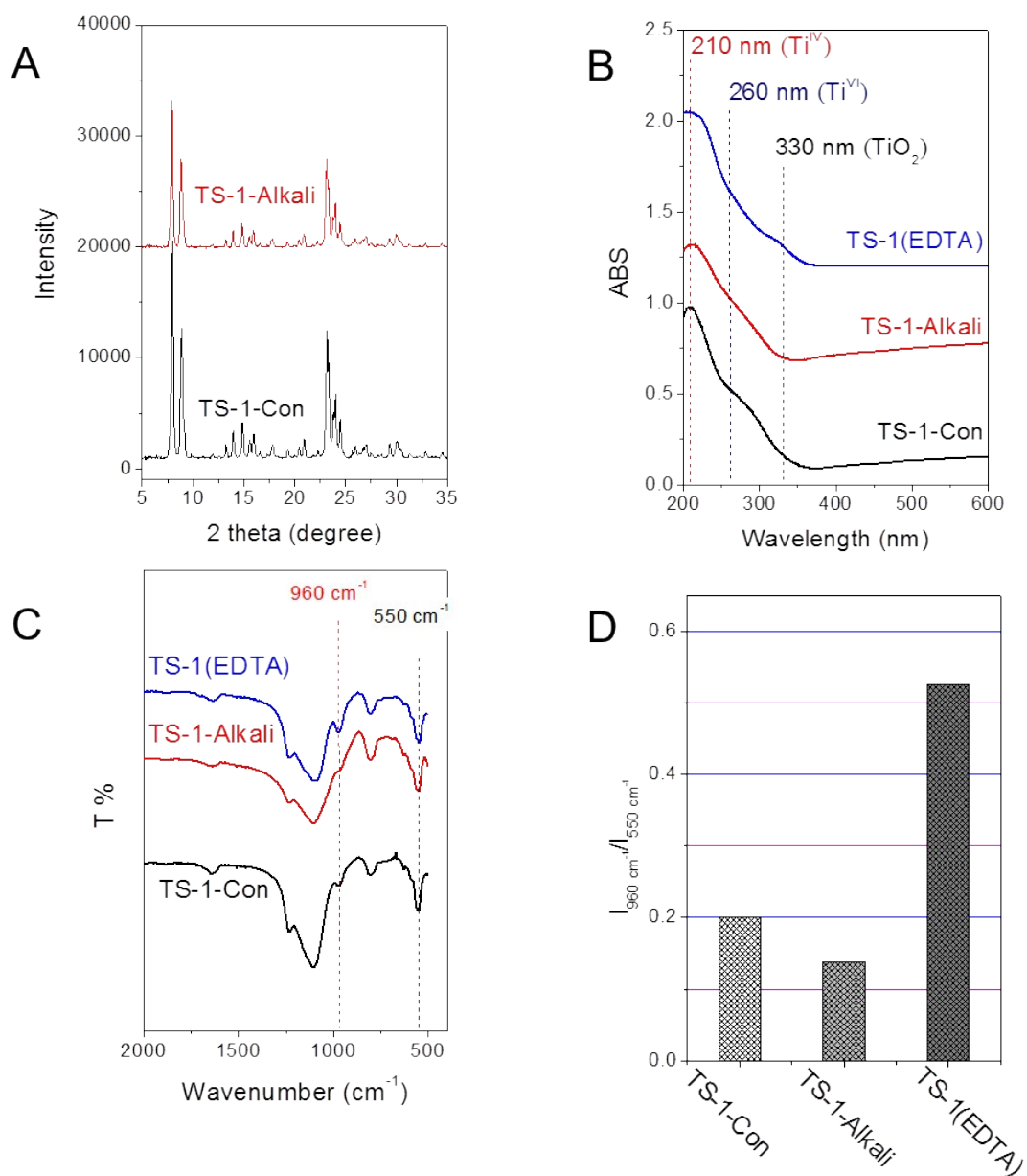


Fig. S3 (A) XRD patterns, (B) DRUV-vis spectra, (C) IR spectra and (D) Intensity of 960 cm^{-1} bands normalized to 550 cm^{-1} in IR spectra of TS-1-Con, TS-1-Alkali and TS-1(EDTA).

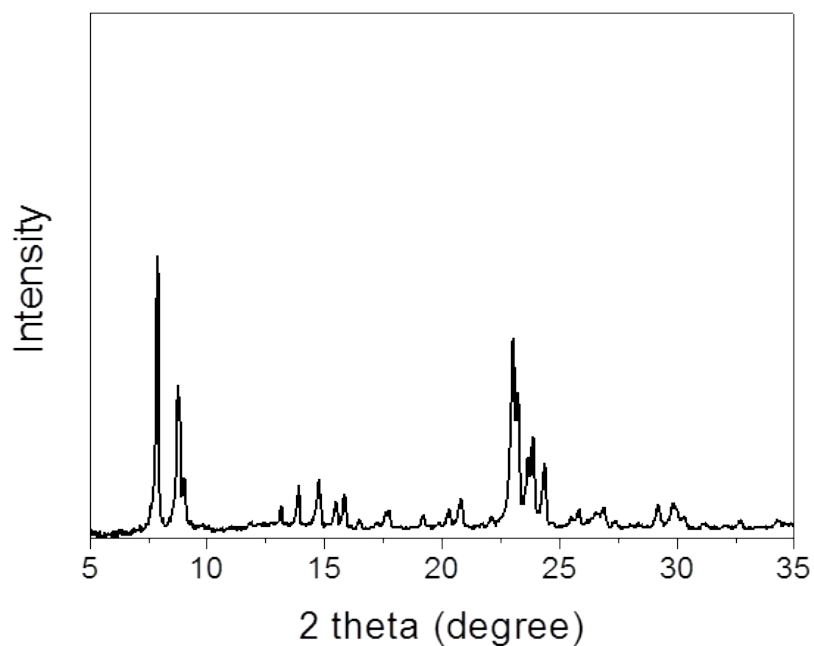


Fig. S4 XRD pattern of TS-1(EDTA) after third use as catalyst for catalytic oxidation of 1-hexene with H_2O_2 . Reaction conditions: catalyst (25 mg), methanol (5 mL), 1-hexene (5 mmol), H_2O_2 (5 mmol), temperature 60 °C, 6 h.

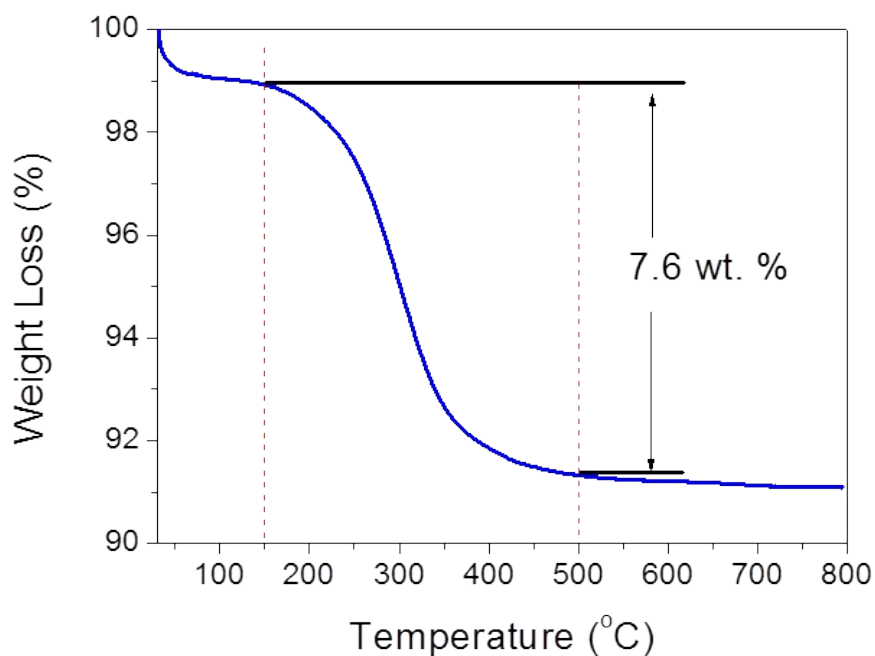


Fig. S5 TG curve of TS-1(EDTA) after third use for catalytic oxidation of 1-hexene with H_2O_2 . Reaction conditions: catalyst (25 mg), methanol (5 mL), 1-hexene (5 mmol), H_2O_2 (5 mmol), temperature 60 °C, 6 h.

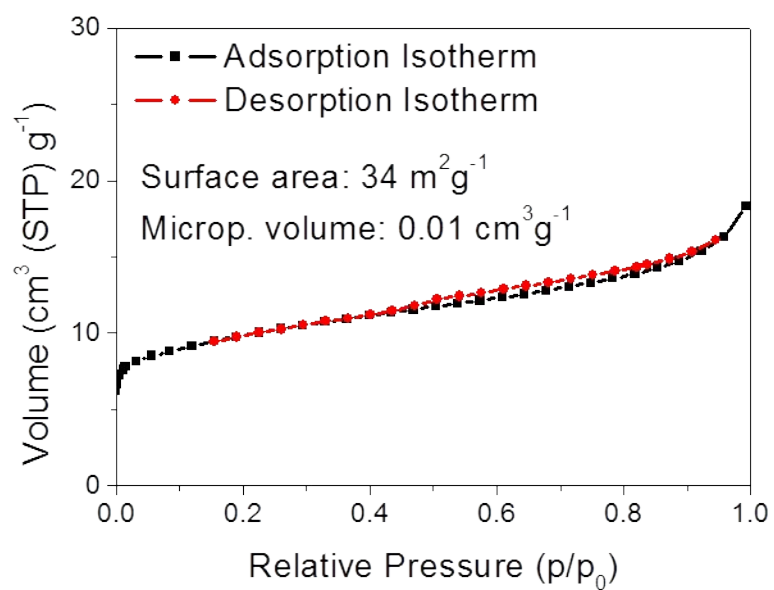


Fig. S6 Nitrogen adsorption-desorption isotherms of TS-1(EDTA) after third use for catalytic oxidation of 1-hexene with H₂O₂. Reaction conditions: catalyst (25 mg), methanol (5 mL), 1-hexene (5 mmol), H₂O₂ (5 mmol), temperature 60 °C, 6 h.