Supplementary Information for

Hierarchical mesoporous TS-1 zeolite: a highly active and extraordinarily stable catalyst for the selective oxidation of 2,3,6-trimethylphenol to trimethyl-*p*-benzoquinone

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Experimental Details

Synthesis of materials

The preparation of *c*-Ti-TUD-1 is similar to that of hierarchical micro/mesostructured aluminosilicate which has been reported elsewhere.[1] It is composed of two independent steps: the first is the synthesis of amorphous mesoporous Ti-TUD-1, and the second, the steam-assisted crystallization (SAC) for *c*-Ti-TUD-1 by employing dried Ti-TUD-1 gel as precursors. The synthesis of wet gel was basically the same as the previous report.[2] Firstly, 0.34 g tetrabutyl titanate ($(C_4H_9O)_4Ti$, 99%, 1.0 mmol) was dissolved in 9.0 g distilled water (0.5 mol) then, 7.5 g triethanolamine (TEA, 99%, 0.05mol) and 10.4 g tetraethylorthosilicate (TEOS, 99%, 0.05mol) were added to the solution under continuous stirring. The resultant mixture was stirred vigorously until a homogenous mixture was obtained. After that, 4.1 g tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution, 5mmol) was added dropwise into the resultant sol. The whole stirring process was carried out at 40 ºC. Therein, the molar ratio of the precursors was TiO_2: SiO_2: TPAOH: TEA: H_2O = 1: 50: 5: 50: 500. The resultant wet gel was dried at 90 ºC for at least 12 h. Finally, this as-prepared dried gel was crystallized by the SAC method at 180 ºC for 12 h. Afterwards, the products were washed repeatedly with distilled water, dried in air and then calcined at 600 ºC for 10 h to remove the organic agents. The white powders obtained were labelled as *c*-Ti-TUD-1.

The synthetic process of amorphous mesoporous Ti-TUD-1 with Si/Ti = 50 was almost the same as the reported procedure.[2]

TS-1 with Si/Ti = 50 was synthesized using the conventional hydrothermal method, in which the mixture sol of precursors was stirred to form a gel, and the as-prepared gel was directly hydrothermally heated at 180 ºC for 24 h.

All the hydrothermal treatments for stability tests were determined in refluxing boiling water at 100 ºC for 48h. For the inherently high hydrothermal stability which has been confirmed, the hydrothermal treatment for stability test wasn't performed on the conventional TS-1 zeolite.

Characterization

Powder XRD patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu Kα radiation (40 kV and 40 mA) with the scanning rate of 4 °min^{-1}.

The N_2 sorption measurements were performed using Micromeritics Tristar 3000 and Micromeritics ASAP 2020 porosimeters at 77 K for mesoporosity and microposity, respectively. The pore specific surface area, pore volume and size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore volume was calculated by the *t*-plot method.

FTIR spectra (Fourier transforming infrared spectroscopy) were obtained in the range of 400–4000 cm^{-1} using a Nicolet 7000-C with a resolution of 8 cm^{-1}.

TEM images were obtained on a JEOL-2010F electron microscope operated at 200 kV. FE-SEM (Field Emission Scanning Electron Microscopy) analysis was performed on a JEOL JSM6700F electron microscope.

UV-Vis spectra were determined by a Shimadzu UV-3600 spectrophotometer using $BaSO_4$ as the reference. The nano TiO_2 used in the test for comparison is bought from Degussa Co., Ltd with average particle size of 25 nm.

The Ti contents analysis of various catalysts were performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Varian Vista AX ICP-AES spectrometer.

Catalytic Reaction

The catalytic reactions were carried out in a three-necked flask equipped a reflux condenser and the conditions were chosen according to the reported procedures[3]. Firstly, 1mmol TMP was dissolved in 10mL acetonitrile (MeCN). Then 0.1 g catalyst was added under continuous stirring. The mixture was stirred for a few minutes at ambient temperature and then the reaction temperature was raised and kept at 80 ºC. After that, 3mmol hydrogen peroxide (H_2O_2, 30% aqueous solution) was added dropwise into the mixture. The stirring with the rotation rate of 250 rpm was held for 3 h and the temperature was kept at 80 ºC all the while in the reaction process. After cooling for a few minutes, the product was centrifugated and the upper solution was collected by a micro-syringe. The samples were analyzed by a GC-MS (Agilent, 6890/5973N). The remained catalyst was filtered off, washed with MeCN for three times and dried at 100 ºC for 4 h. The dried catalyst was reused and then recycled for four times, subsequently. After five cycles, the final remained catalyst was collected for ICP-AES test.

In this communication, we focus on the performance difference among crystallized zeolite, amorphous mesoporous material and mesoporous TS-1 zeolite, especially their catalytic activities and stabilities, and try to reveal the structure reasons for the enhanced catalytic performance of mesoporous TS-1 zeolite. Therein, we don't care about how to improve the catalytic efficiency so the reaction time period chosen in the catalytic process is long enough to ensure the reaction is equivalent and consequently, the turnover frequency (TOF) data calculated in our tests is not meaningful.

References

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3. O.A. Kholdeeva, I. D. Invanchikova, M. Guidotti, N. Ravasio, M. Sgobba, M. V. Barmatova, *Catal. Today*, 2009, **141**, 330.

4. H. Xin, A. Koekkoek, Q. Yang, R. van Santen, C. Li, E. J. M. Hensen, *Chem. Commun.*, 2009, 7590.

Figures

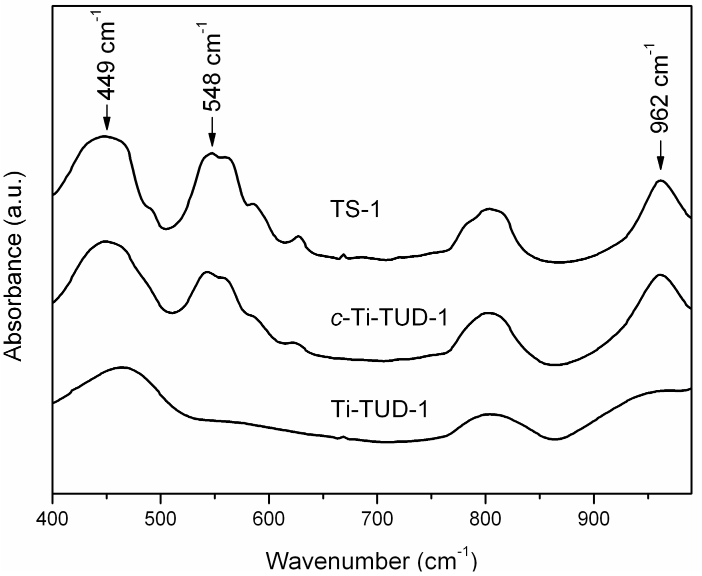

Fig. S1 FTIR spectra of amorphous mesoporous Ti-TUD-1, hierarchically structured *c*-Ti-TUD-1 and conventional TS-1 zeolite (from bottom to top).

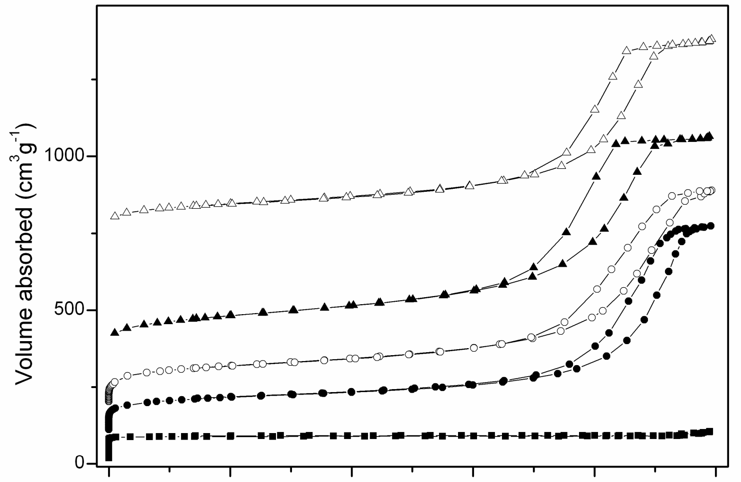

Fig. S2 N_2 sorption isotherms of various materials: (■) conventional TS-1 zeolite, (●) hierarchically structured *c*-Ti-TUD-1 and (○) hydrothermally treated *c*-Ti-TUD-1, (▲) amorphous mesoporous material Ti-TUD-1 and (□) hydrothermally treated Ti-TUD-1. For comparison, isotherms of *c*-Ti-TUD-1 without and with hydrothermal treatments, Ti-TUD-1without and with hydrothermal treatments are offset by 100, 200, 350 and 750 $cm^{-3}g^{-1}$, respectively.

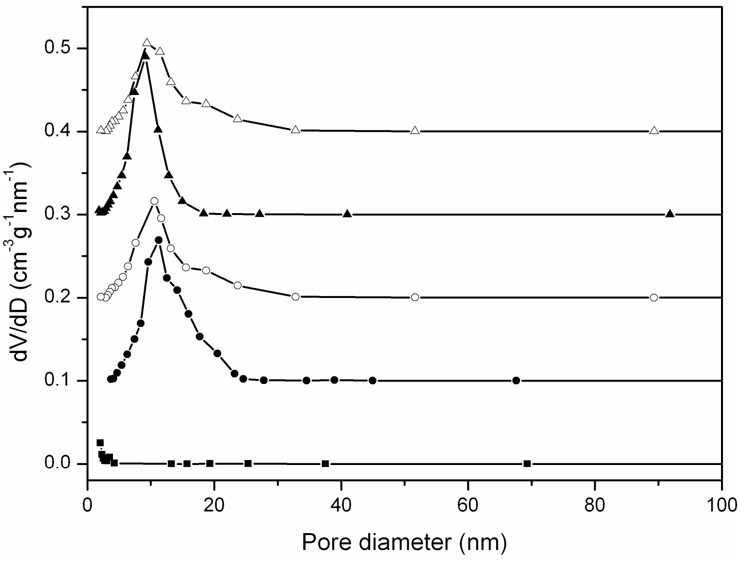

Fig. S3 BJH mesopore size distributions of various materials: (■) conventional TS-1 zeolite, (●) hierarchically structured *c*-Ti-TUD-1 and (○) hydrothermally treated *c*-Ti-TUD-1, (▲) amorphous mesoporous material Ti-TUD-1 and (△) hydrothermally treated Ti-TUD-1.

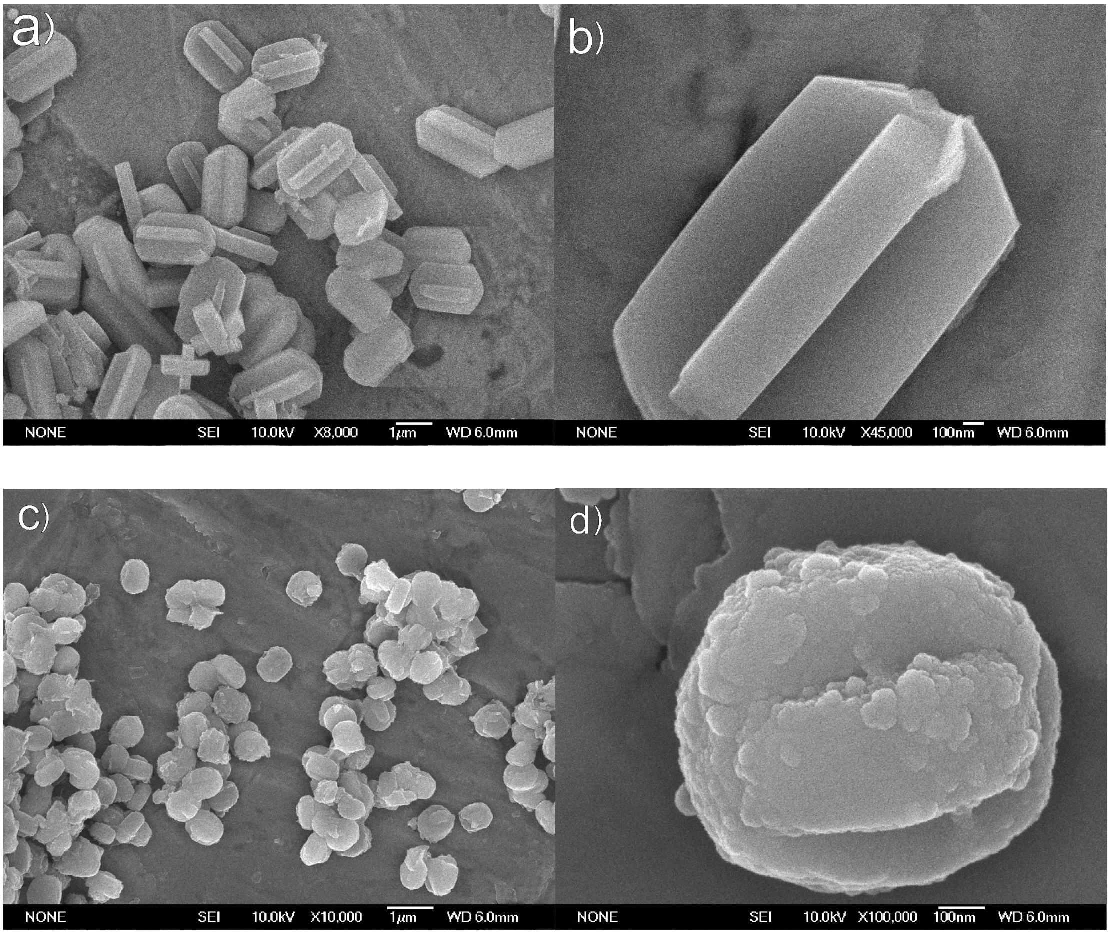

Fig. S4 FE-SEM images of conventional TS-1 zeolite (a, b) and hierarchically structured *c*-Ti-TUD-1 (c, d) at different magnifications.

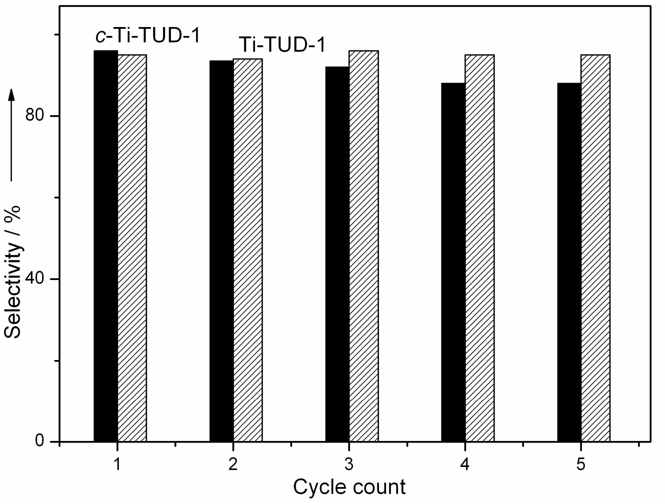

Fig. S5 Selectivities to TMBQ in the selective oxidation of TMP for up to five cycles using amorphous mesoporous Ti-TUD-1 and hierarchically structured *c*-Ti-TUD-1 as catalysts, respectively.

Tables

Table S1. Textural properties of amorphous mesoporous material Ti-TUD-1, hierarchically structured *c*-Ti-TUD-1, conventional TS-1 zeolite and their hydrothermally treated counterparts (Ti-TUD-1(HT) and *c*-Ti-TUD-1 (HT), respectively).

Catalyst	S_{BET} / m^2g^{-1}	S_{micro} / cm^3g^{-1}	D_{meso} / nm	V_{BJH} / cm^3g^{-1}	V_{micro} / cm^3g^{-1}
Ti-TUD-1	445	29	8.5	1.08	0.007
Ti-TUD-1(HT)	349	45	9.6	0.96	0.016
c-Ti-TUD-1	456	97	11.2	1.37	0.049
c-Ti-TUD-1 (HT)	424	103	9.4	1.08	0.045
TS-1	378	196	_	0.17	0.087

Table S2. Structural and catalytic properties of amorphous mesoporous material Ti-TUD-1, hierarchically structured *c*-Ti-TUD-1, conventional TS-1 zeolite.

Catalyst	Ti (wt %)	I_{548}/I_{449}[b]	LWHM[c]	C_{TMP}[d]	S_{TMBQ}[e]
Ti-TUD-1	1.80 (1.51)[a]	_	82	86%	95.0%
c-Ti-TUD-1	1.54 (1.63)[a]	0.57	51	>99%	96.1%
TS-1	1.53(1.55)[a]	0.84	45	<1%	_

[a]: Numbers in the brackets are the Ti contents of the recycled (reused for five times) catalysts; [b]: Ratio of intensities of bands in FTIR spectra was assigned to understand the crystallinity.[4] I_{548} and I_{449} are the intensities of the infrared bands at 548 and 449 cm^{-1} which have been marked in Fig. S2, respectively; [c]: LWHM is the line width at half maximum in the corresponding UV-Vis spectrum; [d]: conversion of TMP; [e]: selectivity for TMBQ in the first cycle.