Support information

Hydrogenated Mesoporous TiO_2-SiO_2 with Increased Moderate Strong Brönsted Acidic Sites for Friedel–Crafts Alkylation Reaction

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Experimental

Synthesis of mTS-x materials: mTS-x (x indicates the Ti/Si mole ratio, x is 0 for m-SiO_2 and ∞ for m-TiO_2) were synthesized by AcHE process. For a typical synthesis of mTS-1.0, 5mmol of $Ti(OBu)_4$ (TBOT), 5mmol $Si(OEt)_4$ (TEOS), 40mmol of HAc, 12mmol of HCl, and 1.6 g of F127 ($EO_{106}PO_{70}EO_{106}$, MW=12600 g/mol) were dissolved in 30mL of ethanol. The mixture was stirred vigorously for 2 h and then transferred into a Petri dish (diameter 125 mm). The ethanol was evaporated at 40 °C with a relative humidity about 40%. After a transparent membrane was formed, the gel was transferred into a 65 °C oven and aged for an additional 24 h. The as-synthesized samples were calcined at 550 °C for 5h in air to obtain final mesoporous products mTS. Non-mesoporous TS materials were synthesized by the similar procedure without using organic templates (F127).

Synthesis of H-mTS-x materials: The hydrogenation is carried out in a quartz tube placed in a tube furnace equipped with a thermocouple and temperature controller. For a typical synthesis of H-mTS-1.0, 0.2g mTS-1.0 material was placed in the quartz tube. The hydrogen was introduced through the quartz tube by a 50 mL/min of Ar stream containing 5 v/v % of hydrogen. The hydrogenation reaction was operated at 550 °C for 12h and then cooled down to room temperature with continuous H_2/Ar gas flow.

Acid-Catalyzed Reaction: The acid catalytic activity of mTS and H-mTS was performed in the F-C reaction of anisole and benzyl alcohol. The reaction was performed using 0.1 g of catalyst, 50 mmol of anisole, and 5 mmol of benzyl alcohol in an oil bath at 153 °C. 50 uL of solution was taken out from the reaction solution every one hour. The solution was centrifuged and mixed with 800 uL of ethanol, to which 50 uL n-decane was added as an internal standard. The concentration of each substrate was analyzed by a gas chromatograph (GC-9790, Fu Li) equipped with a capillary column.

Characterization: The particle size of the titania and silica precursors in the AcHE solution was assessed by Nano-ZS ZEN 3600 (MALVERN Instrument) at 25 °C. SAXRD and WAXRD patterns were recorded on a Bruker D8 diffractometer with Cu KR radiation. Diffuse reflectance UV-Vis spectra (DRUV-vis) were recorded under ambient conditions on a Perkin-Elmer Lambda 14 spectrometer using $BaSO_4$ as a reference; the spectra were plotted using the Kubelka Munk function. Nitrogen adsorption-desorption analysis was carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, samples were out gassed under a vacuum at 300 °C in the port of the adsorption analyzer. Transmission electron microscopy (TEM) images were taken using a JEOL 2010 electron microscope operating at 80 KeV. X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3486.85G; sweep width, 2000.7 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 20.23 mW; conversion time, 30 ms. Infrared measurements were performed on a TENSOR 27 Spectrum One FT-IR spectrometer, with a spectral resolution of 2 cm^{-1}. 11 mg of catalyst was dehydrated in an IR cell for 2h under vacuum prior to pyridine adsorption. Pyridine was introduced to the IR cell at 150 °C, Pyridine adsorption IR spectra of samples were measured at ambient temperature after desorption at 200 °C.

NMR Experiment: The ^{31}P magic-angle spinning nuclear magnetic resonance (^{31}P-MAS-NMR) spectroscopy were collected on a Varian Infinity Plus-400 spectrometer at 9.4 T, equipped with a triple-resonance 5.0 mm probe, with resonance frequencies of 161.9 MHz for ^{31}P. The Pulse widths ($\pi/2$) for ^{31}P was measured to be 10.5 μs, Pulse delay is 10s, Spin rate is set to be 8 kHz. The ^{31}P NMR chemical shift was externally referenced to $(NH_4)_2HPO_4$. Prior to the NMR experiment, each sample was subjected to dehydration treatment at 400 °C for 8 h under vacuum (10^{-5} Pa). After the sample was cooled down to room temperature, a controlled amount of trimethylphosphine (TMP) was introduced by cooling the sample tube with liquid N_2, the physisorbed TMP were removed under vacuum at a temperature of 60 °C for 30 min. Finally, the glass tube was flame sealed. The adsorption procedure of trimethylphosphine oxides (TMPO) was different from that for TMP. Dehydrated samples were mixed with CH_2Cl_2 solution containing 0.1 M TMPO and followed by a 3h ultrasonic treatment, and then solvent was evacuated completely at 433 K for 8 h under vacuum. Finally, the glass tube was flame sealed. Prior to NMR measurements, the samples were transferred into NMR rotors (tightly sealed by a Kel-F cap) under a dry nitrogen atmosphere in a glovebox.

H_2-TPR Experiment: The H_2-TPR (Hydrogen-Temperature Programmed Reduction) analysis was carried out in a quartz tube placed in a tube furnace equipped with a thermocouple and temperature controller. 10mg of mTS-1.0 sample was place in the quartz tube and firstly activated at 300 °C for 1 h in a flow of 30mL/min of N_2 and then cooled down to room temperature naturally prior to the test. After the activation, hydrogen gas was introduced through the quartz tube by a 30 mL/min of N_2 stream containing 5 v/v % of H_2 at room temperature. After the N_2 atmosphere in quartz tube was substituted by the H_2/N_2 stream totally at room temperature, the temperature rose from 65 °C to 930 °C at a ramp rate of 20 °C/min.

Pulse H_2-titration Experiment: Pulse H_2-titration experiment was performed to quantify the amount of reduced Ti species in H-mTS-1.0. H_2 consumption profiles were recorded on a homemade apparatus. The fresh mTS-1.0 was placed in a quartz tube and treated at 550 °C with Ar flow (25 ml/min) for 120 min and cooled down to room temperature before the measurement. The pulse H_2-titration was started by repeatedly inject H_2/Ar pulse (1.0 ml, 5 v/v%) with a ramping rate of 5 °C/min to a final temperature stage at 550 °C. Hydrogen consumption of every pulse was monitored by GC-TCD. The total amount of H_2 was then calculated by summing up the proportions of all pulses consumed. The calculated result shows that 35.0% Ti^{4+} atoms in mTS-1.0 were reduced.

Figure S1. Size evolution of individual titania, silica and titania-silica precursor solution in AcHE system as monitored by time-resolved dynamic light scattering (DLS).

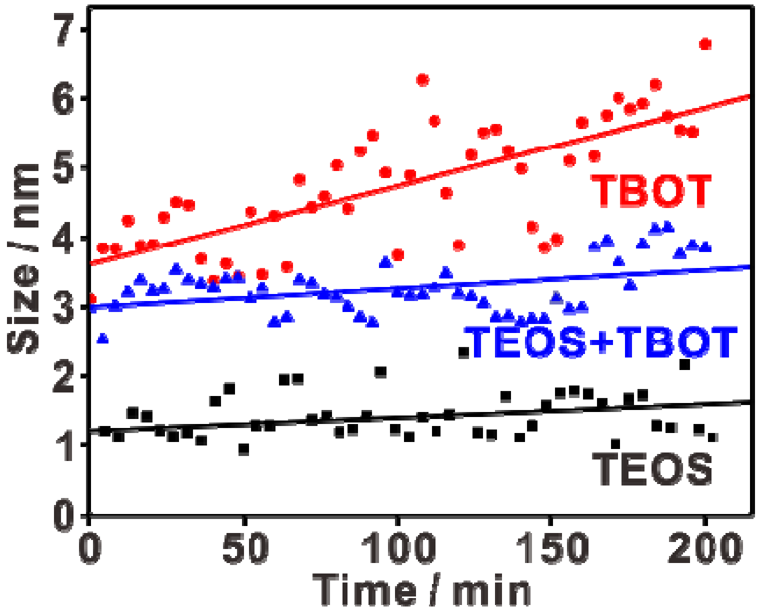

Figure S2. WAXRD patterns of mTS-1.0, H-mTS-1.0 and m-TiO_2.

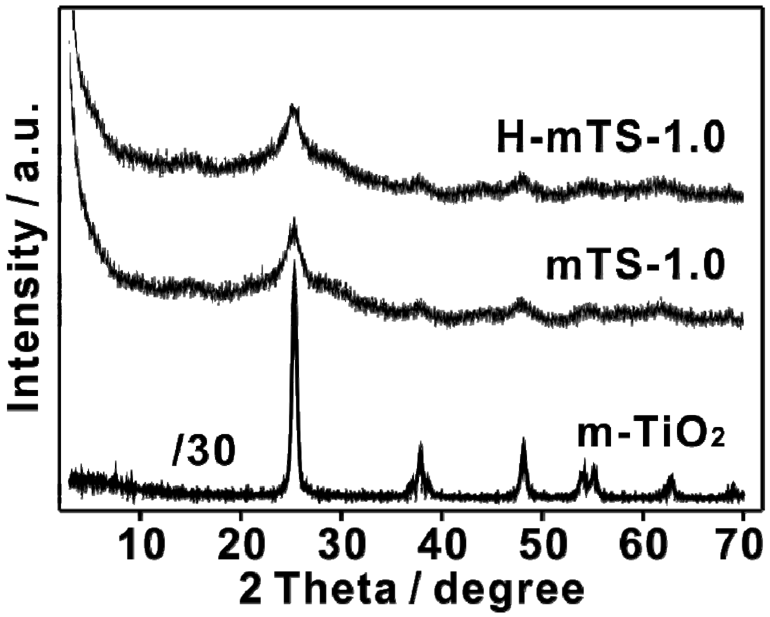

Figure S3. (a) N_2 adsorption-desorption curve of mTS-1.0 and H-mTS-1.0; (b) Pore size distribution of mTS-1.0 and H-mTS-1.0 calculated by BJH model.

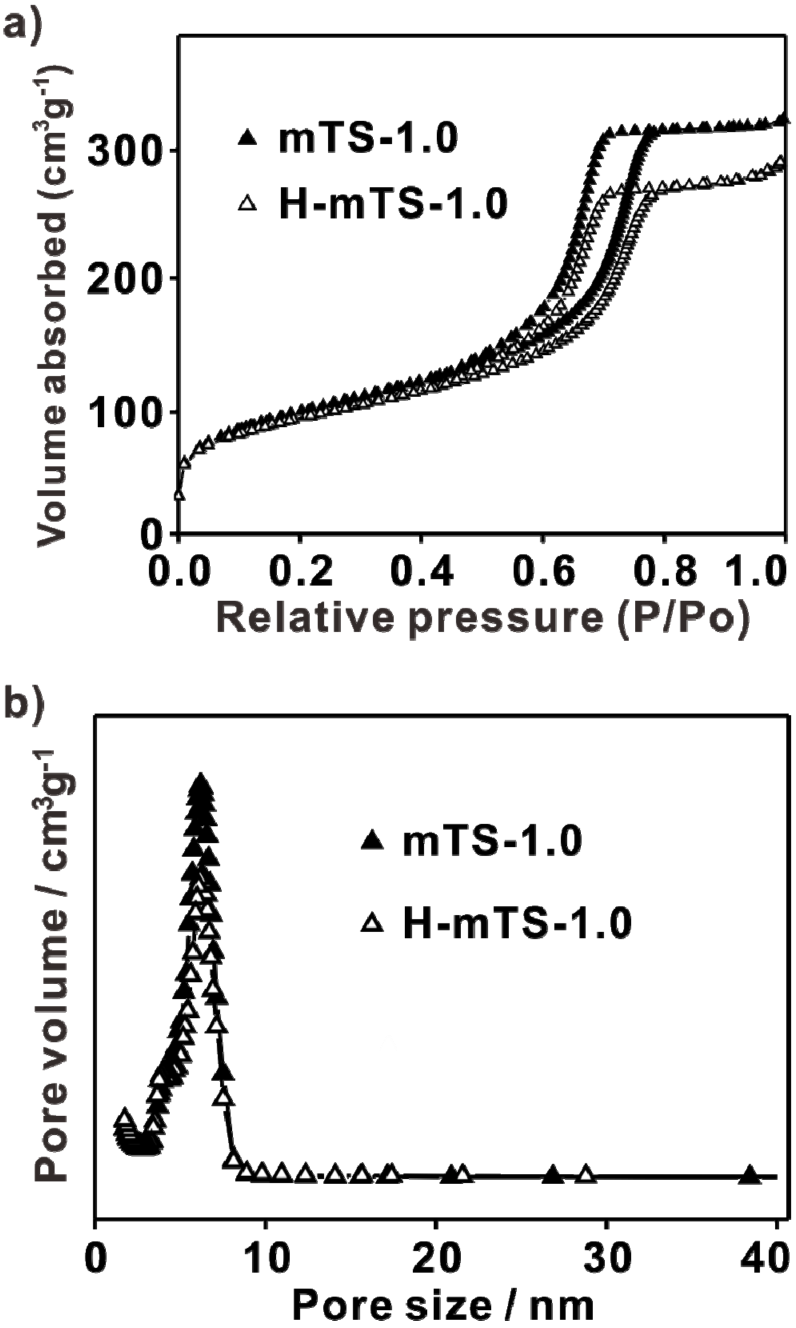

Figure S4. H_2-TPR profile of mTS-1.0.

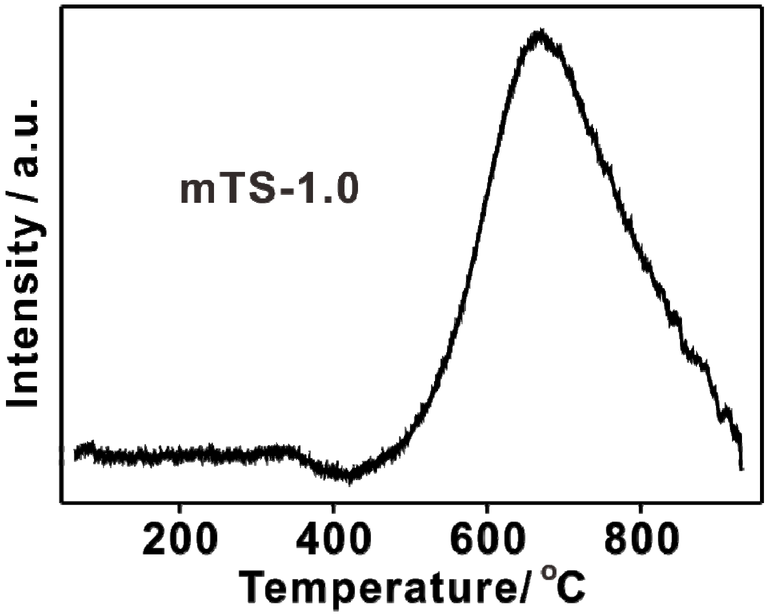

Figure S5. FTIR spectra of mTS-1 and H-mTS-1 adsorbed pyridine.

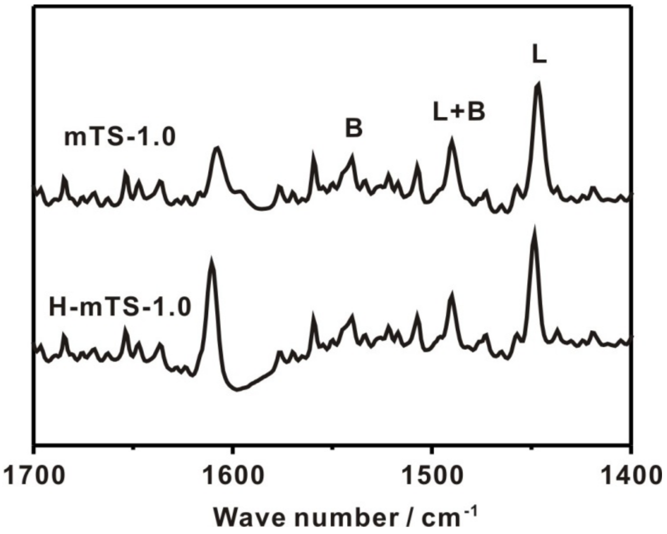

Figure S6. The BA conversion (3h) as the function of different reaction temperature when using mTS-1.0 and H-mTS-1.0 as the catalysts.

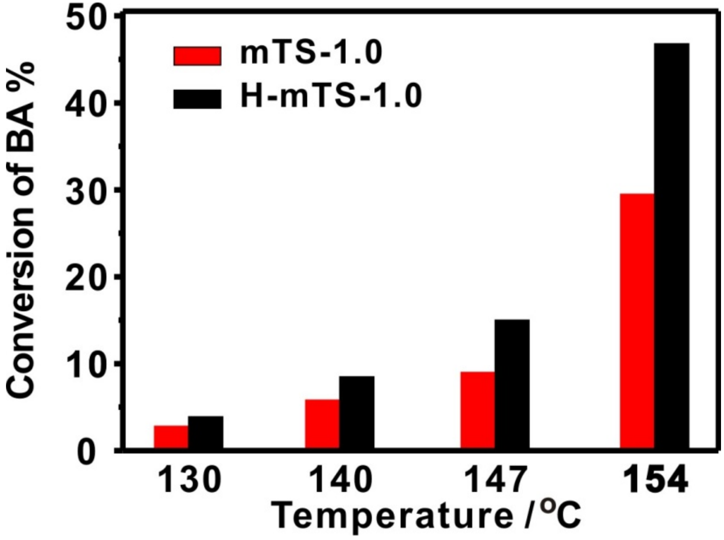

Figure S7. DRUV absorbance spectra of m-SiO_2, m-TiO_2 and mTS with different Ti/Si molar ratio.

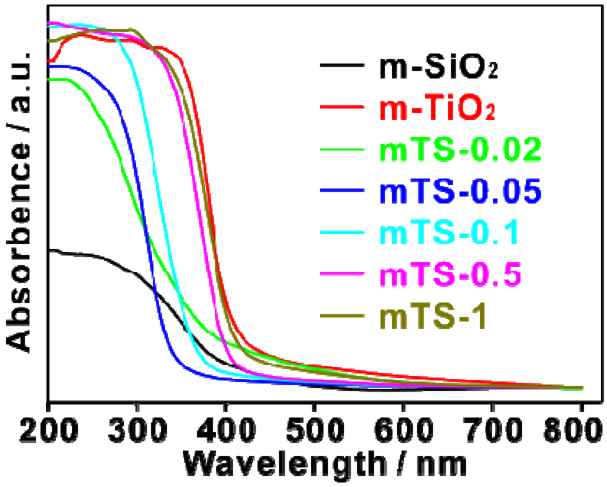

Figure S8. Charge difference in Ti(III)O_2-SiO_2 and Ti(IV)O_2-SiO_2 mixed metal oxides according to Tanabe model.