Electronic Supplementary Information

Uniform Core-Shell Titanium Phosphate Nanospheres with Orderly Open Nanopores: a High Active Brönsted Acid Catalyst

Jiehua Liu,[┤] Xiangfeng Wei,[┤] Yaolun Yu,[├]Junling Song,[┤] Xin Wang,[├] An Li,[┤] Xue-Wei Liu,[┤]* and Weiqiao Deng[┼]*

[┤]*School of Physical & Mathematical Sciences, Nanyang Technological University, 637371, Singapore.*

[├]*School of Chemical and Biomedical Engineering, Nanyang Technological University, 639798, Singapore.*

[┼]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

E-mail: WQDeng@ntu.edu.sg; xuewei@ntu.edu.sg.

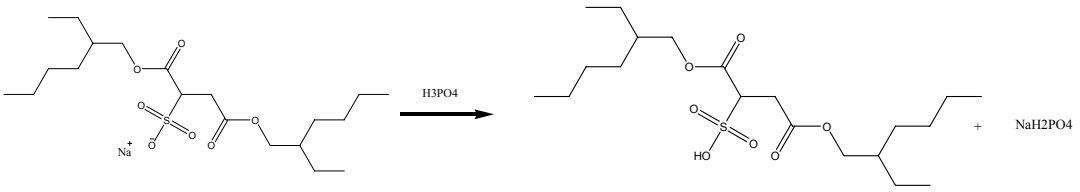
Experiments

Stating materials

Orthophosphoric acid (85%) and titanium (IV) n-butoxide was purchased from Alfa Aesar. Docusate sodium salt and ethanol were supplied by Sigma-Adrich.

Synthesis procedure

In a typical experiment, Docusate sodium salt (AOT, 5 g) was first added and dissolved into 25 g ethanol to prepare AOT/ethanol solution. Then phosphoric acid (10g) was added to get a turbid solution and was still for 2 hours to produce white NaH_2PO_4 precipitate because of the restriction of its solubility in the ethanol solution After the precipitate removed, 1.75 g tetrabutyl titanate in 25g anhydrous ethanol solution was fast dropped into the AOT/ethanol solution to get a stable mixture solution with aid of ultrasonic. The mixture was then placed in an oven at 80°C for 5-24h. The solid product was separated by centrifugation and was washed several times with ethanol to remove residual phosphoric acid and surfactant and then dried at 80 °C for 10 hrs.



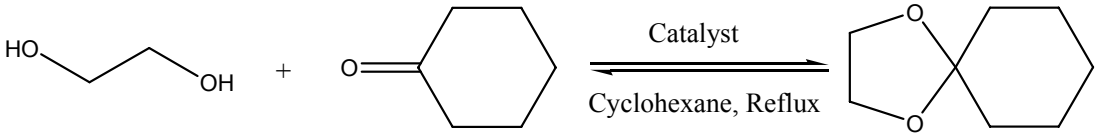
Scheme 1: Acidification of docusate sodium salt.

Characterization

XRD patterns were performed with a Rigaku D/max-2500 diffractometer with Cu-KR radiation (λ=1.54056Å). Field emission scanning electron microscopy (FESEM) image and Transmission electron micrographs (TEMs) were obtained with JEOL JSM 6700F and JEOL JEM-1400 respectively. BET N_2 adsorption-desorption isotherms were conducted at 77 K on a Micromeritics Tristar 3000 analyzer. The BET surface areas and pore-size distribution curves were concluded

using adsorption data. Thermogravimetric analysis was determined using a thermal gravity analyzer (TGA) at an increasing temperature rate of 10°C min^{-1} from 80 to 1000°C under a continuous nitrogen gas flow. Infrared (IR) spectrum was recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer. For ^{31}P Cross Polarization/ Magic-Angle Spinning (CP/MAS) and ^{1}H MAS NMR measurements, a JNM-ECA400 spectrometer was used at 161.73 and 400 MHz respectively. The chemical shifts on ^{31}P NMR were referenced to $NH_4H_2PO_4$.

Catalytic reaction



Scheme S2: Ketalization of cyclohexanone and 1,2-ethanediol to cyclohexanone ethylene ketal.

The ketalization reaction is shown in Scheme S2. The apparatus and procedures for the reaction were similar to that reported in reference [S1]. In a typical experiment, cyclohexanone (100mmol, 2000 equiv), 1,2-ethanediol (100 mmol, 2000 equiv), TiP catalyst (0.012 g (ca. 0.05mmol), based on Ti (1 equiv)) and cyclohexane (30 cm^3) were charged into a round-bottomed flask fitted with a Dean–Stark apparatus to remove the water continuously from the reaction mixture. The progress of the reaction was monitored by GC analysis of small aliquots withdrawn at 30-min intervals. GC analysis was performed on an Agilent 6879N instrument. The structure of the product was confirmed by ^{1}H NMR spectroscopy.

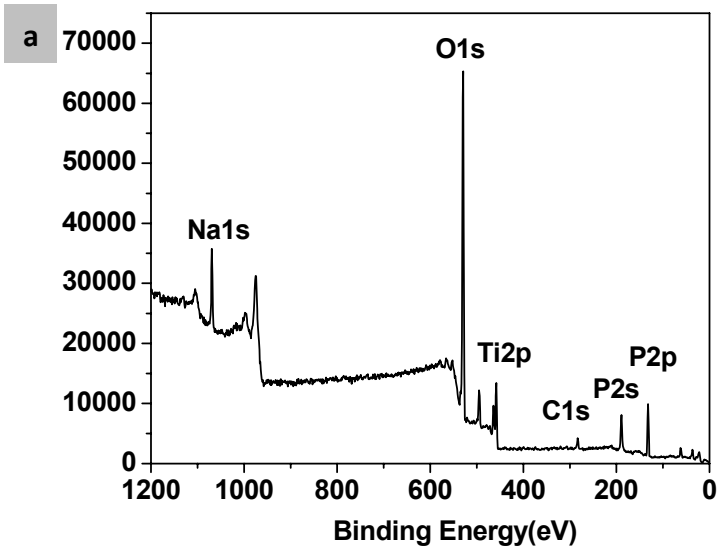


Figure S1a. XPS spectra of the TiP sample annealed at 400 °C

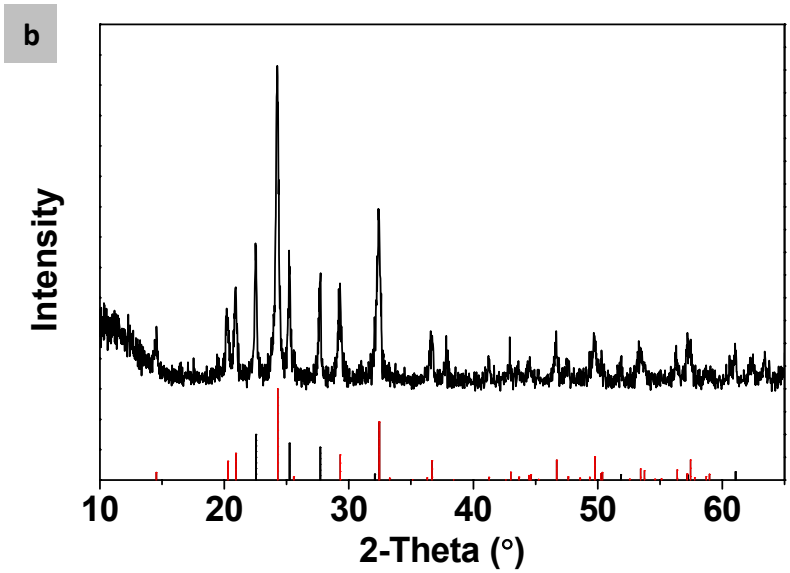


Figure S1b. XRD pattern of TiP material after calcination at 600 °C.

Red and black vertical lines are relative to $NaTi_2(PO_4)_3$ (JPCDS No.33-1296) and TiP_2O_7 (JPCDS No.38-1468) respectively.

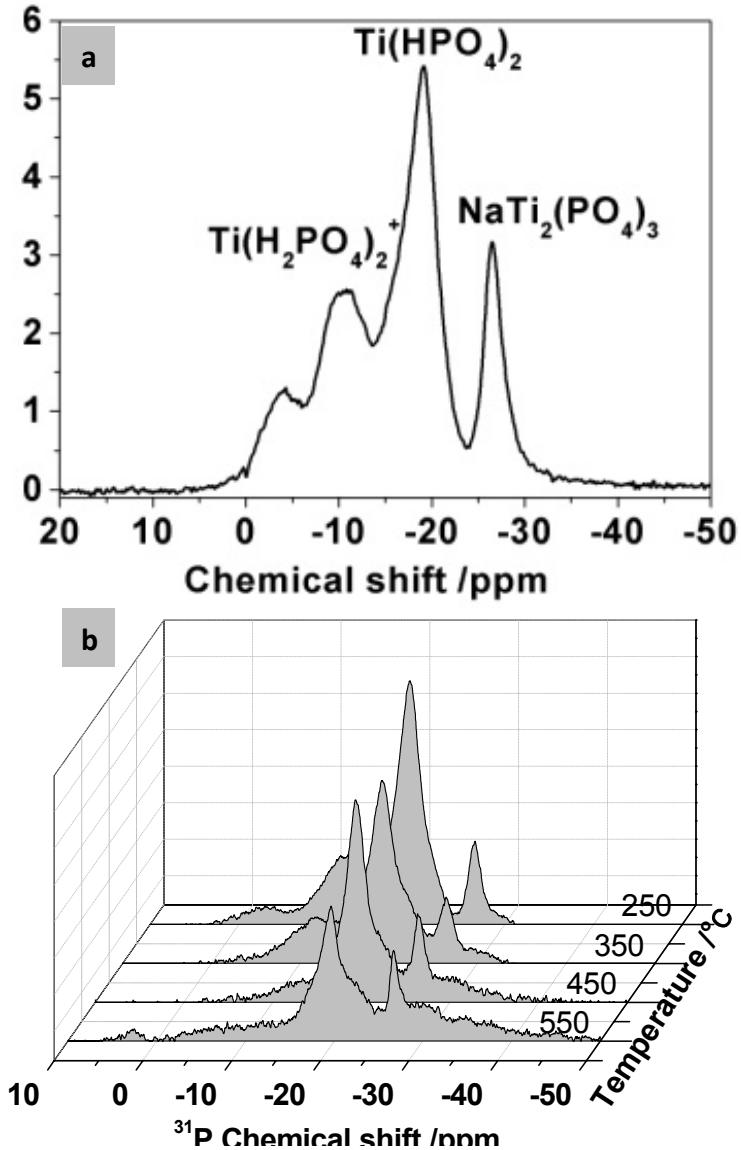


Figure S2. ^{31}P CPMAS NMR spectra calcined at 100 (a) and, 250, 350, 450 and 550 °C (b), respectively.

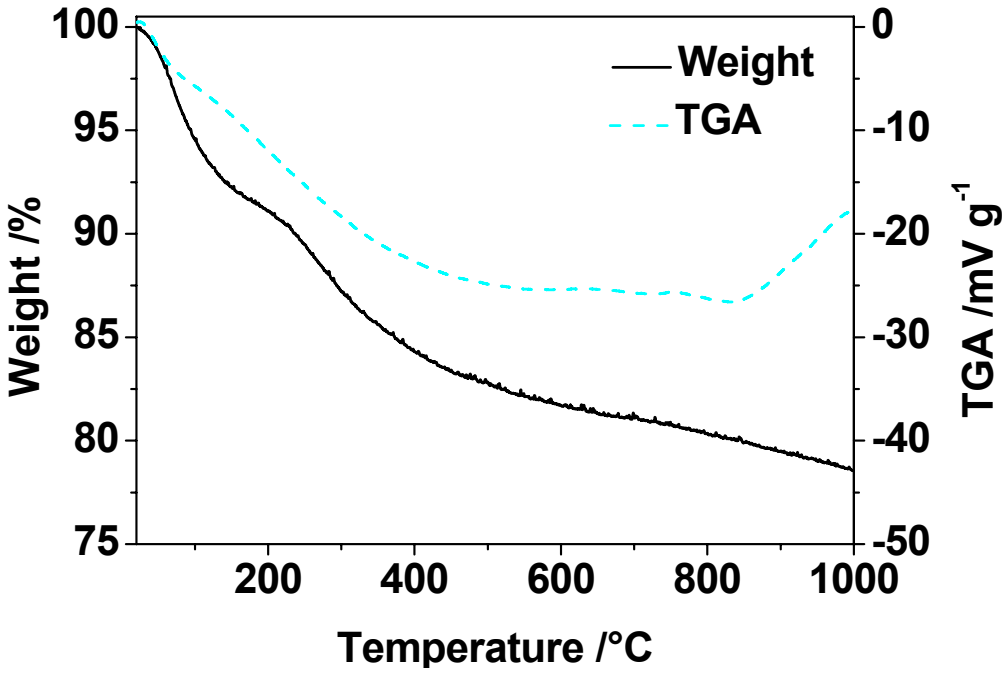


Figure S3：TGA and DTA curves of TiP material

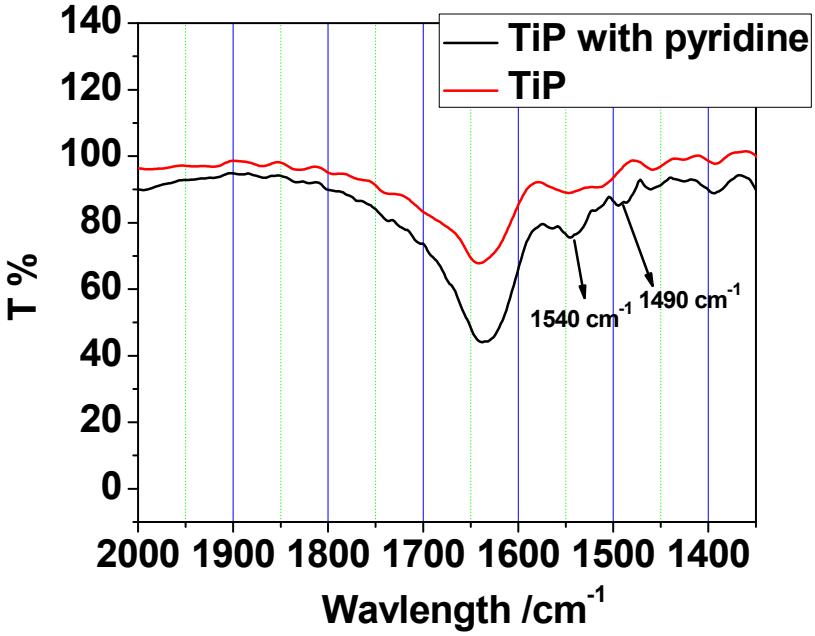


Figure S4. FTIR spectra of TiP calcined at 400 °C (red line) and the sample with pyridine annealed at 250°C (black line) respectively

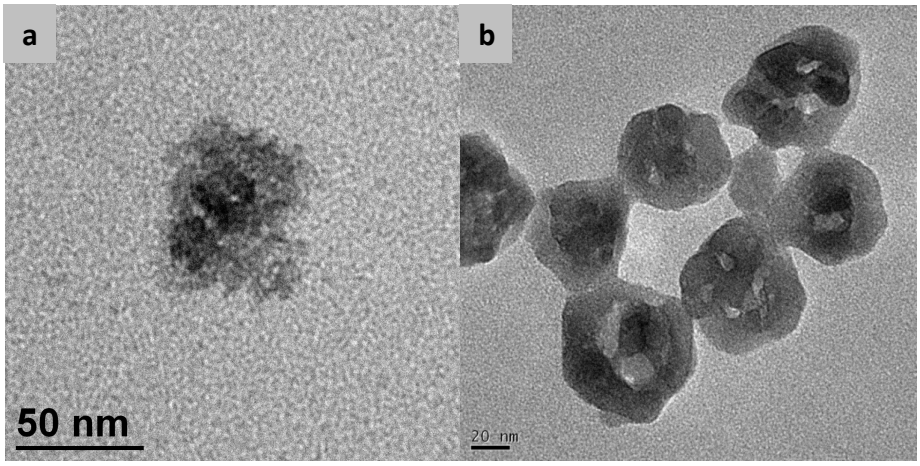


Figure S5. TEM images of product separated the sample from the solution with faint turbidity at the early stage (a) and TiP sample after calcination at 600 °C (b)

a) b)

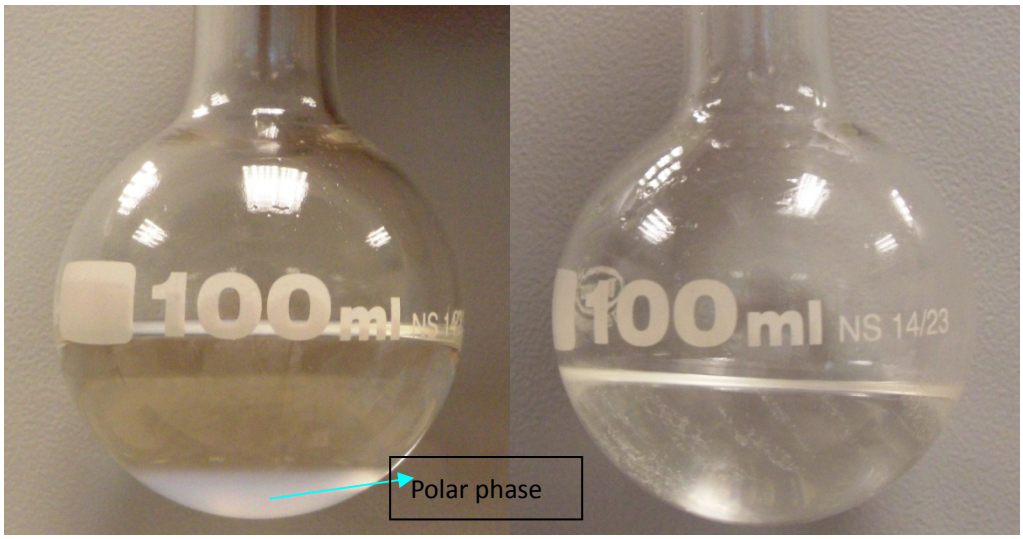


Figure S6. The phase behavior of ketalization of cyclohexanone and 1,2-ethanediol to cyclohexanone system at the very beginning of reaction (a) and the end of reaction (b).

Reference

(S1) Patel, S. M.; Chudasama, U. V.; Ganeshpure, P. A. *Journal of Molecular Catalysis a-Chemical* **2003**, *194*, 267-271.