

Supplementary Information:

Increasing the H⁺ exchange capacity of porous titanium phosphonate materials by protecting defective P–OH groups

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Experimental Section

Materials. Tetrabutyl titanate was obtained from Tianjin Kermel Chemical Co. Diethylenetriamine penta(methylene phosphonic acid) (DTPMPA) was received from Henan Qingyuan Chemical Co. Acetone, methanol, n-propylamine, n-butylamine and n-pentylamine were provided by Tianjin Hongfengke industrial & trading Co., Ltd. Commercial acidic resin NKC-9 was obtained from Nankai University Chemical Plant. D-ribose was provided by Xinxiang Tuoxin Biochemical Science & Technology Co., Ltd. All chemicals were used as received without further purification.

Synthesis of hierarchically macro-/mesoporous titanium phosphonate materials. In a typical synthesis procedure, 0.005 mol of DTPMPA was added into a mixed solution of 30 ml water and 10 ml ethanol in the presence of n-propylamine, n-butylamine and n-pentylamine with different concentrations (alkyl amine/DTPMPA molar ratio of 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) to form a homogenous solution, followed by stirring for 30 min. Tetrabutyl titanate (P/Ti molar ratio ranging from 0.6 to 4.0) was dropwise added into the obtained solution very slow, followed by stirring for another 24 h

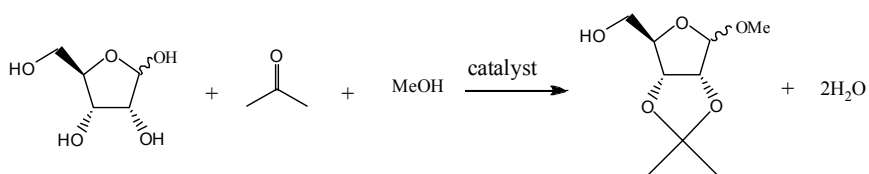
at room temperature. The resultant mixture was filtered, dried, and extracted by hydrochloric acid (pH =1) for three times at 70 °C to remove the alkyl amines, and then washed with water repeatedly. Titanium phosphonate materials synthesized with added P/Ti ratio of 2.5 and n-butylamine/DTPMPA ratio of 0.3 were chosen for detailed discussions, marked as TiPPh-butylamine. Titanium phosphonate materials synthesized without amines and titanium phosphate materials synthesized with n-butylamine were marked as TiPPh-non and TiP-butylamine, respectively, for comparison.

Characterization. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out on a Shimadzu SS-550 microscope at 15 keV and a Philips Tecnai G20 at 200 kV, respectively. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VECTOR 22 spectrometer with KBr pellet technique, and the ranges of spectrograms were 4000 to 400 cm^{-1} . X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with $\text{CuK}\alpha$ radiation operated at 40 kV and 100 mA. The chemical compositions of Ti and P were analyzed by inductively coupled plasma (ICP) emission spectroscopy on a Thermo Jarrell-Ash ICP-9000 (N+M) spectrometer. Solid-state ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurement was performed on a Varian Unity plus-400 spectrometer at spinning rate of 12 kHz and resonance frequency of 161.9 MHz with recycle time of 5 s. N_2 adsorption-desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 150 °C overnight prior to the measurement. The surface areas were calculated by the multi-point Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated from the adsorption branch of the isotherms by the Barret-Joyner-Halenda (BJH) model.

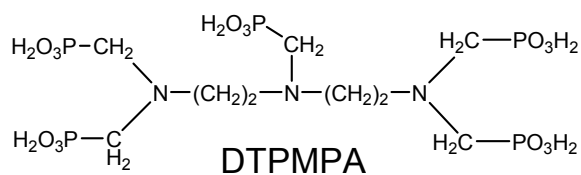
Determination of H^+ exchange capacity. The ion exchange capacity was determined from the titration curve according to the literatures [S. Inagaki, et al. *Nature*, 2002, 416, 304; T. Y. Ma, et al. *Chem. Commun.*, 2010, 46, 2325.]. The obtained titanium phosphonate material (50 mg) was immersed in 10 wt.% sodium chloride aqueous solution for 24 hours to fully exchange the H^+ ions. The solution was

titrated with NaOH solution (0.05 mol/L) to produce the titration curve. Differential titration curve was drawn to determine the ion exchange capacity of titanium phosphonates at the inflexion.

Catalytic activity test. The synthesized titanium phosphonate materials were used as the acid catalyst in the synthesis of methyl-2,3-*O*-isopropylidene- β -D-ribofuranoside from D-ribose. 1.5 g of D-ribose was first dissolved into the mixed solution of acetone (6 ml) and methanol (6 ml), and then 0.5 g of the obtained catalyst was added. After the reaction was refluxed at 70 °C for 3 h, the mixture was cooled and filtrated to separate the solid catalysts and the residues. For concentrated HCl (conc. HCl, 37.5 wt.%) catalytic reaction, the filtrate was neutralized (pH 6–7) with NaHCO₃ solution. The resulting solution was once again filtered through a Celite bed and evaporated to remove acetone and methanol. The organic layer thus obtained was extracted with ethyl ether (3×10 ml), washed with brine, dried by anhydrous Na₂SO₄ and evaporated in vacuo to yield methyl-2,3-*O*-isopropylidene- β -D-ribofuranoside according to the reference [P. Sairam, et al. *Carbohydr. Res.*, 2003, 338, 303.]. The products were characterized by ¹H NMR (400M, CDCl₃): 4.91 (s, 1 H), 4.78 (d, 1 H, *J* = 6 Hz), 4.53 (d, 1 H, *J* = 6 Hz), 4.37 (m, 1 H), 3.61 (m, 2 H), 3.56 (s, 3 H), 3.37 (m, 1 H), 1.42 (s, 3 H), 1.25 (s, 3 H); ¹³C NMR (300 MHz, CDCl₃): 112.0, 109.6, 87.9, 85.5, 81.4, 63.6, 55.1, 26.2, 24.6, which was in agreement with those reported in the literature [P. Sairam, et al. *Carbohydr. Res.*, 2003, 338, 303; A. K. Gosh, et al. *J. Org. Chem.*, 1996, 61, 6175.]. Performances of various catalysts were evaluated in terms of the percentage of product yields, which is defined as follows: Product yield (%) = [Actual moles of product formed] / [Expected moles of product formed based on D-ribose consumed] × 100%. The formation reaction of methyl-2,3-*O*-isopropylidene- β -D-ribofuranoside from D-ribose was expressed in Scheme S1.



Scheme S1



Scheme S2 Structure of the phosphonic acid DTPMPA.

Table S1 Hammett acidities of the synthesized catalysts.

Hammett indicators	TiPPh-butylamine	TiPPh-non	TiP-butylamine	PMTP-1	NKC-9
Anthraquinone (pK _a = -8.20)	+	-	+	-	+
<i>p</i> -nitrotoluene (pK _a = -11.35)	-	-	-	-	+
<i>p</i> -nitrochlorobenzene (pK _a = -12.70)	-	-	-	-	-
2,4-dinitrotoluene (pK _a = -13.75)	-	-	-	-	-

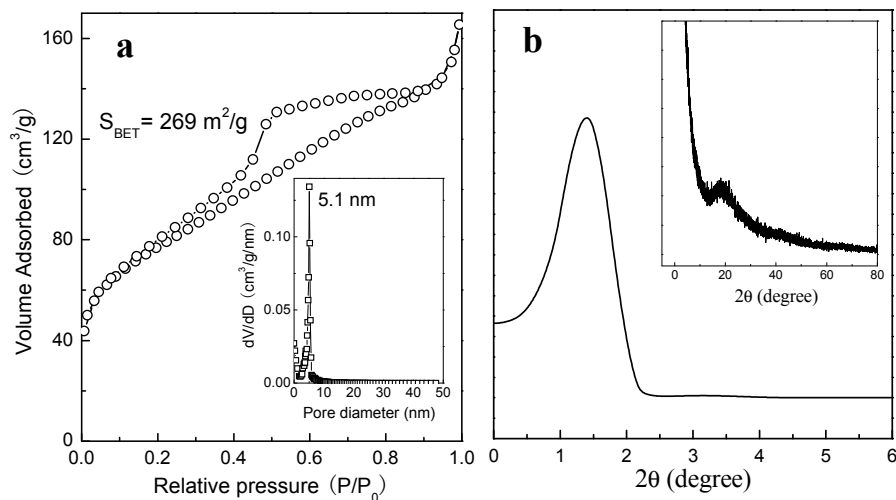


Fig. S1 (a) N₂ sorption isotherms and (*inset*) the corresponding pore size distribution curve calculated by BJH method, and (b) small and wide (*inset*) angle XRD patterns of TiPPh-amine and TiPPh-non.

The N₂ sorption isotherm of TiPPh-butylamine is of type IV with a hysteresis loop of type H2 (Fig. S1a), characteristic of mesoporous materials according to the IUPAC classification. An increase in the volume of nitrogen adsorbed at high relative pressure ($P/P_0 > 0.9$) can be observed on the isotherm, indicating an appreciable amount of macroporosity [M. Kruk, M. Jaroniec, *Chem. Mater.* **2001**, *13*, 3169.], as observed in the SEM images. The surface area is 269 m²/g with pore volume of 0.22 cm³/g. The pore size distribution, obtained from the adsorption branch of the isotherms by the BJH method (Fig. S1a *inset*), presents one narrow peak at 5.1 nm, which is consistent to TEM observation. The synthesized TiPPh-amine sample possesses amorphous framework walls, as revealed by wide angle XRD pattern (Fig. S1b *inset*). One single and broad diffraction peak is present in the low-angle region (Fig. S1b), suggestive of the wormhole-like mesopores without long-range order [X. Wang, J.C. Yu, et al., *Langmuir* **2005**, *21*, 2552.].

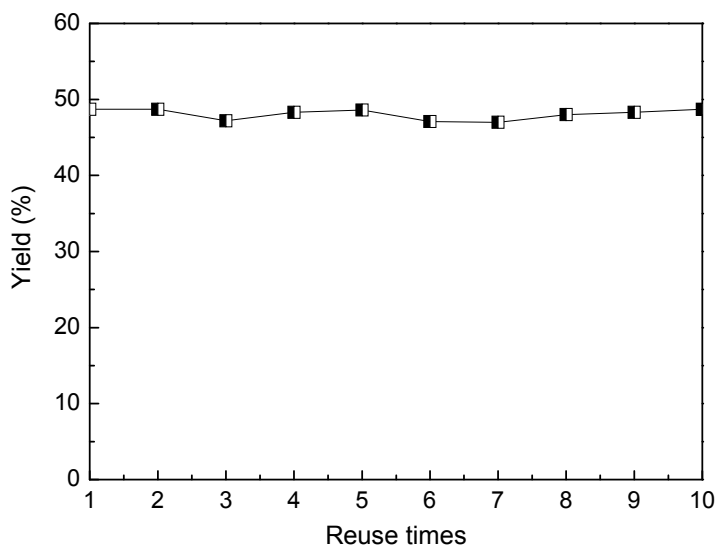


Fig. S2 Catalytic recycle study of the TiPPh-butylamine material.

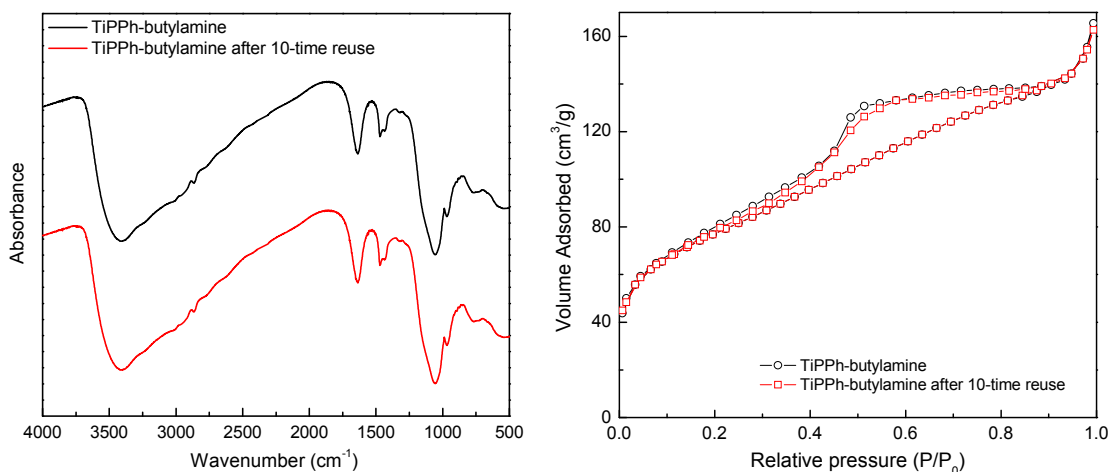


Fig. S3 FT-IR (*left*) and N₂ sorption (*right*) measurements of TiPPh-butylamine catalyst before and after 10-time reuse.

The recyclability of TiPPh-butylamine was examined by isolating it from the reaction mixture (centrifugation, washing with acetone and drying). After 10-time reuse, the product yield was hardly decreased (Fig. S2). The FT-IR and N₂ sorption measurements were also performed, showing no obvious changes compared with that of the fresh TiPPh-butylamine catalyst, which confirmed the good retention of organic groups within the hybrid framework and the porous structure (Fig. S3).