Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Supplemental Materials:

Depolymerization of Crystalline Cellulose Catalyzed by Acidic Ionic Liquids Grafted on Sponge-Like Nanoporous Polymers

Fujian Liu [a,b], Ranjan K. Kamat [b], Iman Noshadi [b], Daniel Peck [c], Richard S. Parnas [b], Anmin Zheng [d], Chenze Qi [a,*] and Yao Lin [b,c,*]

[a] Key Laboratory of Alternative Technologies for Fine Chemicals Process of Zhejiang Province, Department of Chemistry, Shaoxing University, Shaoxing, 312000, People's Republic of China.

[b] Polymer Program, Institute of Materials Science.

[c] Department of Chemistry, University of Connecticut, Storrs, CT, 06269, United States.

[d] Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

Experimental details

Chemicals and reagents. All reagents were of analytical grade and used as purchased without further purification. Divinylbenzene (DVB), 1-*n*-butyl-3-methylimidazolium ([C_4mim]Cl), 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac), 1-vinylimidazolate (vim), Amberlyst 15, sodium *p*-styrene sulfonate, nonionic block copolymer surfactant poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) block copolymer (Pluronic 123, molecular weight of about 5800) and Avicel cellulose were purchased from Sigma-Aldrich Co. Azobisisobutyronitrile (AIBN), THF, 1,3-propanesultone, HSO_3CF_3, H_2SO_4, HCl, toluene and CH_2Cl_2 were obtained from Beijing Chemical Agents Company.

Characterization methods. Nitrogen isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 150 °C before the measurements. The pore-size distribution was calculated using Barrett-Joyner-Halenda (BJH) model. FTIR spectra were collected by using a Bruker 66V FTIR spectrometer. X-ray powder diffraction (XRD) of samples was recorded on a Rigaku D/max2550 PC powder diffractometer using nickel-filtered CuKα radiation in the range of $10° \leq 2\theta \leq 35°$. SEM images were performed on JEOL 6335F field emission scanning electron microscope (FESEM) attached with a Thermo Noran EDX detector. Transmission electron microscopy (TEM) images were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV.

CHNS elemental analysis was performed on a Perkin-Elmer series II CHNS analyzer 2400. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα radition at y=901 for the X-ray sources, the binding energies were calibrated using the C1s peak at 284.9 eV.

The solid ^{31}P NMR spectrum over PDVB-SO_3H-[C_3vim][SO_3CF_3] catalyst was performed as follows: prior to trimethylphosphine (TMP) sorption of probe molecules, the sample was placed in a glass tube and then connected to a vacuum line for dehydration. The sample was kept at final temperature of 393 K with the pressure below 10^{-3} Pa over a period of 24 h and then cooled. After TMP sorption, the sealed sample tube was opened and the sample was transferred into a NMR rotor with a Kel-F end cap under a dry nitrogen atmosphere in a glove box.

All ^{31}P NMR experiments were performed on a Bruker Ascend-500 spectrometer at a resonance frequency of 202.34 MHz with a 4 mm triple-resonance MAS probe at a sample spinning rate of 12.5 kHz. Pulse width ($\pi/2$) for ^{31}P was measured to be 4.5 μs. ^{31}P MAS NMR spectra were recorded with a recycle delay of 30 s. The chemical shifts for the ^{31}P resonance were referred to 1M aqueous H_3PO_4.

Synthesis of functional nanoporous polymers (PDVB-SO_3Na-vim). 1-vinylimidazolate (vim) and sodium *p*-styrene sulfonate functionalized nanoporous polymer (PDVB-vim) was hydrothermally synthesized by copolymerization of DVB with vim and sodium *p*-styrene sulfonate in the starting mixture of DVB/vim/sodium *p*-styrene sulfonate/AIBN/THF/H_2O at molar ratios of 1/0.5/0.2/0.027/24.1/10.8. In a typical synthesis of PDVB-vim, 2.0 g of DVB, 0.483 g of vim and 0.56 g of sodium *p*-styrene sulfonate were added into a solution containing 0.07 g of AIBN and 30 mL of THF and 3 mL of water. After stirring at room temperature for 3 h, the mixture was hydrothermally treated at 100 °C for 24 h, followed by slow evaporation of the solvent at room temperature for 2 days. The product (PDVB-SO_3Na-vim) shows monolith morphology.

Synthesis of ionic liquids and sulfonic group functionalized nanoporous polymers (PDVB-SO3H-[C3vim][X]). PDVB-SO_3H-[C_3vim][SO_3CF_3], PDVB-SO_3H-[C_3vim][SO_4H] or PDVB-SO_3H-[C_3vim][Cl] (C_3 stands for quaternary ammoniation reagent of 1,3-propanesultone) were synthesized by quaternary ammoniation of PDVB-SO_3Na-vim with 1,3-propanesultone, followed by ion exchanging with HSO_3CF_3, H_2SO_4 or HCl, respectively. In the synthesis of PDVB-SO_3H-[C_3vim][SO_3CF_3], 1.0 g of PDVB-SO_3Na-vim was added into 25 mL of toluene under vigorous stirring, followed by addition of 0.25 g of 1,3-propanesultone. After reacting at 100 °C for 12 h, the product was collected by filtration, washing with a large amount of ethanol and drying at 60 °C. The polymer was then treated with HSO_3CF_3 in toluene solvent for 24 h at room temperature, washed with large amount of CH_2Cl_2 and dried at 80 °C for 8 h, to obtain the final product of PDVB-SO_3H-[C_3vim][SO_3CF_3]. PDVB-SO_3H and PDVB-[C_3vim][SO_3CF_3] [S1, S2] were prepared in a similar way for comparison.

Synthesis of homogeneous ionic liquids ([C_3vim][SO_3CF_3]). 2.0 g of vim monomer was added to 20 mL of toluene under vigorous stirring, followed by addition of 0.4 g of 1,3-propanesultone. The reaction was kept at 50 °C for 48 h, to give [C_3vim]. [C_3vim] was then treated by 3-5 mL HSO_3CF_3 in toluene for 24 h, followed by washing with a large amount of CH_2Cl_2. The process was repeated for two times to give [C_3vim][SO_3CF_3].

Preparation of DNS Reagent. 182 g of potassium sodium tartrate was added into 500 mL of hot deionized water at 50 °C, followed by addition of 6.3 g of 3, 5-dinitrosalicylic acid (DNS) and 262 mL of 2 M NaOH. 5 g of phenol and 5 g of sodium sulfite were then introduced into the solution under vigorous stirring to obtain homogeneous solution. The solution was cooled to room temperature and diluted with deionized water to 1000 mL to give the DNS reagent.

Depolymerization of Avicel cellulose. 100 mg of Avicel cellulose was dissolved into 2.0 g of [C_4mim]Cl ionic liquid at 100 °C for 1 h under vigorous stirring, until a clear solution was obtained. 20 mg of specific catalyst was added, and 600 μL of water was slowly introduced into the reaction mixture and the reaction temperature was kept at 100 °C. At different time intervals, samples were withdrawn, weighed (recorded as M_1), quenched immediately with cold water, and centrifuged at 14,800 rpm for 5 min for removing of catalysts and unreacted cellulose, to give the reaction mixtures for subsequent analysis, the volume was measured and recorded as V_1.[S3] Unreacted

Avicel was separated, washed and weighted. The contents of mineral acids of H_2SO_4 and HCl used for depolymerization of Avicel cellulose were the same number of catalytic site (H^+) as that in PDVB-SO_3H-[C_3vim][SO_3CF_3].

Depolymerization of Gracilaria. 50 mg of *Gracilaria* was dissolved into 3.0 g of [EMIM]Ac ionic liquid at 110 °C for 12 h under vigorous stirring until a clear solution was obtained, followed by addition of 30 mg of catalysts. 600 μL of water was slowly introduced into the reaction mixture and the reaction temperature was kept at 110 °C. At different time intervals, samples were withdrawn, weighed, quenched immediately with cold water, and centrifuged at 14,800 rpm for 5 min for removing of catalysts and unreacted *Gracilaria*, to give the reaction mixture for subsequent analysis. Unreacted *Gracilaria* was separated, washed and weighted. The content of HCl used for depolymerization of *Gracilaria* cellulose was the same number of catalytic sites (H^+) as that in PDVB-SO_3H-[C_3vim][SO_3CF_3].

Total Reducing Sugar (TRS) tests. TRS was measured by DNS method [S3, S4]. 0.5 mL of DNS regent was added into 0.5 mL of the reaction solution and heated at 100 °C for 5 min. The mixture was then cooled to room temperature, and 4 mL of deionized water was added to dilute the solution. The adsorption at 540 nm was measured in a calibrated NanoDrop 2000 UV-spectrophotometer. The yield of TRS was then determined based on a standard curve obtained with glucose.

Measuring the yields of glucose and cellobiose. The concentrations of glucose and cellobiose in the reaction mixture were measured by a Water 717plus high-performance liquid chromatography (HPLC) system, with an Aminex HPX-87H column and a refraction index detector. The temperature of the column was set to 65 °C. The flow rate was 0.5 mL/min. The eluent consisted of a filtered and degasified solution of sulfuric acid (5 mM). The volume of each injection was 10 μL. Pre-measured glucose and cellobiose was used to establish the calibration curves for the HPLC. The concentrations of soluble sugars from the reactions were then determined from the calibration curves (e.g., Glucose Yield %=carbon mass of glucose/mass of cellulose; Cellobiose Yield %=carbon mass of cellobiose/carbon mass of cellulose).

Table S1 The textural and acidic parameters of various catalysts.

Run	Samples	S content (mmol/g)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm) [b]
1	PDVB-SO_3H-[C_3vim][SO_3CF_3]	2.90 [a]	179	0.58	36.2
2	PDVB-SO_3H-[C_3vim][SO_3CF_3] [c]	2.88 [a]	184	0.59	34.2
3	PDVB-SO_3H-[C_3vim][SO_3CF_3] [d]	2.83 [a]	171	0.54	33.2
4	PDVB-SO_3H-[C_3vim][Cl]	2.30 [a]	182	0.65	37.5
5	Amberlyst 15	4.30 [a]	45	0.31	40
6	HCl	27.40 [e]	-	-	-
7	H_2SO_4	10.20 [e]	-	-	-

[a] Measured by elemental analysis.

[b] Pore size distribution estimated from BJH model.

[c] The catalyst has been recycled for three times.

[d] The catalyst has been recycled for five times.

[e] Calculated from molecular formula.

Table S2 Catalytic performances and recyclability of PDVB-SO_3H-[C_3vim][SO_3CF_3] in the reaction of depolymerization of Avicel.

Catalysts	Glucose yield (%) [a]	Cellobiose yield (%) [a]	TRS (%) [b]
PDVB-SO_3H-[C_3vim][SO_3CF_3]	77.0±2.7	8.2±1.8	99.6±0.4
PDVB-SO_3H-[C_3vim][SO_3CF_3] [c]	75.1±3.5	6.1±1.9	97.2±1.7
PDVB-SO_3H-[C_3vim][SO_3CF_3] [d]	72.7±3.7	5.9±1.3	94.3±3.6

[a] Measured by HPLC method, the reaction time was 5 h. [b] Measured by DNS method. [c] The catalyst has been recycled for three times. [d] The catalyst has been recycled for five times.

Figure Captions

Figure S1 XPS spectra of (A) wide-scan survey, (B) C1s, (C) N1s and (D) O1s in PDVB-SO_3H-[C_3vim][SO_3CF_3].

Figure S2 FT-IR spectra of PDVB-SO_3H-[C_3vim][SO_3CF_3].

Figure S3 TEM images of (A&B) PDVB-SO_3H-[C_3vim][SO_3CF_3] and (C&D) PDVB-SO_3H-[C_3vim][Cl].

Figure S4 N_2 isotherms and pore size distribution of PDVB-SO_3H-[C_3vim][SO_3CF_3] (in red) and PDVB-SO_3H-[C_3vim][Cl] (in black).

Figure S5 Room temperature ^{31}P MAS NMR spectra of TMP acquired (a) with proton decoupling, and (b) without proton decoupling of PDVB-SO_3H-[C_3vim][SO_3CF_3].

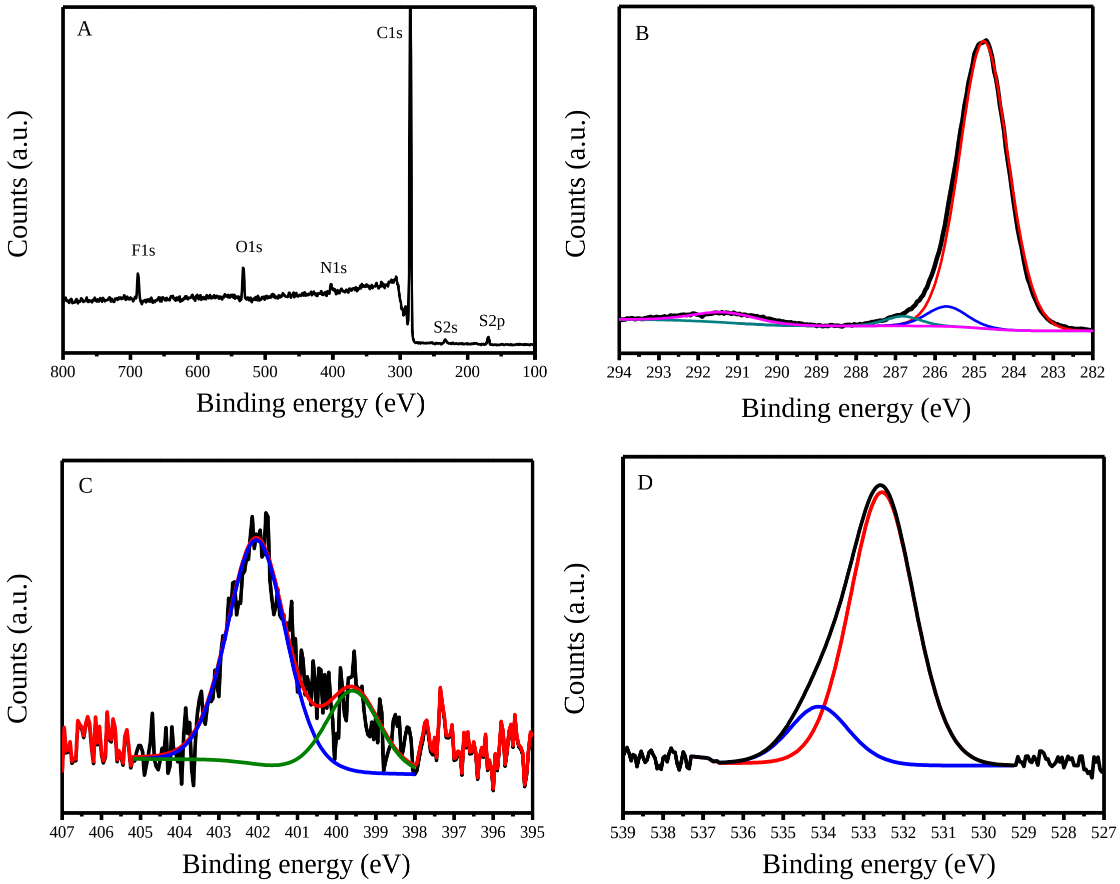
A
C1s
F1s
O1s
N1s
S2s
S2p
Counts (a.u.)
800
700
600
500
400
300
200
100
Binding energy (eV)
B
Counts (a.u.)
294
293
292
291
290
289
288
287
286
285
284
283
282
Binding energy (eV)
C
Counts (a.u.)
407
406
405
404
403
402
401
400
399
398
397
396
395
Binding energy (eV)
D
Counts (a.u.)
539
538
537
536
535
534
533
532
531
530
529
528
527
Binding energy (eV)

Figure S1

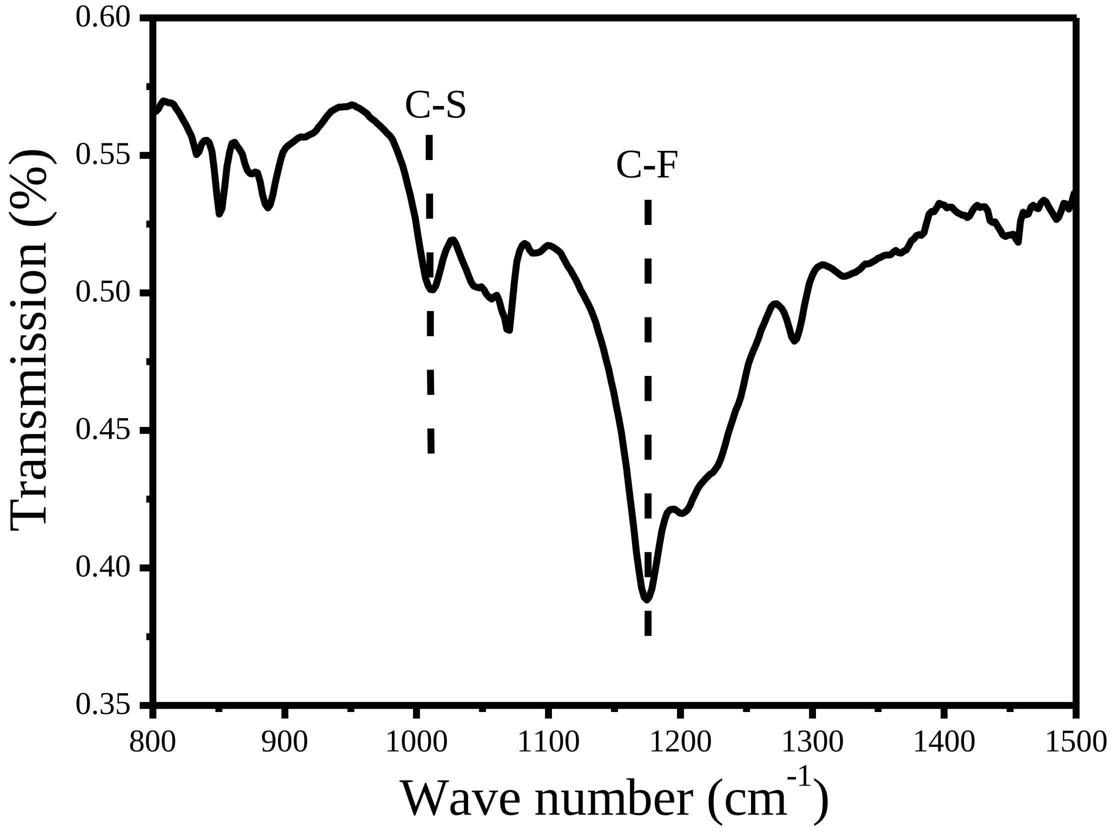
C-S
C-F
Transmission (%)
0.60
0.55
0.50
0.45
0.40
0.35
800
900
1000
1100
1200
1300
1400
1500
Wave number (cm^{-1})

Figure S2

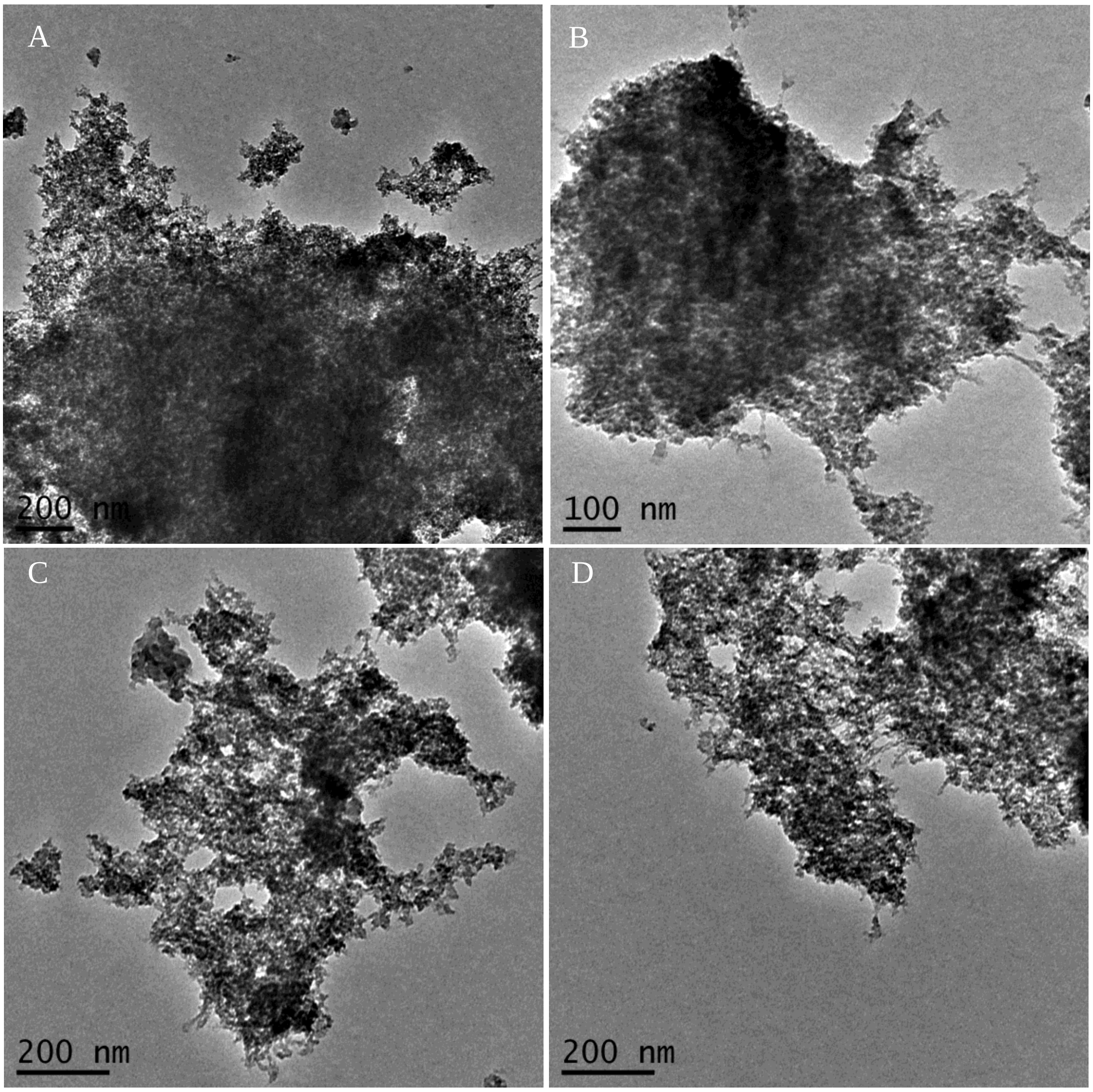

Figure S3

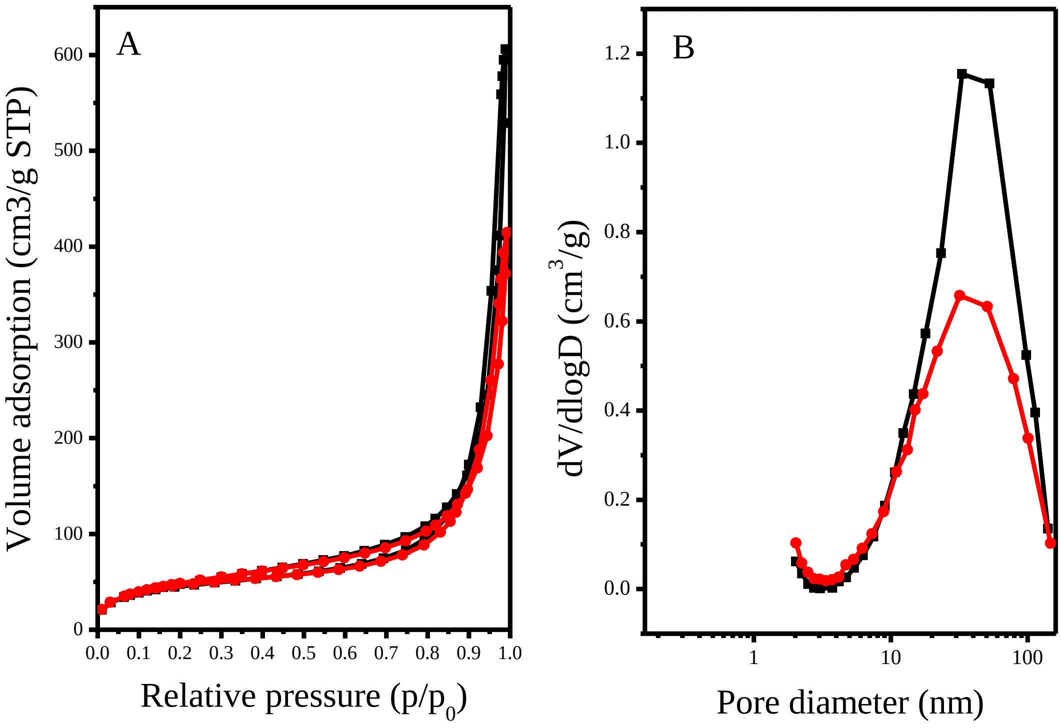
A
Volume adsorption (cm3/g STP)
0
100
200
300
400
500
600
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Relative pressure (p/p0)
B
dV/dlogD (cm3/g)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1
10
100
Pore diameter (nm)

Figure S4

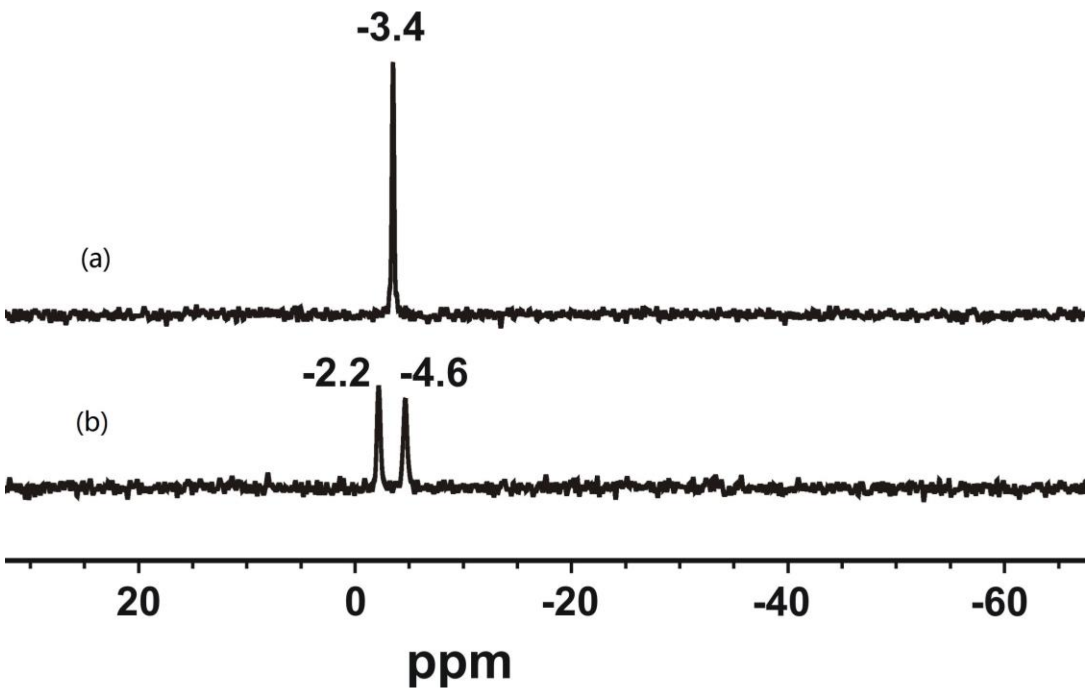

Figure S5

^{31}P NMR of adsorbed trimethylphosphine (TMP) has been demonstrated to be a sensitive and reliable technique for the determination of the Brønsted and Lewis acid sites in solid catalysts. The adsorption of TMP on the Brønsted acid will give rise to ^{31}P resonances in a rather narrow range (ca. -2 ~ -5 ppm). However, TMP bound to Lewis acid sites, may result in ^{31}P peaks in the range of ca. -20 ~ -60 ppm. [S5, S6] As shown in Figure S5a, using TMP as a probe molecule, the ^{31}P resonances at -3.4 ppm was assigned to the protonated adducts, $[(CH_3)_3P\text{-}H]^+$, attributed by the reaction of TMP and the Brønsted acidic protons. It's noteworthy that no resonances were observed in the range of -20 to -60 ppm due to interaction with Lewis acid sites, [S5, S6] therefore, it's indicative that no Lewis acid was formed over PDVB-SO_3H-[C_3vim][SO_3CF_3]. In order to reveal the interaction strength of P-H bond in the $[(CH_3)_3P\text{–}H]^+$ complexes, the NMR experiment without the proton decoupling was done as well. The single ^{31}P resonance (-3.4 ppm) was split into double peaks (at -2.2 and -4.6 ppm) and the JP-H coupling was determined to ca. 500 Hz (see Figure. S5b). This JP-H coupling was very close to the coupling values for TMPH^{+} inside aqueous HCl solution and related solid catalysts **S7**, which is indicative the stronger Brønsted acidity formed in PDVB-SO_3H-[C_3vim][SO_3CF_3].

References

(S1) F. J. Liu, W. P. Kong, C. Z. Qi, L. F. Zhu and F.-S. Xiao, *ACS Catalysis* 2012, **2**, 565.

(S2) F. J. Liu, L. Wang, Q. Sun, L. F. Zhu, X. J. Meng and F.-S. Xiao, *J. Am. Chem. Soc.* 2012, **134**, 16948.

(S3) R. Rinaldi, R. Palkovits and F. Schüth, *Angew. Chem., Int. Ed.* 2008, **47**, 8047.

(S4) C. Z. Li and Z. K. Zhao, *Adv. Synth. Catal.* 2007, **349**, 1847.

(S5) A. Zheng, S. J. Huang, S. B. Liu, F. Deng, *Phys. Chem. Chem. Phys.* 2011, **13**, 14889.

(S6) Y. Chu, Z. Yu, A. Zheng, H. Fang, H. Zhang, S. J. Huang, S. B. Liu, F. Deng, *J. Phys. Chem. C* 2011, **115**, 7660.

(S7) J. H. Lunsford, *Top Catal.* 1997, **4**, 91.