

Supplementary Information

One pot production of 5-hydroxymethylfurfural with high yield from cellulose by a Brønsted-Lewis- surfactant- combined heteropolyacid catalyst

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Experimental Methods

General Information

Microcrystalline cellulose (white, average particle size 50 μm) was obtained from J & K chemical Ltd (Beijing, China). SDS, CrCl_3 and other solvents were purchased from Beijing chemical industry and used without any purification. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was prepared following the Ref.1. FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. TEM image was measured on TECNAI G2 microscope. Centrifugation was performed on T4C Centrifuge (4000 rpm, 5 min, Beijing Yiyao). Energy dispersive X-ray analysis (EDX) was performed taking into account of the C, P, W and Cr elements using XL30ESEM-FEG. The concentration of HMF in the aqueous phase was determined by High-performance liquid chromatography (HPLC) with ION-300H column using a 2: 8 v/v methanol: water (pH = 2) gradient at a flow rate of 0.7 ml/min and a column temperature of 303 K using a UV detector. The concentration of HMF in the organic phase was determined by gas chromatography (Agilent 6890) equipped with Agilent 19091J-416 capillary column and flame ionization detector. Qualitative analysis was performed by Gas chromatography-mass spectrometry (GC-MS, Agilent 5970) with scan parameters: low mass 20.0, high mass 700.0, and threshold 150. Mass spectrometric measurement of the catalyst was collected using an autoflex III samrtbeam MALDI-TOF/TOF instrument supplied by Bruker Ltd with smartbeam laser with 355nm wavelength in positive ion mode. The ^{31}P MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CPMAS probehead whose X channel was tuned to 162 MHz for ^{31}P , using a magnetic field of 9.39 T at 297 K. The ^{13}C MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CPMAS probehead whose X channel was tuned to 100.62 MHz for ^{13}C using a magnetic field of 9.39 T at 297 K. The surface acidity was investigated ^{2a} using the irreversible adsorption of pyridine on the solid surfaces.

Preparation of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$

Chromium dodecyl sulfate ($\text{Cr}(\text{DS})_3$ abbreviated as CDS) was prepared as follows: dissolving 0.55 g SDS in 1 mL of water by ultrasonic dispersion, and then a saturated aqueous solution containing 0.1 g CrCl_3 was added with stirring at 60 $^\circ\text{C}$. The CDS precipitated by ethanol and was collected and dried.

$\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ was prepared by addition of 25 mL aqueous solution containing 0.189 mmol of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ into 25 mL solution containing 48 mg of CDS at 60 $^\circ\text{C}$. The molar ratio of CDS and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was 1:3. The precipitate was collected by centrifugation. The resulting $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ was obtained with yield 50 %. IR (1 % KBr pellet, $4000\text{--}400\text{ cm}^{-1}$): 1080 (sh, vas P-O_a , internal oxygen connecting P and W), 976 (s, vas W-O_d , terminal oxygen bonding to W atom), 922 (m, vas W-O_b , edge-sharing oxygen connecting W), 794 cm^{-1} (s, vas W-O_c , corner- sharing oxygen connecting W_3O_{13} units). Anal. Calcd for $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$: W, 69.78; Cr, 0.55; C, 4.56; H, 0.85; P, 0.98 %. Found: W, 68.95; Cr, 0.69; C, 4.64; H, 0.89; P, 0.94 %. The EDX analysis of the catalyst: C, 12.47; Cr, 0.39; W, 4.12; P, 0.36 (At %). The EDX measurement results showed that the approximate ratio of atomic percentage of C, Cr, W and P was 12: 1: 11.4: 1. The MALDI-TOF mass spectrum was recorded by using a LDI-1700: 9385.3 m/z corresponding to the mass of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}\text{H}^+]_3$ (m/z (calcd) 9386.2). The critical micelle concentration (CMC) of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ was $9.0 \times 10^{-3}\text{ M}$ determined by conductivity versus concentration plot, indicating that $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ existed in water as a micellar state.

The surface acidity of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$

The FTIR spectrum of adsorbed pyridine was recorded at 300 K to determine the above suggestion (Figure S1). The intense peak at 1490 cm^{-1} is attributed to Lewis acid sites, and the peaks at 1540 cm^{-1} and 1640 cm^{-1} are related to Brønsted (B) acid sites as well. Compared with pure HPW, which showed intense peaks at 1533, 1638 and 1545 cm^{-1} characterized by Brønsted type acidity,^{2b} the Lewis acid sites were successfully introduced to $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ molecules by H^+ partial exchange with Cr^{3+} .

Typical Procedures for Cellulose Hydrolysis

A typical catalytic reaction procedure was as follow: cellulose (0.2g), catalyst (0.06mmol), distilled water (4mL) were introduced in a **steel** autoclave lined with Teflon under air, and the autoclave was heated at $150\text{ }^\circ\text{C}$ for 2 h with agitation (30 rpm). The reaction was stopped by rapidly cooling the reactor in an ice bath at 0°C . Cellulose was decanted into the bottom, was filtered and weighed (recorded as W_1). The cellulose conversions were determined by the change of cellulose weight before (W_0) and after the reaction (W_1). The mixture was extracted twice by methylisobutylketone (MIBK) in order to confirm HMF entering into it. And the catalyst existed between water phase and MIBK phase, which was easy to be separated. All experiments were repeated three times. The catalyst $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ was separated and calcinated at 80°C for 3h. The total amount of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ leaching into the reaction solution through six runs were detected using a Leeman Plasma Spec (I) ICP-ES.

1. C. Rocchiccioli-Deltcheff C, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem.1983, 22, 207.
2. (a). C.A. Emeis, J. Catal. 1993, 141, 347. (b). E. P. Parry, J. Catal. 1963, 2, 371.

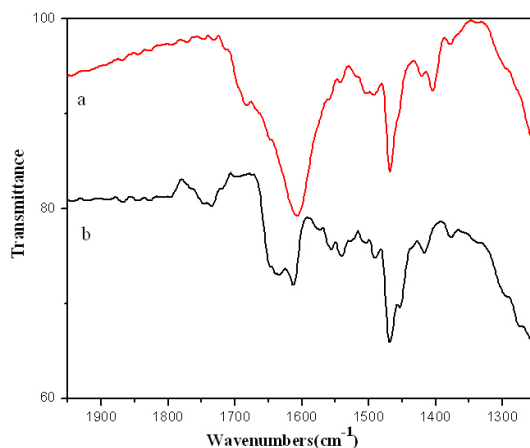


Fig. S1. The IR spectra of adsorbed pyridine at 300 K of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$
a. Before adsorption b. After adsorption

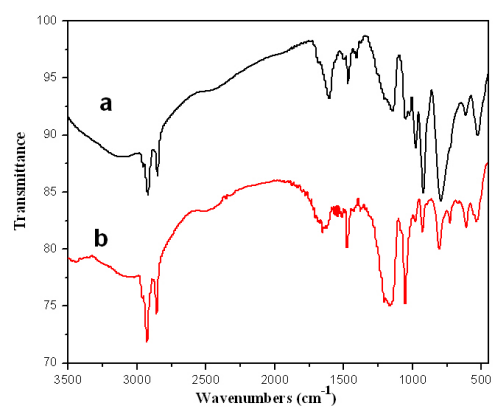


Fig. S2. The IR spectra of Cr[(DS)H₂PW₁₂O₄₀]₃ (a) and Cr[(DS)H₂PW₁₂O₄₀]₃ adsorption of cellulose (b).

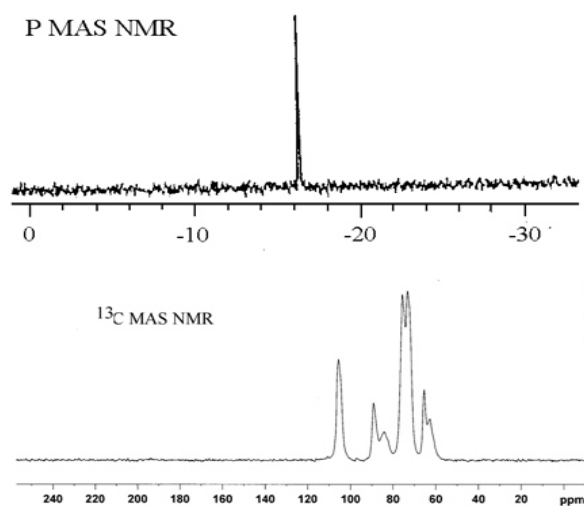


Fig. S3. The ^{31}P (a) and ^{13}C (b) MAS NMR spectra of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ adsorption of cellulose.

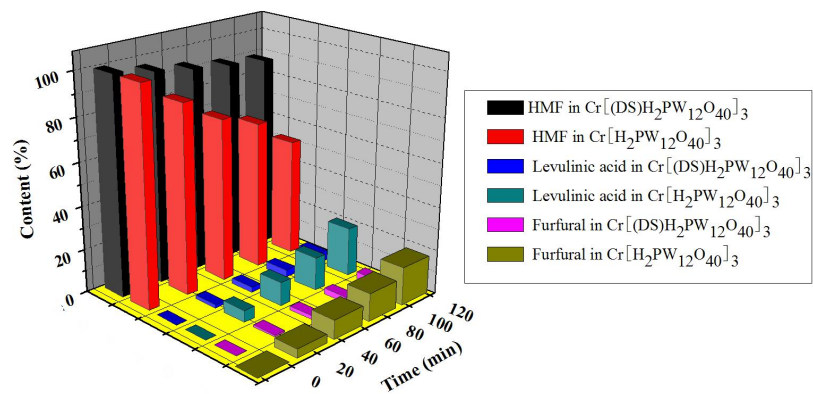


Fig. S4. The stability of HMF in $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ or $\text{Cr}[\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$

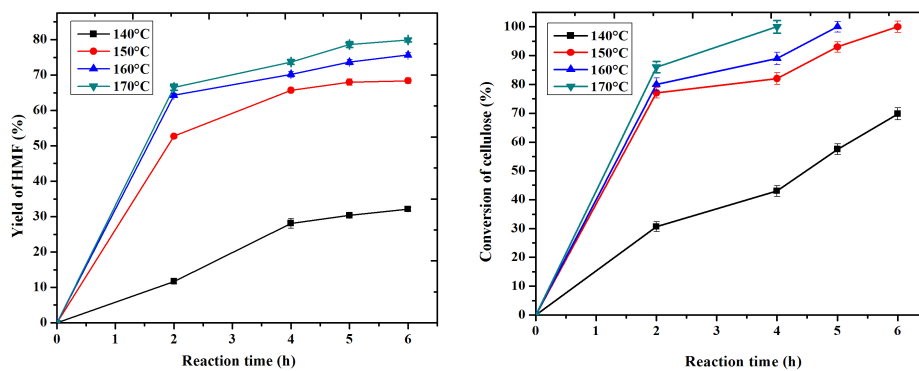


Fig. S5. The influence of reaction time and temperature on the conversion of cellulose into HMF

Reaction conditions: 0.2g of cellulose, 0.06mmol of catalyst, 4mL of water

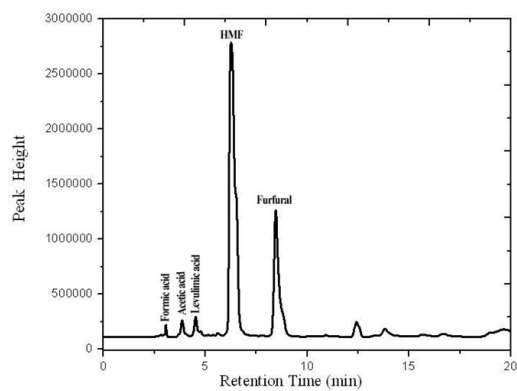


Fig. S6. Refractive index HPLC traces of representative reaction mixtures from XSB

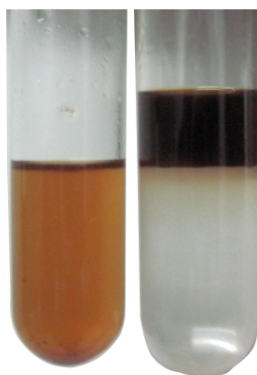


Fig. S7. The separation process of catalyst $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ from the reaction mixture: Left is the mixture of the reaction containing cellulose, HMF and catalyst. Right is the mixture after extraction of HMF by MIBK.

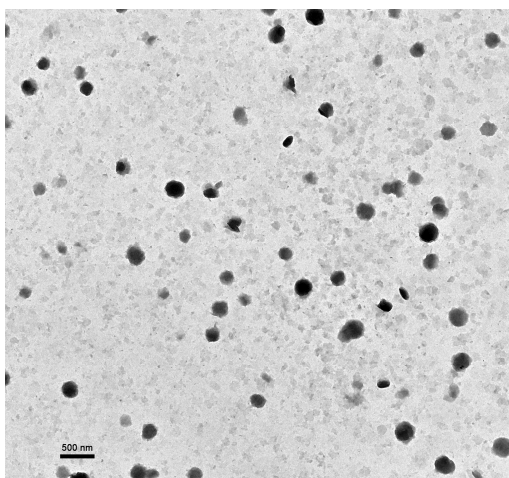


Fig. S8. The cryo-TEM image of the HPA micellar catalyst after the reaction.

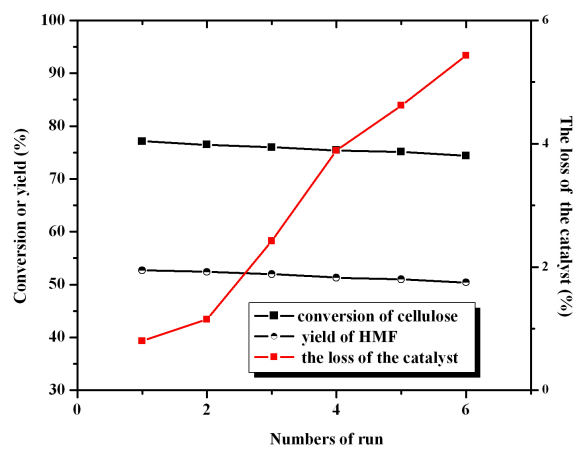


Fig. S9. Cycling runs in the conversion of cellulose (0.2g) in the presence of $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ (0.06 mM) at 150°C for 2h