

Supporting Information

CePO₄, a multi-functional catalyst for carbohydrate biomass conversion: Production of 5-hydroxymethylfurfural, 2,5-diformylfuran, and γ -valerolactone

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Synthesis of CePO₄

CePO₄ was synthesized by following the reported procedure.⁴³ In a synthesis procedure, P123 (1 g), H₃PO₄ (10 mmol), and water (15 g) were charged into a polypropylene bottle and agitated with a magnetic stirrer at ambient temperature for 2 h. Then CeCl₃·7H₂O (10 mmol) dissolved in 5 g water was slowly added to the above solution under stirring condition and stirring was continued for another 3 h. Then, the above white gel was subjected to hydrothermal treatment in an oven at 373 K for 72 h. The white precipitate of CePO₄ was recovered by centrifugation at 8000 rpm and washing three times with distilled water followed by drying in an oven at 343 K for 12 h.

Synthesis procedure of CePO₄ decorated H-Beta nanocomposites (CePO₄@H-Beta)

To obtain CePO₄@H-Beta nanocomposite, CePO₄ and H-Beta zeolite was mixed by grinding in a mortar and pestle. Ethanol was added during mixing to make the mixture homogeneous and mixture was grinded until complete removal of ethanol, which became powder again. Finally, the powder mixture was heated at 473 K for 2 h and then calcined at 773 K for 12 h to obtain the material. Three nanocomposites with 20, 30, and 40 % weight ratio of CePO₄ were synthesized and designated as CePO₄(20%)@H-Beta, CePO₄(30%)@H-Beta, and CePO₄(40%)@H-Beta respectively.

Catalyst characterization

The materials were characterized by X-ray diffraction (XRD) analysis using a RIGAKU Mini-flex diffractometer in 2θ range of 5-70° with Cu Kα (λ = 0.154 nm) radiation. The specific surface area and porous nature of the synthesized materials were analysed using N₂ sorption measurements on a Quantachrome Instrument, Autosorb-IQ, USA. Before analysis, the samples were degassed at 423 K for 5 h in the degassing port. The surface area was measured in the relative pressure range of 0.05 to 0.3 using Brunauer-Emmett-Teller (BET) equation. The distribution of pores was calculated using Barrett-Joyner-Halenda (BJH) method. The morphologies and microstructures of the synthesized materials were analysed using Field Emission Scanning Electron Microscopy (FE-SEM), Nova Nano SEM-450, JFEI, USA and high-resolution transmission electron microscope (HR-TEM) operated at an accelerating voltage of 300 KV (Tecnai G2, F30) at SAIF centre, IIT Bombay. The compositions of the various elements present in the material were calculated using energy dispersive X-ray spectroscopy (EDX). The X-Ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5000 VersaProbeII XPS system (ULVAC-PHI, INC, Japan) with a

microfocussed (100 μm , 25 W, 15 kV) monochromatic Al-K α source. A Bruker Tensor-II F-27 instrument with Pt-ATR assembly was used for Fourier transform-Infra red (FT-IR) analysis. The estimation of the nature of acid sites present in the materials were carry out on the same FT-IR instrument using pyridine as a probe molecule. The total acidity measurement of the materials was carried out using NH₃ temperature programmed desorption (NH₃-TPD) technique on a Quantachrome, CHEMBET™ TPR/TPD instrument. Before NH₃-TPD analysis, the sample was preheated at 423 K at a heating rate of 10 deg/min under a continuous He gas flow for 30 min. Then, after cooling to 323 K, NH₃ was allowed to adsorb on the sample for 1 h. After adsorption, the excess or physically adsorbed NH₃ was removed by flushing He gas (50 mL/min) for 30 min. Finally, the temperature controlled device (TCD) device became on and the temperature was ramped from 323-873 K at a rate of 10 deg/min.

Catalytic reaction Procedure

Conversion of carbohydrates into HMF

The reaction was performed in a Teflon lined 15 mL autoclave. In a typical reaction, carbohydrate (100 mg), catalyst (50 mg), and solvent (4 mL) were charged in the autoclave. The solvent was a mixture of aqueous phase (saturated NaCl solution) and diglyme in a volume ratio of 1:3. The autoclave was heated to 413 K in an oil bath with a vigorous stirring for the required period of time. The starting time of the reaction was recorded when the temperature of the oil bath was reached to 413 K and stirring was started at the same time. After completion of the reaction, the autoclave was allowed to cool down naturally to room temperature. The catalyst was removed from the reaction mixture by centrifugation. The recovered catalyst was washed three times with water, followed by acetone and dried in an oven at 343 K for 12 h, followed by activation at 673 K for 1 h. Carbohydrate conversion and HMF selectivity were based on ¹H NMR investigation. The carbohydrate conversion and HMF selectivity were obtained by analyzing the crude reaction mixture using ¹H NMR (Jeol, 400 MHz) in DMSO-d⁶. Analytical method for the determination of HMF yield is given below.

Analytic methods for the determination of yield using ¹H NMR

Conversion of carbohydrates to 5-HMF and formic acid were monitored using ¹H NMR. ¹H NMR was recorded at a regular interval by following a reported procedure.¹⁰ A small portion of the reaction mixture was centrifuged at regular time interval to remove the catalyst, and

then few-drops of reaction mixture was transferred to NMR tube, and diluted with DMSO- D_6 . One illustrative example is given below for the quantification of HMF yield using 1H NMR.

When sucrose was taken as starting material, HMF as the product and sucrose conversion is defined as follows:

Sucrose ($C_{12}H_{22}O_{11}$)

HMF ($C_6H_6O_2$)

No. of hydrogen= 22

No. of hydrogen= (6) x (3.67)

= 22

Areas under the peak correspond to chemical shift value for sucrose (ppm) based on proton content.

Say, area under the peaks correspond to sucrose = y

And area under the peaks correspond to HMF = w. factor = (w) x (3.67) = z

% Unreacted sucrose = $[y/(y+z)] \times 100$

Sucrose conversion (%) = $[100 - y/(y+z)]$.

HMF selectivity (%) = $[HMF \text{ (product) i.e area under the peaks correspond to HMF protons}]/[\text{Total product formed (area under the peaks based on proton content of all products)}] \times 100$.

HMF yield (%) = $[\text{Sucrose conversion (\%)} \times (\%) \text{ HMF selectivity}]/100$

Oxidation of HMF to DFF

The DFF was prepared from HMF oxidation using $CePO_4$ as the catalyst by using similar reaction setup describe in our previous report.¹¹ In brief, in a 25 mL round bottom flask, connected to a water condenser, HMF (0.5 mmol), DMSO (5 mL), and catalyst (50 mg) were heated at 413 K in a preheated oil bath and stirring was continued during the reaction. The reaction was performed under a continuous bubbling of molecular oxygen (10 mL/min). On completion of the reaction, the reaction mixture was centrifuged for catalyst removal. For recyclability test, the catalyst was washed three times with water, followed by acetone and dried at 343 K for 12 h, followed by activation at 473 K for 1 h. The reaction mixture was poured in water and the extraction of the reactants and products were carried out by the

addition of ethyl acetate. The reaction mixture was extracted three times and the ethyl acetate portions were combined and evaporated using rota-evaporator. The concentrated reaction mixture was diluted with 2 mL of ethyl acetate and then analyzed with gas chromatography (GC) (Yonglin; 6100; GC column: BP-5; 30 m×0.25 mm×0.25µm) fitted with FID detector. High purity N₂ gas (99.99%, GC grade) was used as the carrier gas with a flow rate of 10 ml/min whereas H₂ (99.99%, GC grade) and Air (99.99%, GC grade) were used as ignition gases. The injector and detector temperature were set at 553 K. GC column oven temperature was programmed as follows: Initial temperature = 353 K, hold time = 2 min followed by temperature ramping to final temperature of 573 K with a ramp rate of 10 K/min. 0.4 µL of sample was injected for the analysis. The calibration curves were constructed for pure HMF and DFF (diluted in ethyl acetate) for the determination of HMF conversion and DFF selectivity. Products were also confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 µm) and ¹H NMR.

¹H NMR of DFF in DMSO-d₆: 9.75 (s, 2H, -CHO), 7.60 (s, 2H, olefin protons)

Catalytic transfer-hydrogenation of LA into GVL

The transfer hydrogenation reaction was carried out in a Teflon-lined autoclave, charged with LA (1mmol), 2-propanol (6 mL), and catalyst (100 mg, pre-treated at 773 K for 5 h) and heated at 413 K in an oil bath for the desired period of time. After completion of the reaction, the stirring was stopped and the autoclave was allowed to cool to room temperature naturally. On completion of the reaction, the reaction mixture was centrifuged for catalyst removal. For recyclability test, the catalyst was washed three times with 2-propanol, followed by acetone and dried at 343 K for 12 h, followed by activation at 673 K for 1 h. The reaction mixture was directly analyzed with gas chromatography (GC) (Yonglin; 6100; GC column: BP-5; 30 m×0.25 mm×0.25µm) fitted with FID detector. High purity N₂ gas (99.99%, GC grade) was used as the carrier gas with a flow rate of 10 ml/min whereas H₂ (99.99%, GC grade) and Air (99.99%, GC grade) were used as ignition gases. The injector and detector temperature were set at 553 K. GC column oven temperature was programmed as follows: Initial temperature = 353 K, hold time = 2 min followed by temperature ramping to final temperature of 573 K with a ramp rate of 10 K/min. 0.4 µL of sample was injected for the analysis. The calibration curves were constructed for pure LA and GVL (diluted in 2-propanol) for the determination of LA conversion and GVL selectivity. Products were also confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 µm).

Table S1. Crystallite size of various materials prepared in this study.

Sr. No.	Catalyst	Mean crystallite size^a (nm)
1	H-Beta (before heat treatment)	8.76
2	H-Beta (after heat treatment at 773 K)	9.03
3	CePO ₄ (before heat treatment)	24.96
4	CePO ₄ - (after heat treatment at 773 K)	22.33
5	CePO ₄ (30%)@H-Beta (before heat treatment)	H-Beta- 9.29 CePO ₄ - 23.14
6	CePO ₄ (30%)@H-Beta (after heat treatment at 773 K)	H-Beta- 8.42 CePO ₄ - 21.49

^a Calculated using Scherrer formula.

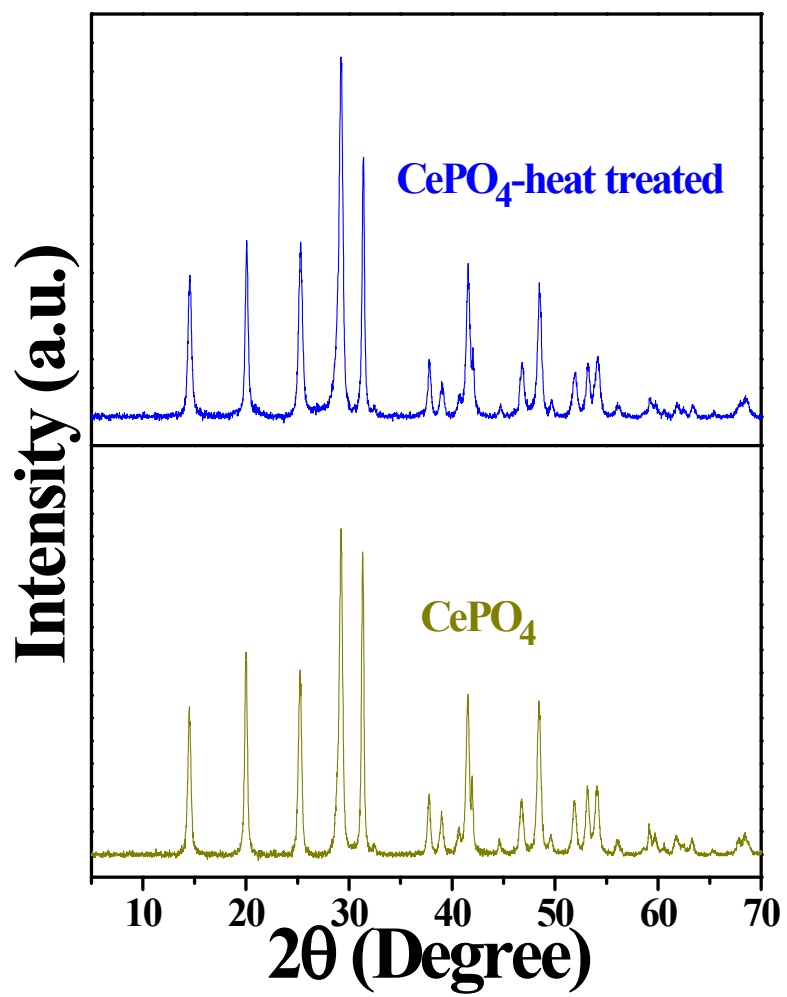


Fig. S1 XRD patterns of CePO₄ and CePO₄-heat treated at 773 K.

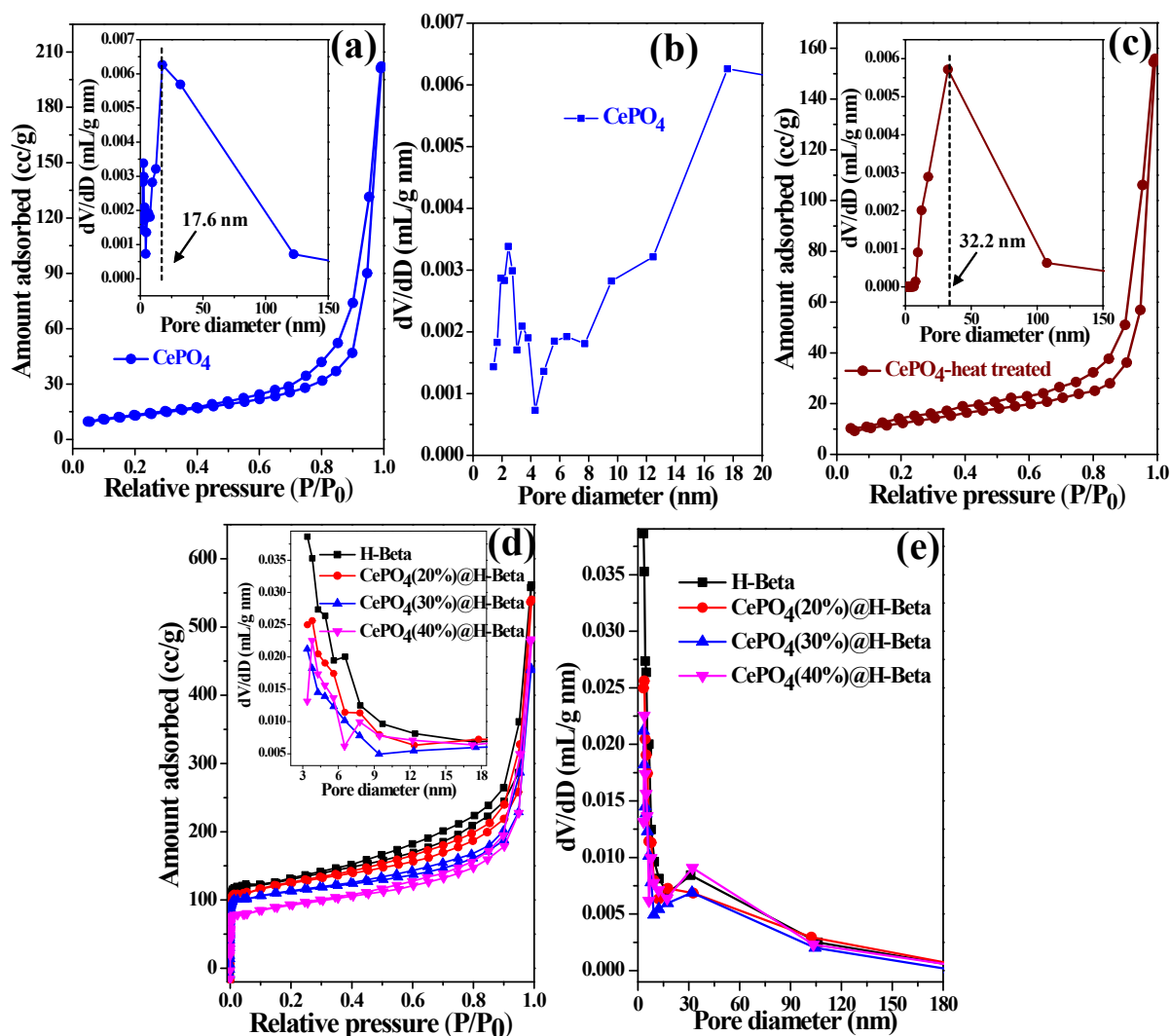


Fig. S2 (a) N₂-adsorption isotherm of CePO₄ (Inset shows the BJH pore size distributions), (b) BJH pore size distribution of CePO₄ in the range of 2-20 nm, (c) N₂-adsorption isotherm of CePO₄ treated at 773 K (Inset shows the BJH pore size distribution), (d) N₂-adsorption isotherm of H-Beta, CePO₄(20%)@H-Beta, CePO₄(30%)@H-Beta, and CePO₄(40%)@H-Beta (Inset shows the BJH pore size distribution in the range of 2-20 nm), and (e) BJH pore size distribution of materials shown in Fig. d in the range of 2-180 nm.

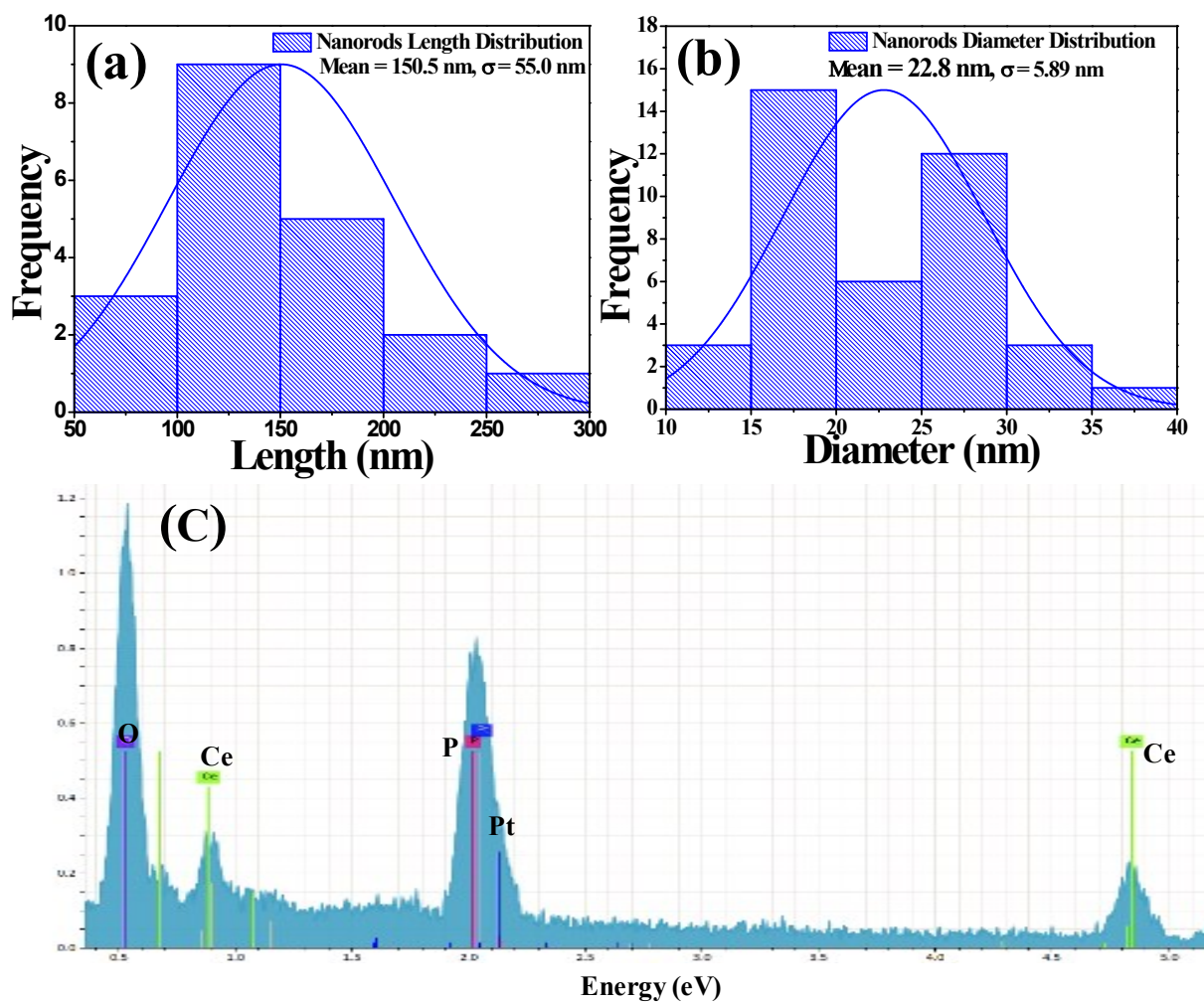


Fig. S3 Distributions of (a) length and (b) diameter of CePO_4 nanorods, (c) EDAX profile for CePO_4 .

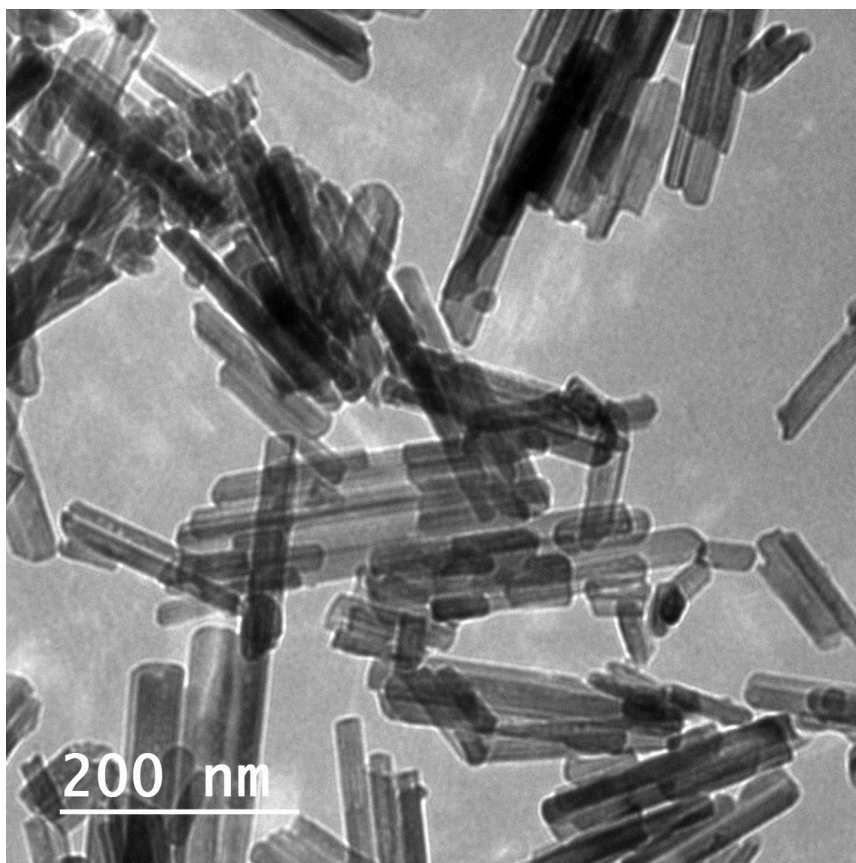


Fig. S4 TEM image of CePO₄ heat-treated at 773 K.

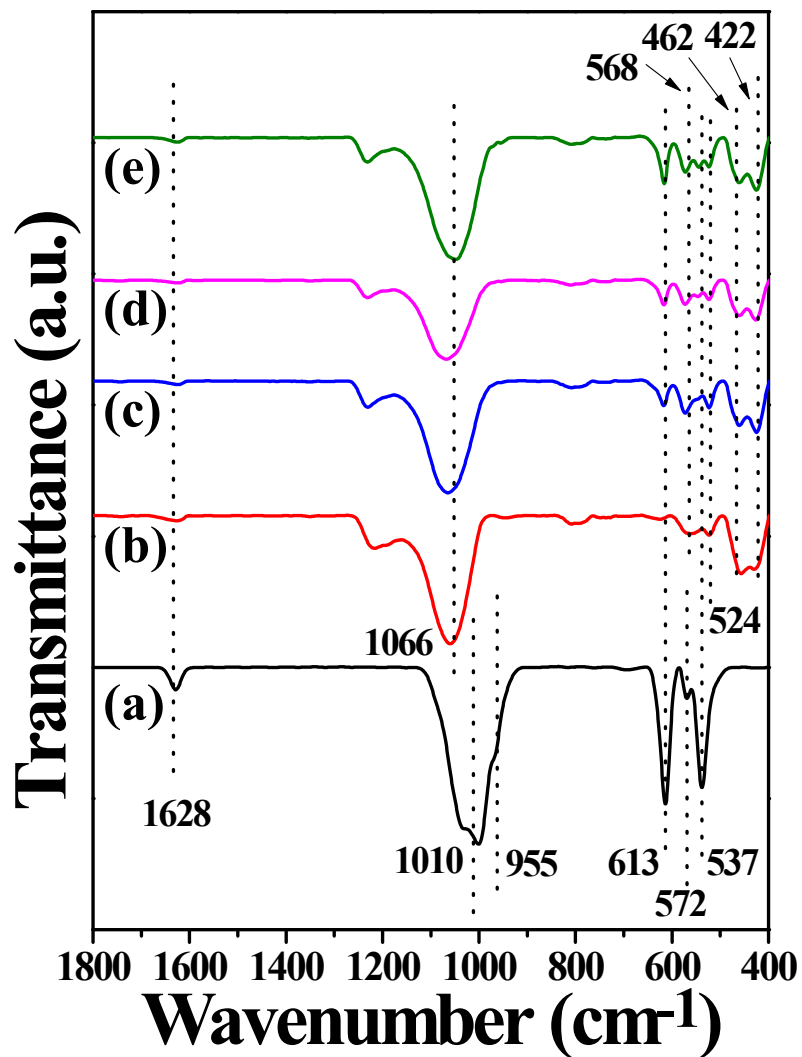


Fig. S5 FT-IR spectra of (a) CePO₄, (b) H-Beta, (c) CePO₄(20%)@H-Beta, (d) CePO₄(30%)@H-Beta, and (e) CePO₄(40%)@H-Beta.

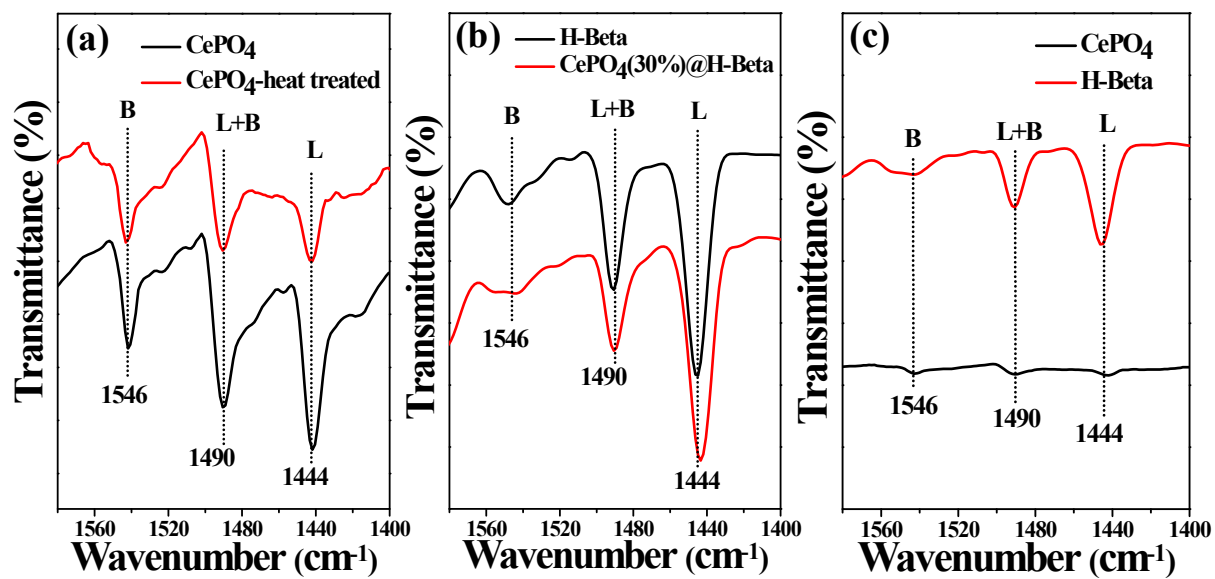


Fig. S6 Pyridine IR spectra of (a) CePO₄ & CePO₄ heat-treated at 773 K, (b) H-Beta & CePO₄(30%)@H-Beta, and (c) comparative PY-IR spectra of CePO₄ & H-Beta.

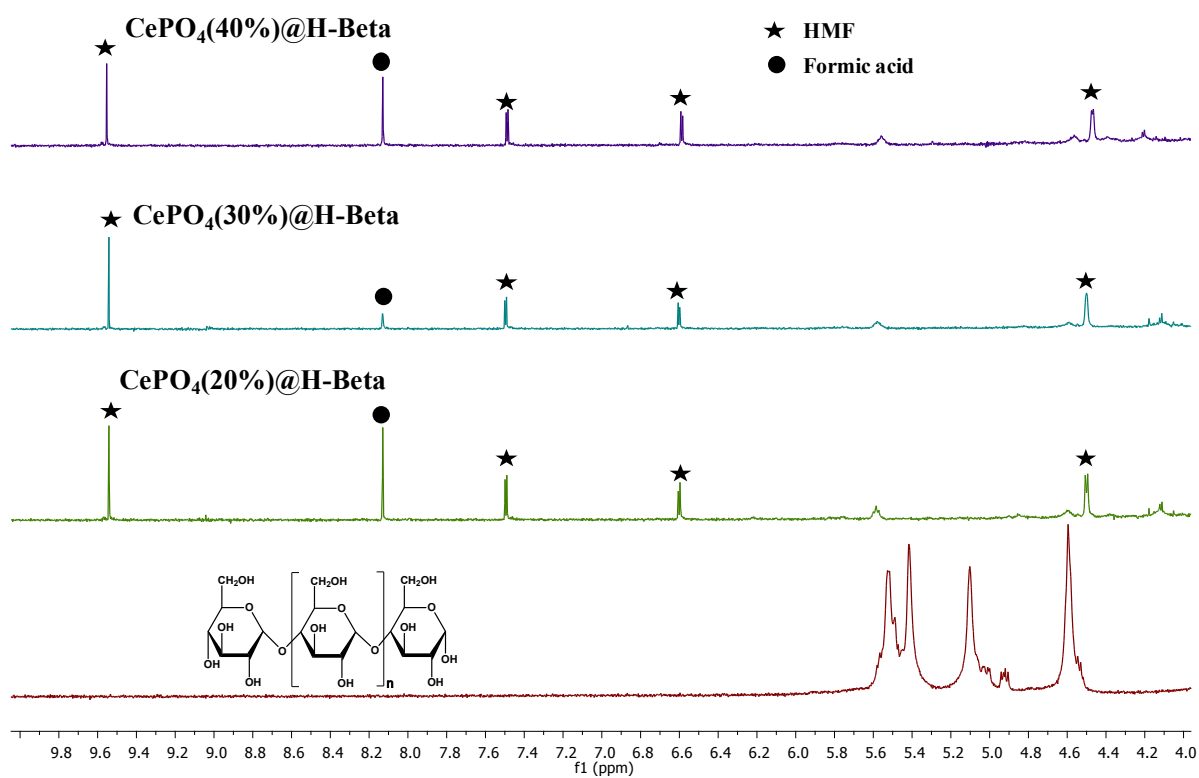


Fig. S7 ^1H NMR spectra for the conversion of starch into HMF over $\text{CePO}_4(20\%)\text{@H-Beta}$, $\text{CePO}_4(30\%)\text{@H-Beta}$, and $\text{CePO}_4(40\%)\text{@H-Beta}$ nanocomposite.

Photographs taken after each step in the sucrose to HMF conversion

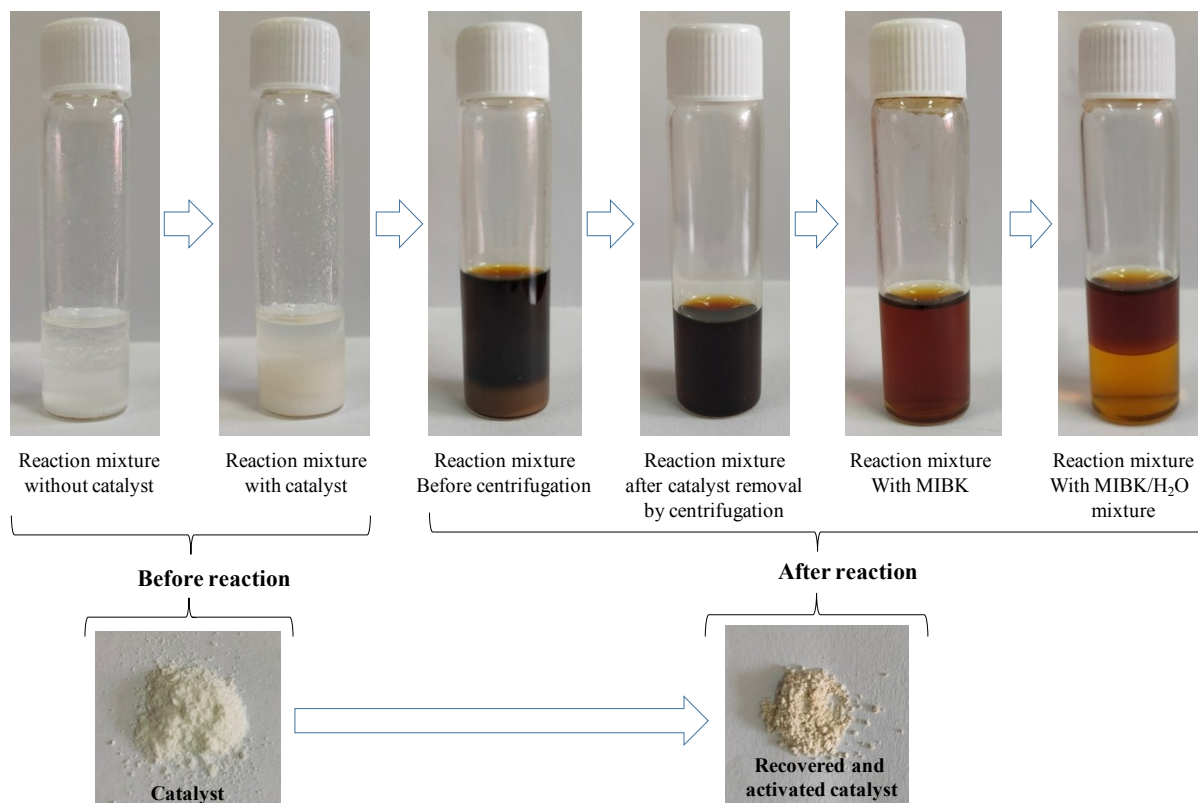


Fig. S8 Photographs recorded after each steps of the sucrose to HMF conversion using $\text{CePO}_4(30\%)\text{@H-Beta}$ catalyst.

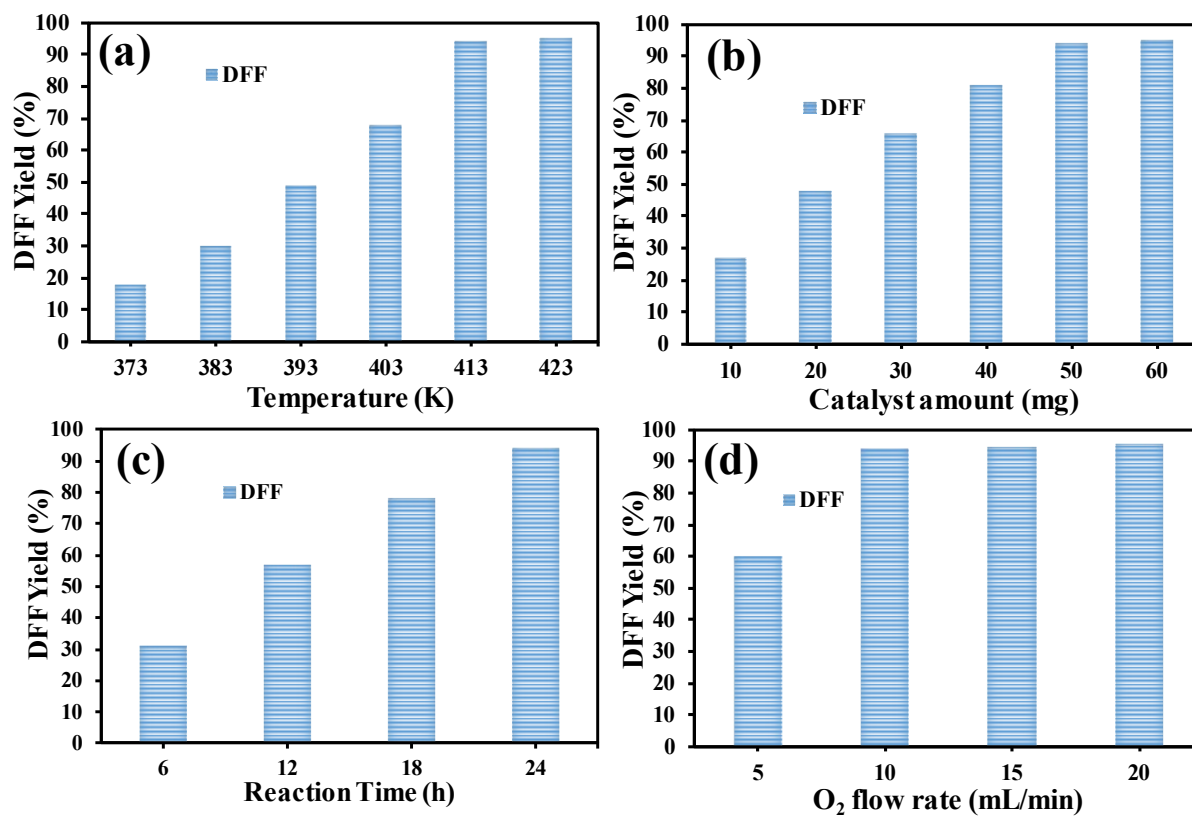


Fig. S9 Optimization of reaction parameters (a) temperature, (b) catalyst amount, (c) reaction time, and (d) O₂ flow rate for the selective conversion of HMF into DFF over CePO₄.

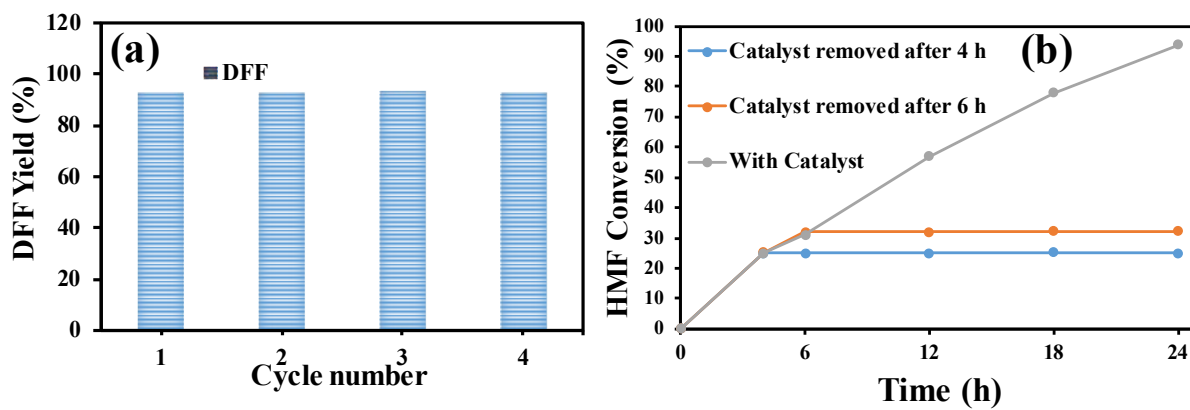


Fig. S10 (a) Catalyst recyclability and **(b)** leaching behaviour of CePO₄ for the conversion of HMF into DFF.

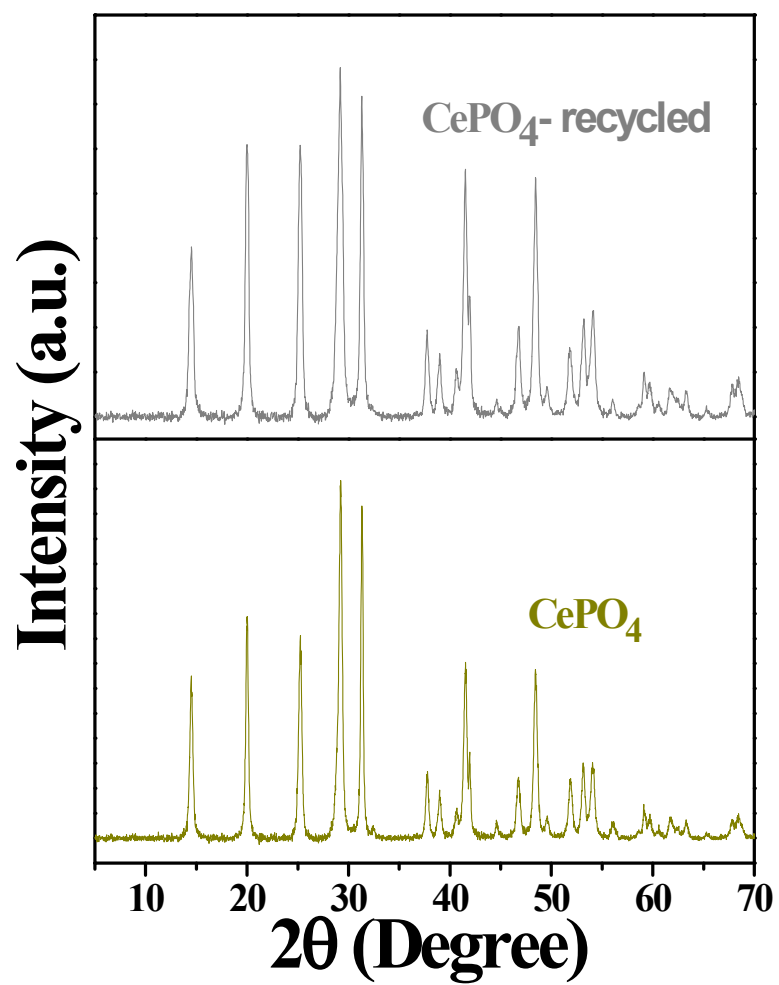
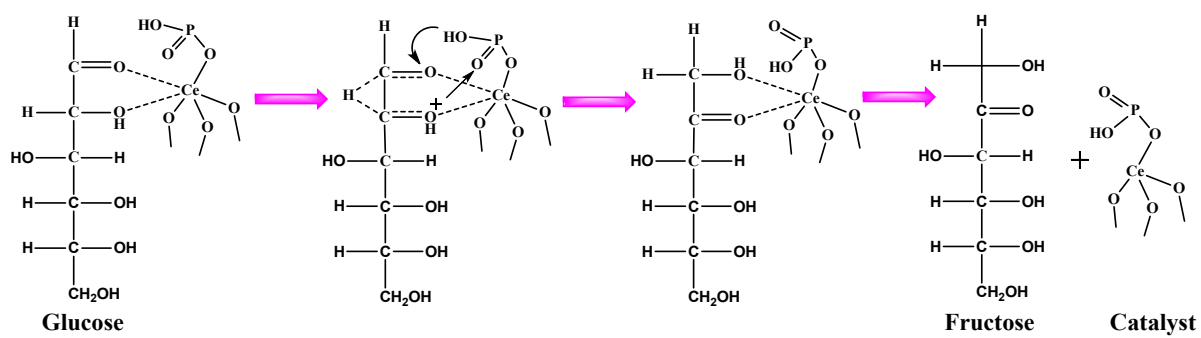
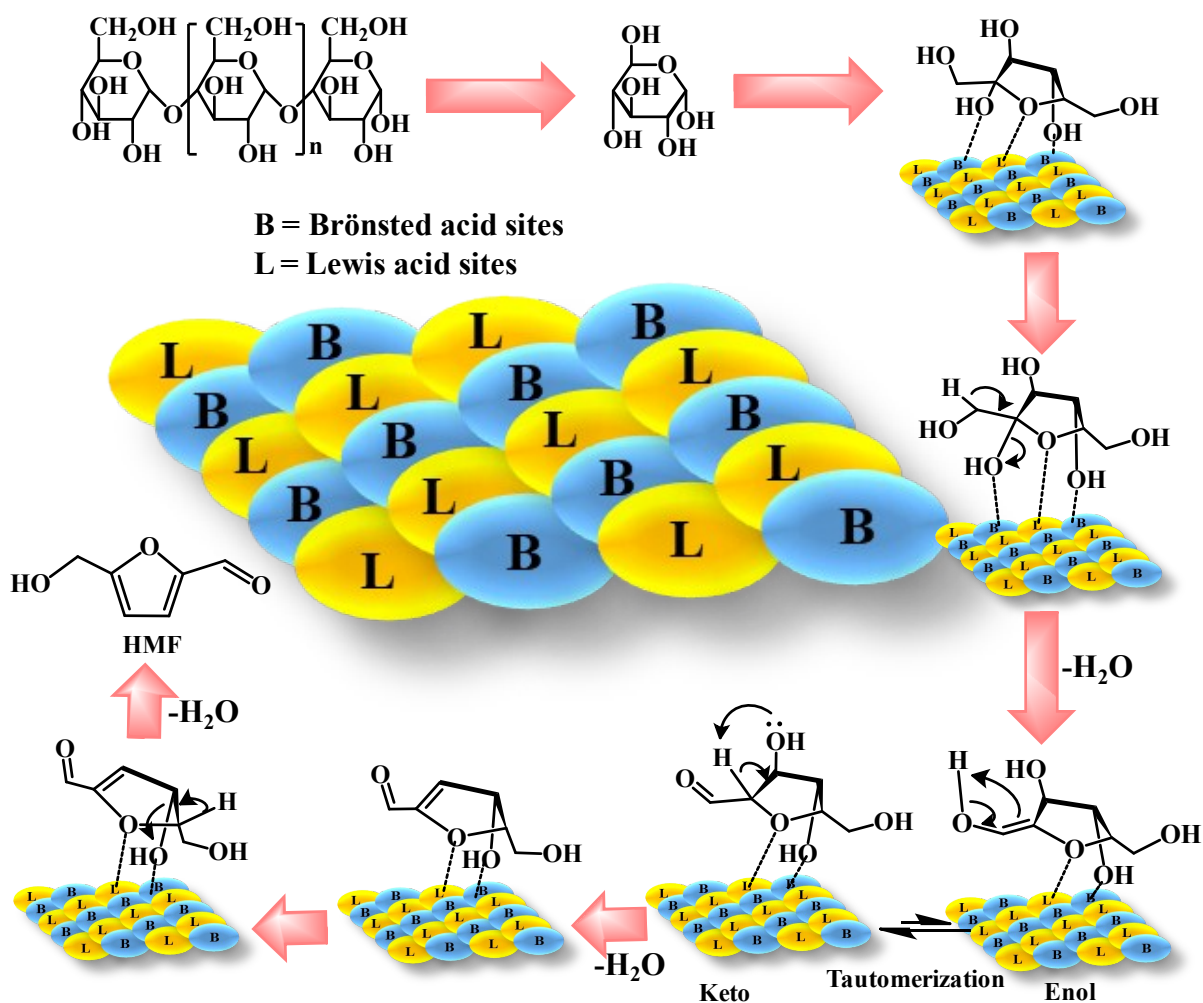


Fig. S11 XRD patterns of the fresh and recycled catalysts recovered after the HMF oxidation.



Scheme S1 Plausible reaction pathways for the isomerisation of glucose to fructose over CePO_4 catalyst.



Scheme S2 Plausible reaction pathways for the transformation of starch into HMF.



Scheme S3 Plausible reaction pathways for the transformation of LA into GVL. Where B is the Brønsted acid sites and L is the Lewis acid sites present in the catalyst.