

Electronic Supplementary Information (ESI)

Efficient, direct synthesis of dimethyl carbonate from CO₂ using solid, calcined zirconium phenylphosphonate phosphite catalyst

Pulikkeel Unnikrishnan,^{a,b} Poonam Varhadi^a and Darbha Srinivas^{*a,b}

^aCatalysis Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India. E-mail: d.srinivas@ncl.res.in. Fax: +91 20 25902633. Tel: +91 20 25902018

^bAcademy of Scientific and Innovative Research, Anusandhan Bhavan, 2, Rafi Marg, New Delhi-110001, India

S1: Catalyst preparation

S2: Catalyst characterization

S3: Reaction procedure and product analysis

S4: Catalytic activity data of ZrPP

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S1: Catalyst preparation

Chemicals

Methanol (AR grade), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, phenyl phosphonic acid, phosphorus acid and concentrated HF (48%) were purchased from Merck, India and used as received. Carbon dioxide (purity = 98 vol%) was procured from De-luxe Industrial Gases, Pune.

Synthesis of ZrPP-HF-C

In a typical synthesis of zirconium phenyl phosphonate phosphite (ZrPP-HF; $\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.29}(\text{HPO}_3)_{1.71} \cdot 0.02 \text{H}_2\text{O}$), solution A was prepared dissolving 4 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 20 ml of distilled water and 9 ml of concentrated HF taken in a polyethylene beaker. Solution B was prepared dissolving 1.06 g of phenyl phosphonic acid and 26.8 g of phosphorous acid in 50 ml of distilled water. Solution A was added to solution B. The beaker containing solution A was rinsed with 14 ml of water and the contents were added to the above reaction mixture which was then, heated at 70 °C for 34 h till it got dried completely. The material (ZrPP-HF), thus formed, was washed with 2 l of distilled water and dried at 90 °C overnight. ZrPP-HF-C was prepared calcining ZrPP-HF at 550 °C for 2 h.

Synthesis of ZrPP-1-C

In the preparation of ZrPP-1 [$\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.99}(\text{HPO}_3)_{1.01} \cdot 0.4 \text{H}_2\text{O}$], phenyl phosphonic acid (1 g) and phosphorous acid (0.52 g) were dissolved in 20 ml of distilled water. To that, 2.04 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ dissolved in 5 ml of distilled water was added. The mixture was heated to dryness at 90 °C for 3 h. The solid was recovered, washed with 500 ml of water and dried at 90 °C overnight. The obtained solid was designated as ZrPP-1. Calcination of ZrPP-1 at 550 °C for 2 h resulted in ZrPP-1-C.

Synthesis of ZrPP-2-C and ZrPP-3-C

ZrPP-2 [$\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.97}(\text{HPO}_3)_{1.03} \cdot 0.15 \text{H}_2\text{O}$] and ZrPP-3 [$\text{Zr}(\text{C}_6\text{H}_5\text{PO}_3)_{0.95}(\text{HPO}_3)_{1.05} \cdot 0.1 \text{H}_2\text{O}$] were prepared in the same manner as described for ZrPP-1 but for using phosphorus acid : phenyl phosphonic acid molar ratios of 2:1 and 3:1, respectively. Calcination of these materials at 550 °C for 2 h yielded ZrPP-2-C and ZrPP-3-C, respectively.

ZrP_2O_7 was prepared as per the procedure reported by Ch. Srilakshmi, K. Ramesh, P. Nagaraju, N. Lingaiah and P. S. Sai Prasad. *Cat. Lett.*, 2006, **106**, 115-122.

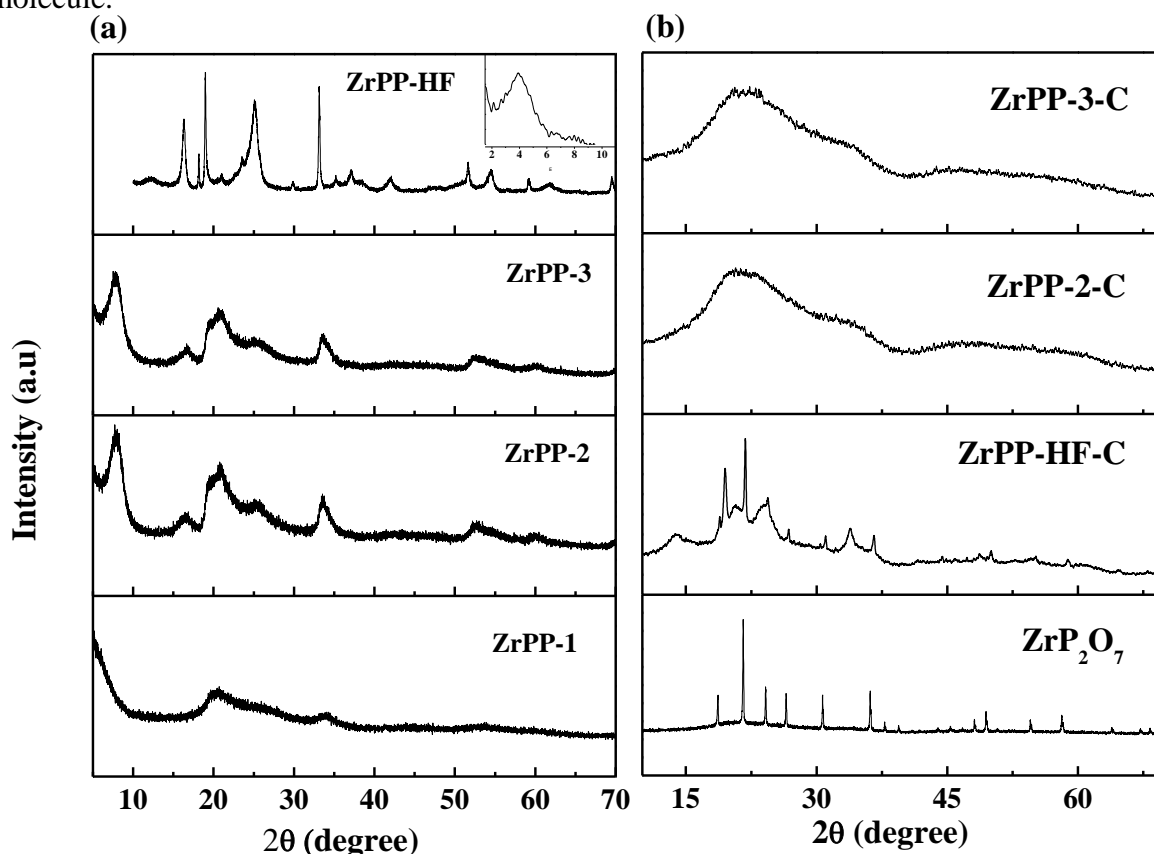
S2: Catalyst characterization

Characterization techniques

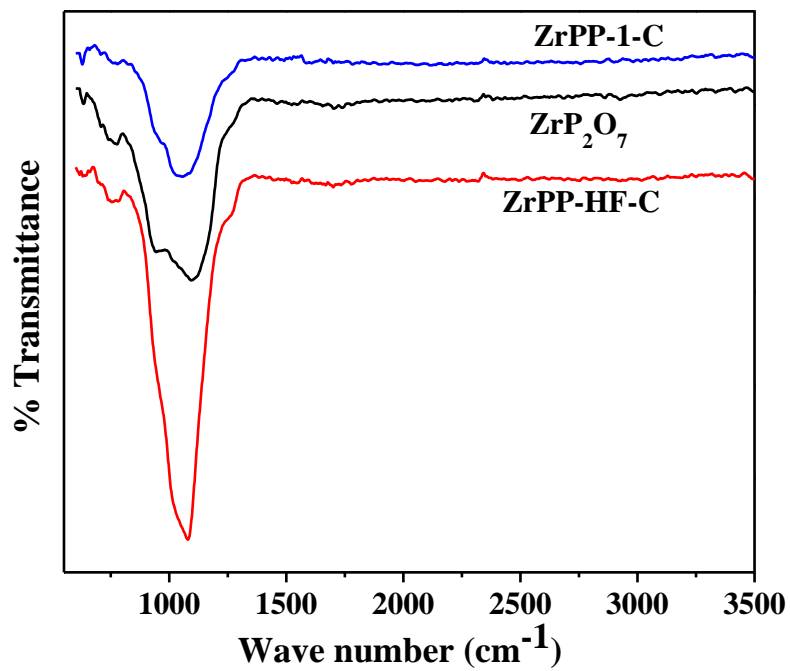
X-ray powder diffraction patterns of the samples were recorded on a Philips X'pert Pro diffractometer using Cu-K α radiation and a proportional counter detector. The diffraction patterns in the low-angle region ($2\theta = 0.5-5^\circ$) were recorded at a scan rate of 0.2 $^\circ$ /min and those in the high-angle region ($2\theta = 10-80^\circ$) were recorded at a scan rate of 4 $^\circ$ /min. The step size in the measurements was 0.02 $^\circ$. Fourier transform infrared (FTIR) spectra of the samples (as KBr pellets) were recorded using a Shimadzu 8201PC spectrophotometer in the region 400-4000 cm^{-1} . Solid state ^{31}P magic angle spin nuclear magnetic resonance (MAS NMR) spectra were recorded at 121.49 MHz on a Bruker AV300 NMR spectrometer using 4 mm sample rotors. Samples were spun at a speed of 8 kHz. A single pulse sequence was applied and the NMR measurements were performed at 25 °C. Thermogravimetric analyses (TGA) of the samples was done under nitrogen (50 ml/min) on a PerkinElmer Diamond TG-DTA instrument in the temperature range 25–600 °C and with a ramp rate of 10 °C/min. Surface area (S_{BET}) of the samples was determined from nitrogen-adsorption measurements carried out at -196 °C using a

NOVA 1200 Quanta Chrome equipment. The percentage compositions of C and H in ZrPP-HF, ZrPP-1, ZrPP-2 and ZrPP-3 were determined using a Carlo-Erba 1106 elemental analyzer.

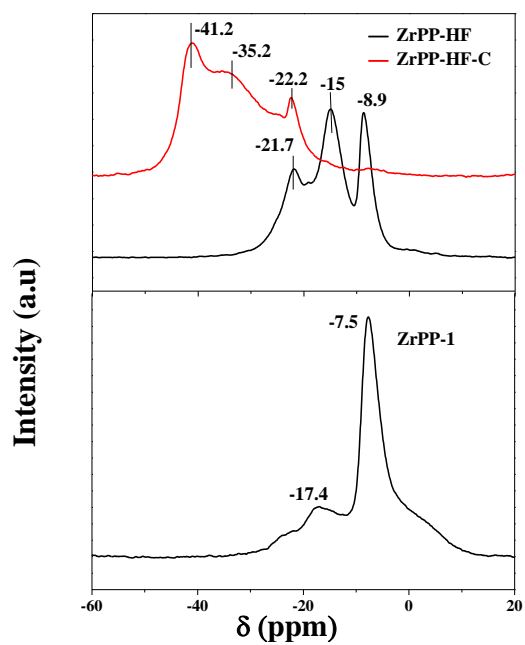
Acidity of the calcined samples was quantified by temperature-programmed desorption of ammonia (NH_3 -TPD) technique (Micromeritics AutoChem 2910). About 100 mg of the sample was placed in a U-shaped, flow-through, quartz sample tube. Before the TPD experiments, the catalyst was activated at 500 °C under a flow of He (30 ml/min). The sample was cooled to 50 °C and NH_3 (10% in He; 30 ml/min) was adsorbed for 30 min. Desorption of NH_3 was followed by raising the temperature from 50 to 500 °C at the ramp rate of 10 °C/min. Basicity of the samples was determined on the same instrument using CO_2 (10% in He; 40 ml/min) as probe molecule.



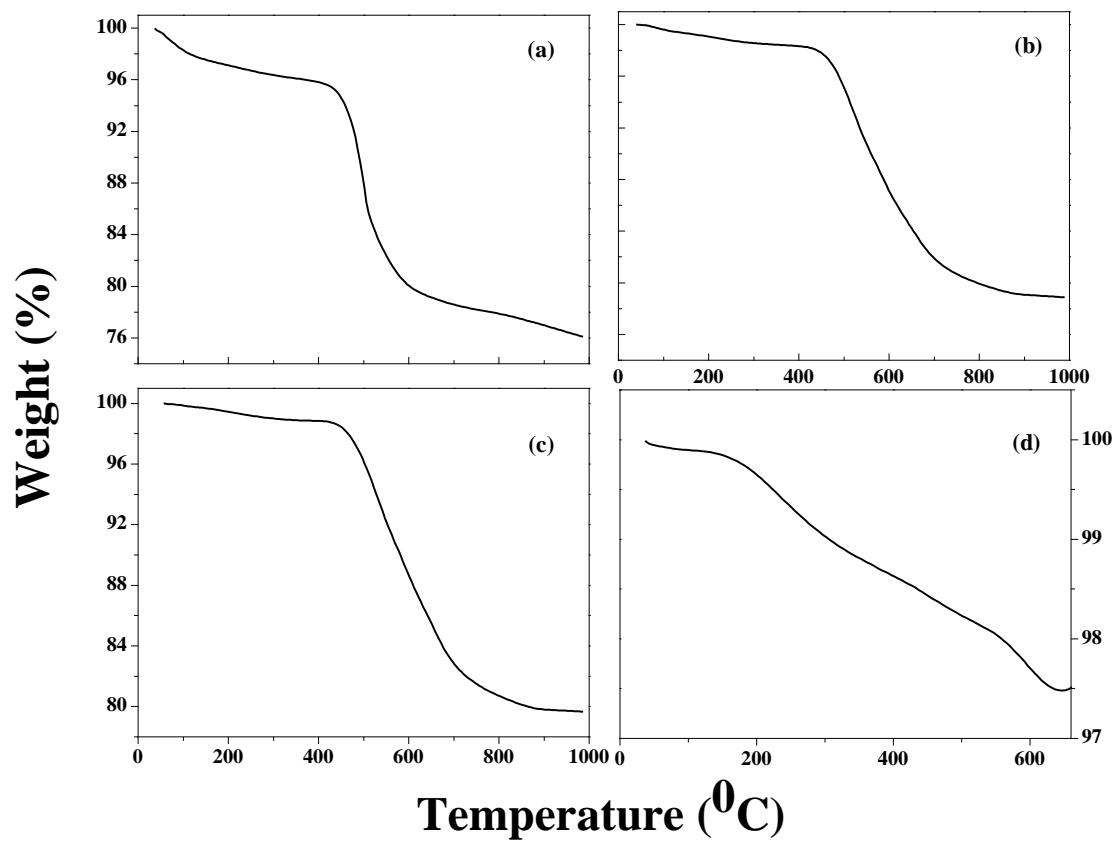
Powder XRD of (a) uncalcined and (b) calcined zirconium phenyl phosphonate phosphite catalysts and ZrP_2O_7 .



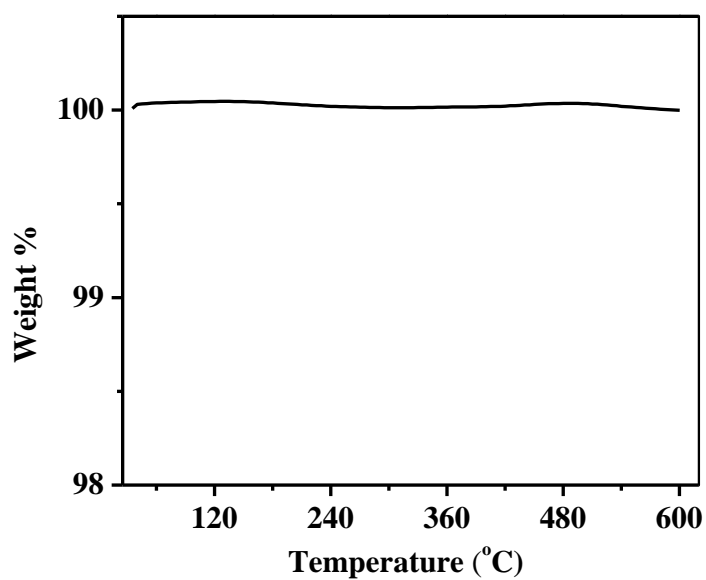
FTIR spectra of calcined ZrPP catalysts and ZrP₂O₇.



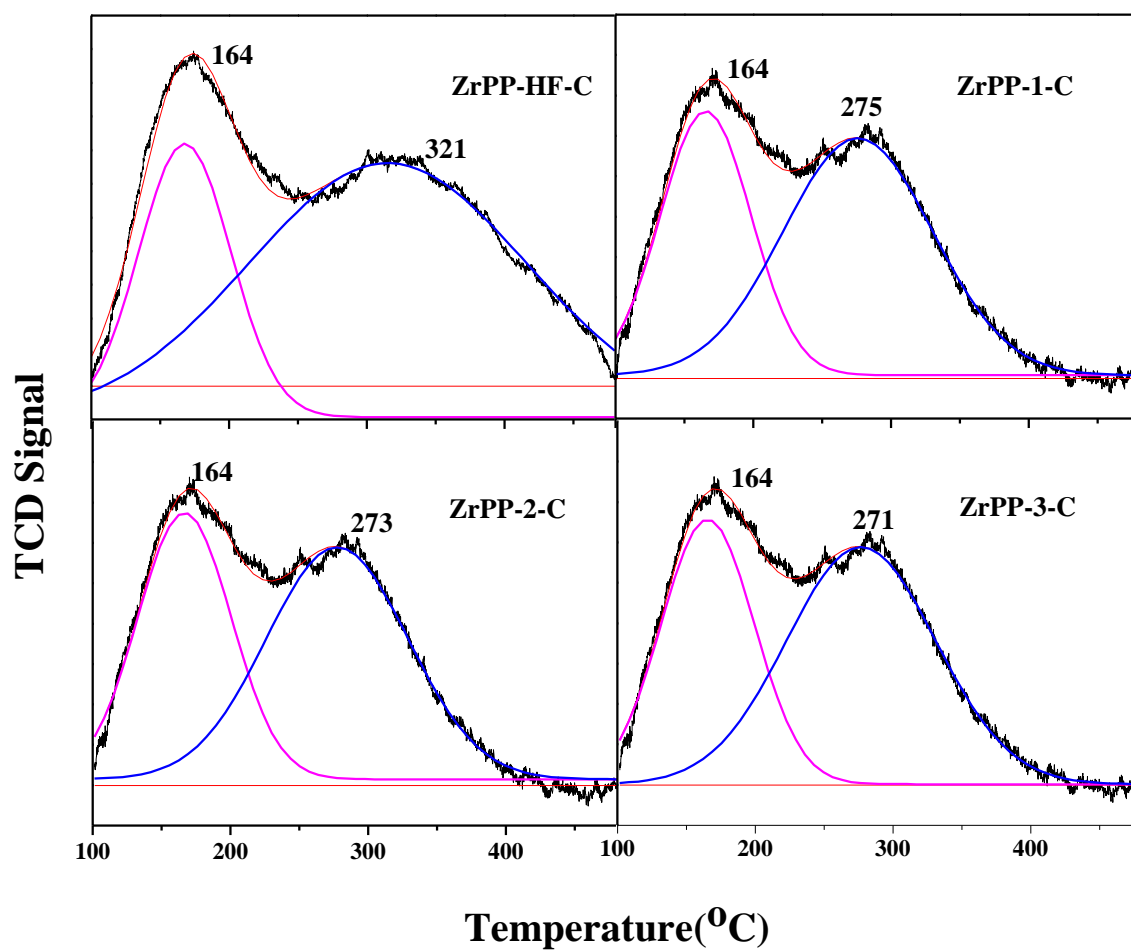
^{31}P MASNMR spectra of uncalcined (ZrPP-1, ZrPP-HF) and calcined (ZrPP-HF-C) zirconium phenylphosphonate phosphites



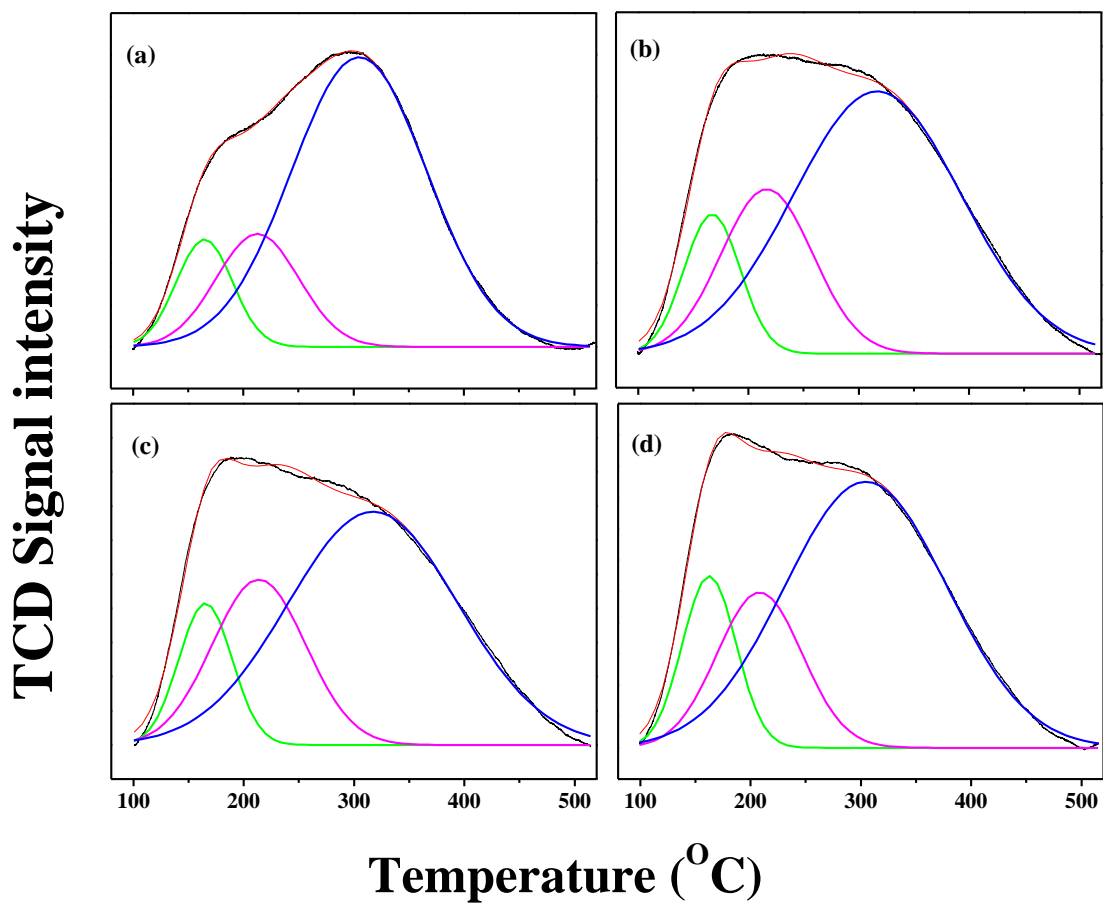
Thermogravimetric plots of (a) ZrPP-1, (b) ZrPP-2, (c) ZrPP-3, (d) ZrPP-HF.



Thermogravimetric plot of ZrPP-HF-C



CO₂-TPD profiles of calcined zirconium phenyl phosphonate phosphite catalysts.

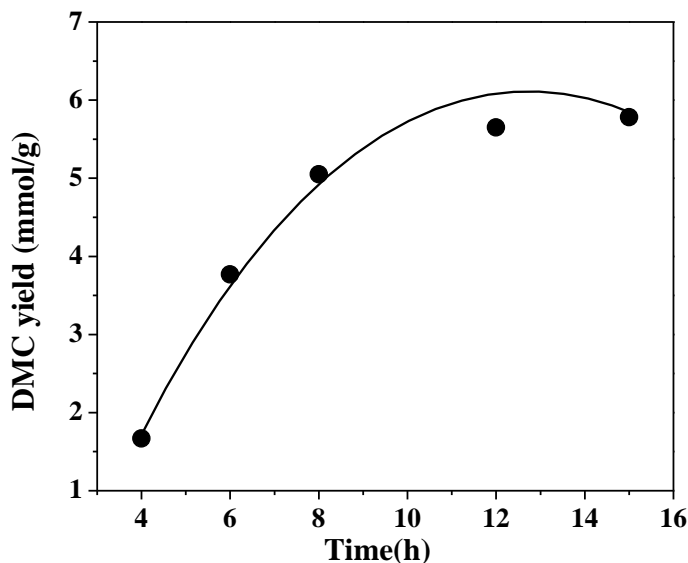


NH_3 -TPD profiles of (a) ZrPP-HF-C, (b) ZrPP-1-C, (c) ZrPP-2-C, (d) ZrPP-3-C.

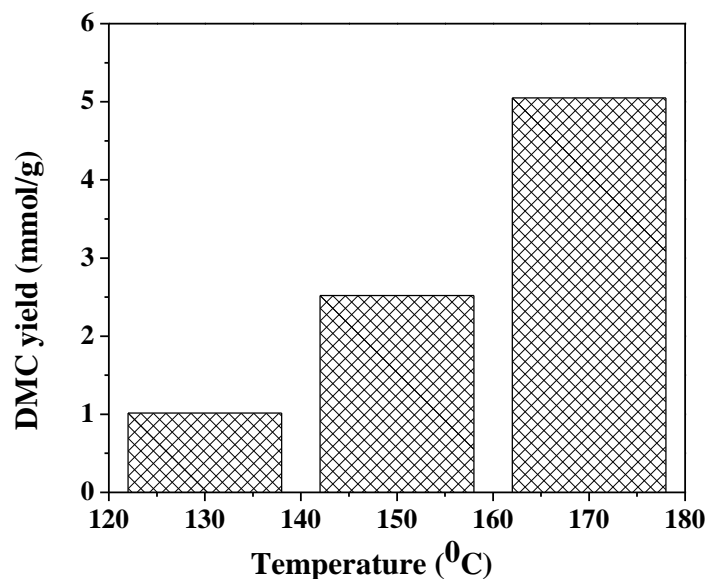
S3: Reaction procedure and product analysis

All the reactions were conducted in a 100 ml stainless steel Parr high pressure autoclave. 16.02 g of methanol (500 mmol) and 0.1-0.4 g of activated catalyst were taken in the reactor which was then pressurized with CO₂ to 1 – 4 MPa. The temperature of the reactor was raised to 120 – 170 °C and the reaction was conducted while stirring at a speed of 600 rpm for 4 – 12 h. Then, the reactor was cooled to 25 °C and gaseous products were vented out. The catalyst was separated out from the liquid products by centrifugation followed by filtration. The liquid products were analyzed and quantified with the help of a Varian 3400 gas chromatograph (GC) equipped with a flame ionization detector and CP-SIL8CB column (30 m-long and 0.53 mm i.d.). Nonane-1-ol was used as an internal standard for quantification of the products by GC. The gas product was analyzed with the above GC but with thermal conductivity detector.

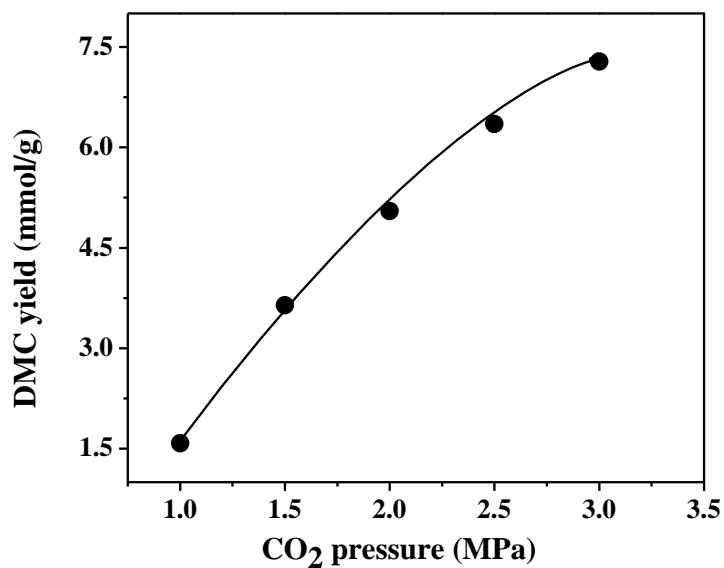
S4: Catalytic activity data of ZrPP catalysts



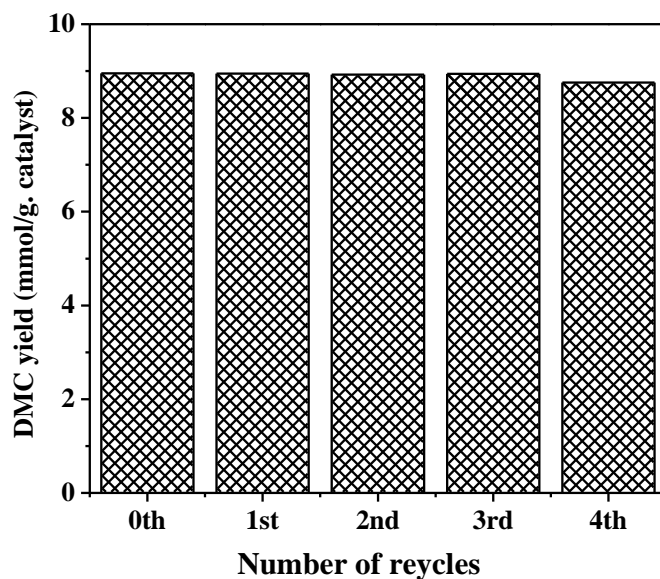
Influence of reaction time on the synthesis of DMC. Reaction conditions: methanol = 16.02 g (500 mmol), CO₂ pressure = 2 MPa, catalyst (ZrPP-HF-C) = 1 wt% of methanol, reaction temperature = 170 °C.



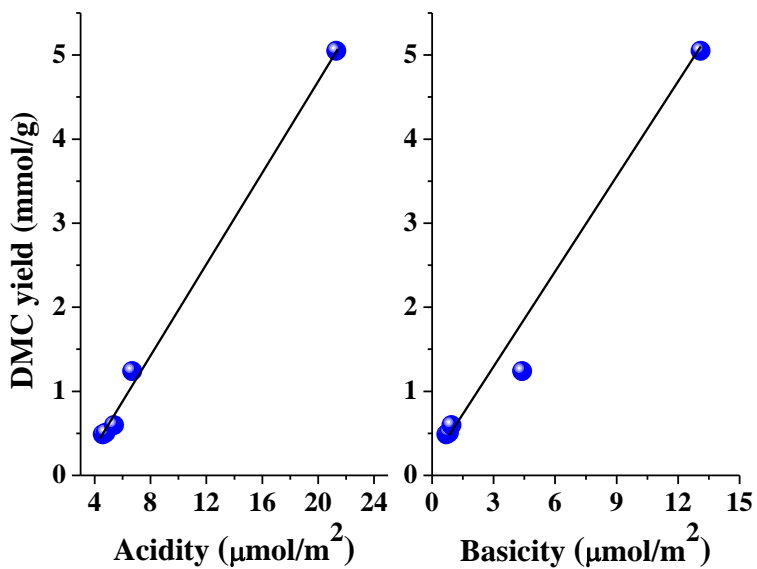
Influence of reaction temperature on the synthesis of DMC: Reaction conditions: methanol = 16.02 g (500 mmol), CO₂ pressure = 2 MPa, catalyst (ZrPP-HF-C) = 1 wt% of methanol, reaction time = 8 h.



Effect of CO₂ pressure on DMC synthesis in the absence of solvent using ZrPP-HF-C catalyst. Reaction conditions: methanol = 16.02 g (500 mmol), catalyst = 1 wt% of methanol, reaction time = 8 h and reaction temperature = 170 °C.



Catalyst recyclability test. Reaction conditions: methanol = 16.02 g; CO₂ pressure = 3 MPa, solvent = DMF (5 ml), catalyst (ZrPP-HF-C) = 1 wt% of methanol, reaction temperature = 170 °C, reaction time = 12 h.



Correlation of DMC yield with acidity and basicity of calcined ZrPP catalysts.

S5: XRD and FTIR of spent ZrPP-HF-C catalyst

