Electronic supplementary information

Exceptionally Stable Core-Shell MOF/COF Bifunctional Catalyst for High Efficient Cascade Deacetalization-Knoevenagel Condensation Reaction†

Ming-Liang Gao‡, Mei-Hong Qi‡ , Lin Liu* and Zheng-Bo Han*

College of Chemistry, Liaoning University. Shenyang 110036 P.R. China
E-mail: ceshzb@lnu.edu.cn; liulin@lnu.edu.cn

Materials and Characterization techniques

All raw materials for synthesis were commercially achieved analytically pure and were used without further purification. FT-IR spectra were recorded from KBr pellets in the 4000-400 cm^{-1} range on a Nicolet 5DX spectrometer. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyrisl (25-800 °C, 5 °C min^{-1}, flowing N_2 gas). Powder X-ray diffraction was recorded with a Bruker D8 ADVANCE automated diffractometer with Cu-Kα radiation. Variable-temperature PXRD studies were conducted by heating the sample at a constant rate of 5 °C min^{-1} from room temperature to target temperature in air, respectively. Inductively coupled plasma-optical emission spectroscopy (ICP) was performed using a 700 Series ICP-OES (Agilent Technologies). UV-vis diffuse reflection spectroscopy (DRS) was measured using Cary 400 UV-Vis spectrophotometer (VARIAN) equipped with an integrating sphere was used to measure the UV-vis DRS of the prepared samples. $BaSO_4$ was used as a white standard reference and the spectral range was 400-800 nm. The products of catalysis reaction were monitored by ^{1}HNMR spectra recorded on a Varian-300 MHz NMR spectrometer. The N_2 adsorption-desorption isotherms and BET surface area were characterized by a 3H-2000PS1 analyzer (Beishide Instrument Co., China). The samples of PCN-222-Co@TpPa-1 were activated by washing with DMF followed by solvent exchange in CH_2Cl_2 and CH_3OH for 3 days, respectively. The solution was refreshed several times daily during this period. In a typical experiment, 80 to 100 mg of each activated sample was transferred to a 6-mm large bulb glass sample cell (dry) and firstly evacuated at room temperature using a turbo molecular vacuum pump and then gradually heated to 150 °C for 24 h and cooled to room temperature.

Preparation of PCN-222-Co

The PCN-222-Co was synthesized according to the previous reported with a slight modification. 500 mg (2.15 mmol) $ZrCl_4$, 515 mg (0.6 mmol) H_4TCPP-Co and 6 mL (0.105 mol) acetic acid were dissolved in 100 mL DMF in a 250 mL three-necked flask, and then 2.5 mL H_2O was added. The resulting homogeneous solution was heated in oil bath under stirring at 120 ^{o}C for 15 min before it was cooled to room temperature. The product was separated via centrifugation at 10000 rpm for 3 minutes and further purified with ethanol for several times.

Preparation of TpPa-1

A 10 mL glass vial was charged with 1, 3, 5-triformylphloroglucinol (TP) (42 mg, 0.2 mmol) and dioxane (1 mL). The mixture was sonicated for 10 min to get a homogenous dispersion. Afterwards, p-phenylenediamine (Pa) (32 mg, 0.3 mmol) in 1 mL of dioxane solution was added, and the resultant suspension was briefly sonicated for 1 min. Subsequently, acetic acid aqueous solution (3 M, 0.35 mL) was added and the vial was then sealed and left undisturbed for 3 days at room temperature. The yielded red precipitate was collected by centrifugation and washed with anhydrous THF, anhydrous acetone, and anhydrous CH_2Cl_2, separately. The collected powder was then activated by solvent exchange with anhydrous CH_3OH for 3 times and dried at 120 °C under vacuum for 12 h to give a red powder.

Synthesis of core-shell PCN-222-Co@TpPa-1 hybrid material

A scintillation vial is charged with PCN-222-Co (48mg), Pa (48 mg, 0.45 mmol), 1.5 mL of mesitylene, 1.5 mL of dioxane were mixture in a 5 mL vial and sonicated 1 h at room temperature to uniformly distribute the PDA on the PCN-222-Co surface. Afterwards, TP and 0.5 mL acetic acid aqueous solution (3 M) was added and continued to sonicate 30 min in order to get a homogenous dispersion. The scintillation vial was sealed and left undisturbed for 3 days at room temperature. A aubergine coloured precipitate formed was collected by centrifugation or filtration and washed with anhydrous acetone. The powder collected was then solvent exchanged with anhydrous acetone 5-6 times and then dried under vacuum for 24 h to give an aubergine coloured powder.

Catalytic Reaction

The potential catalytic performance of PCN-222-Co@TpPa-1 was studied by continuous cascade reaction. First, the catalyst was activated at 393 K for 24 h under vacuum to remove the solvent molecules in the channels of hybrid material. Second, the catalytic reaction was performed with using benzaldehyde dimethylacetal (0.2 mmol) and malononitrile (0.21 mmol) in DMSO-d_6 (2.0 mL) for 10 h. The conversions and yields were calculated from ^1H NMR spectroscopy. The benzaldehydedimethylacetal (reactant) appears at δ 5.3 ppm, benzaldehyde is around 10.0 ppm and benzylidenemalononitrile is around 8.5 ppm. Due to hygroscopic DMSO, water was not added into the reaction mixture. The yields were calculated by integration of benzylic protons at the end of the reaction. Finally, the catalyst was removed by filtration and was washed repeatedly with CH_3OH and CH_2Cl_2.

Calculation of the % conversion in the Cascade Deacetalization-Knoevenagel Condensation Reaction

The conversion and yield was calculated by the integral area of benzaldehydedimethylacetal (a), benzaldehyde (b) and benzylidenemalononitrile (c) according to the formula:

Conversion = (b+c)/(a+b+c)*100%

Yield = c/(a+b+c)*100%

For PCN-222-Co@TpPa-1

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (0) and benzylidenemalononitrile (141.86): (141.86+0)/(141.86+0+1)*100% = 99.3%.

The yield of benzaldehyde: 0/(141.86+0+1)*100% = 0%

The yield of benzylidenemalononitrile: 141.86/(141.86+0+1)*100%*100%=6%

For PCN-222-Co

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (69.6) and benzylidenemalononitrile (4.5): (69.6+4.5)/(1+69.6+4.5)*100% = 98.7%.

The yield of benzaldehyde: 69.6/(1+69.6+4.5)*100% = 91.7%

The yield of benzylidenemalononitrile: 4.5/(1+69.6+4.5)*100% = 6%.

For PCN-222 @TpPa-1

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (0) and benzylidenemalononitrile (0.9): (0.9+0)/(0.9+0+1)*100% = 47.6%.

The yield of benzaldehyde: 0/(141.86+0+1)*100% = 0%

The yield of benzylidenemalononitrile: 0.9/(0.9+0+1)*100%*100% = 47.6%

For PCN-222-Co+TpPa-1

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (17.04) and benzylidenemalononitrile (93.07): (17.04+93.07)/(17.04+93.07+1)*100% = 99.1%.

The yield of benzaldehyde: 17.04/(17.04+93.07+1)*100%=15.2%

The yield of benzylidenemalononitrile: 93.07/(17.04+93.07+1)*100%*100% = 83.9%.

For PCN-222-Co@TpPa-1(thin)

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (12.71) and benzylidenemalononitrile (57.71): (12.71+57.71)/(12.71+57.71+1)*100% = 98.6%.

The yield of benzaldehyde: 12.71/(12.71+57.71+1)*100% = 17.8%

The yield of benzylidenemalononitrile: 57.71/(12.71+57.71+1)*100%*100% = 80.8%

For PCN-222-Co@TpPa-1(thick)

The conversion of benzaldehydedimethylacetal was calculated by the integral area of benzaldehydedimethylacetal (1), benzaldehyde (0) and benzylidenemalononitrile (3.03): (3.03+0)/(3.03+0+1)*100% = 75.2%.

The yield of benzaldehyde: 0/(3.03+0+1)*100% = 0%

The yield of benzylidenemalononitrile: 3.03/(3.03+0+1)*100%*100% = 75.2%

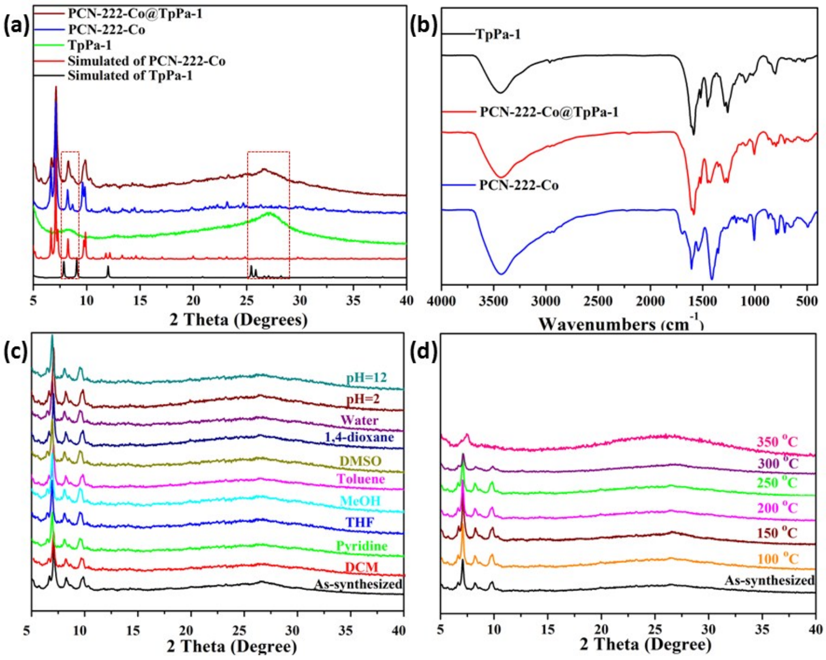


Fig. S1 a) The PXRD patterns of PCN-222-Co, TpPa-1 and PCN-222-Co@TpPa-1 hybrid materials; b) FT-IR spectra of the PCN-222-Co@TpPa-1 hybrid material, TpPa-1 and PCN-222-Co; c) Chemical stability tests for PCN-222-Co@TpPa-1 monitored by PXRD; d) Thermal stability tests for PCN-222-Co@TpPa-1 monitored by variable-temperature PXRD analysis.

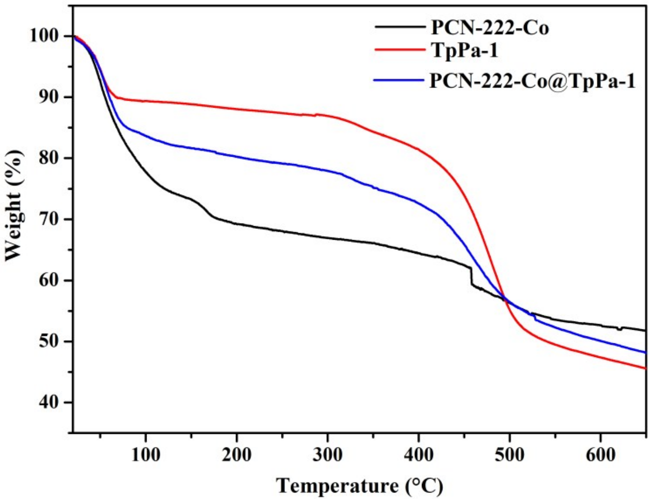


Fig. S2 TGA curves of PCN-222-Co@TpPa-1 hybrid material, PCN-222-Co and TpPa-1.

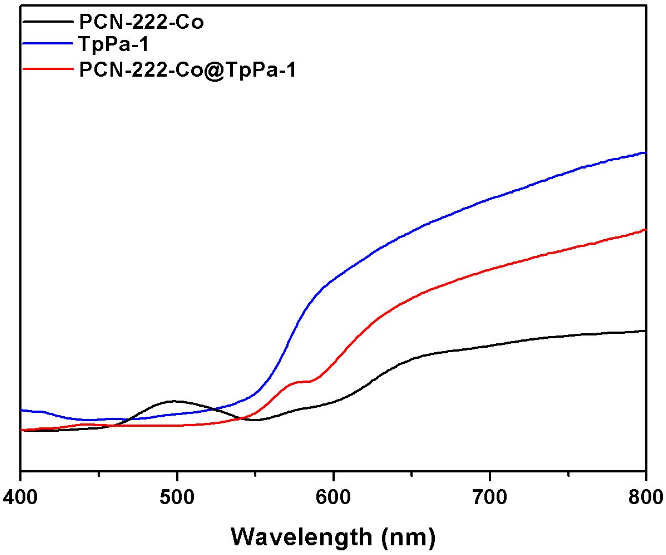
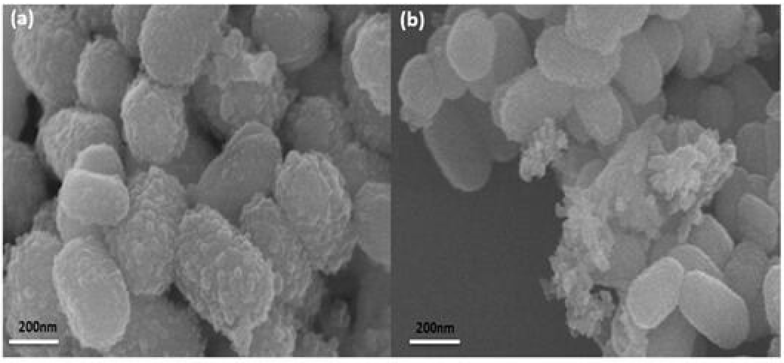


Fig. S3 The solid UV-Vis absorption spectra of PCN-222-Co, TpPa-1 and PCN-222-Co@TpPa-1 hybrid materials.



	PCN-222-Co	Pa	Tp
PCN-222-Co@TpPa-1(thick)	20 mg	48 mg	62 mg
PCN-222-Co@TpPa-1	20 mg	24 mg	31 mg
PCN-222-Co@TpPa-1(thin)	20 mg	12 mg	15.5 mg

Fig. S4 SEM images of PCN-222-Co@TpPa-1 prepared with different MOFs:COFs ratios: (a) PCN-222-Co@TpPa-1(thick); (b) PCN-222-Co@TpPa-1(thin).

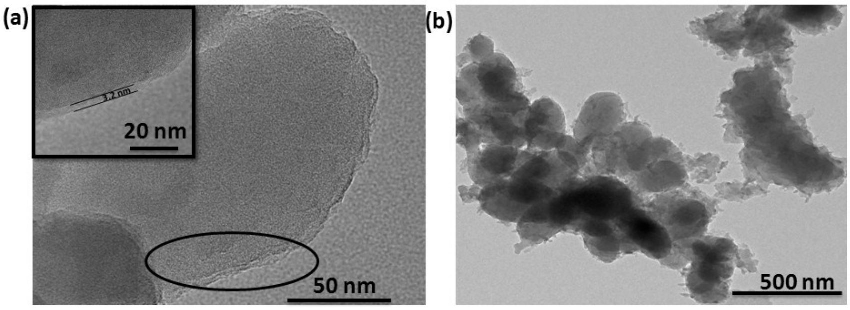


Fig. S5 TEM images of PCN-222-Co@TpPa-1 prepared with different MOFs:COFs ratios: (a) PCN-222-Co@TpPa-1(thin); (b) PCN-222-Co@TpPa-1(thick).

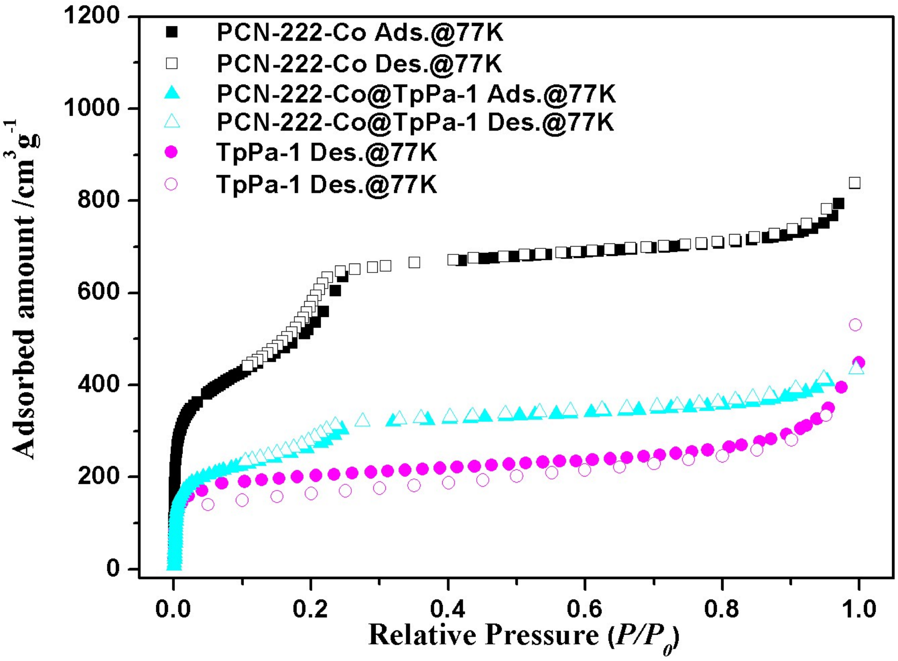


Fig. S6 N_2 sorption isotherms for PCN-222-Co, TpPa-1-COF, PCN-222-Co@TpPa-1 measured at 77 K.

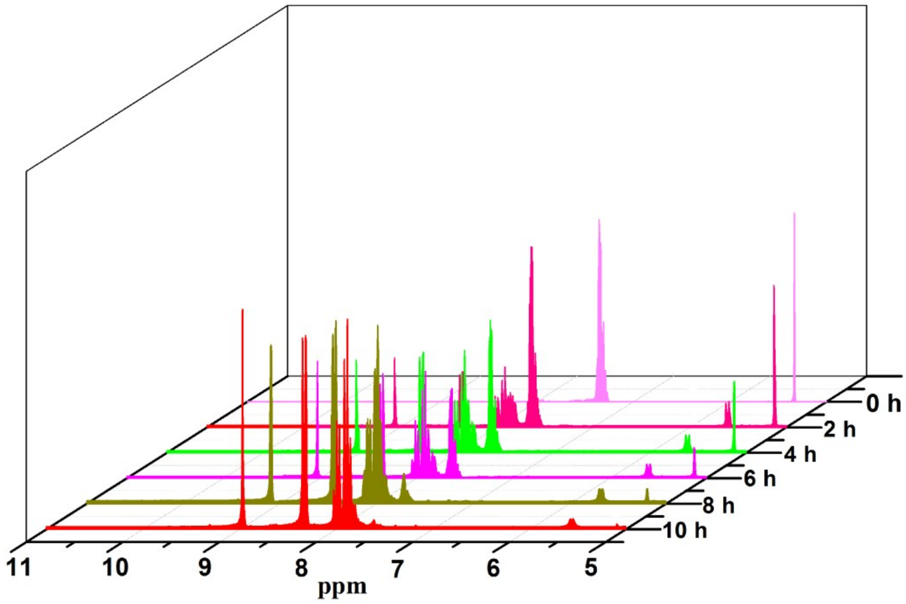


Fig. S7 ^{1}H NMR spectra of the deacetalization-Knoevenagel condensation reaction were catalyzed by PCN-222-Co@TpPa-1 hybrid material.

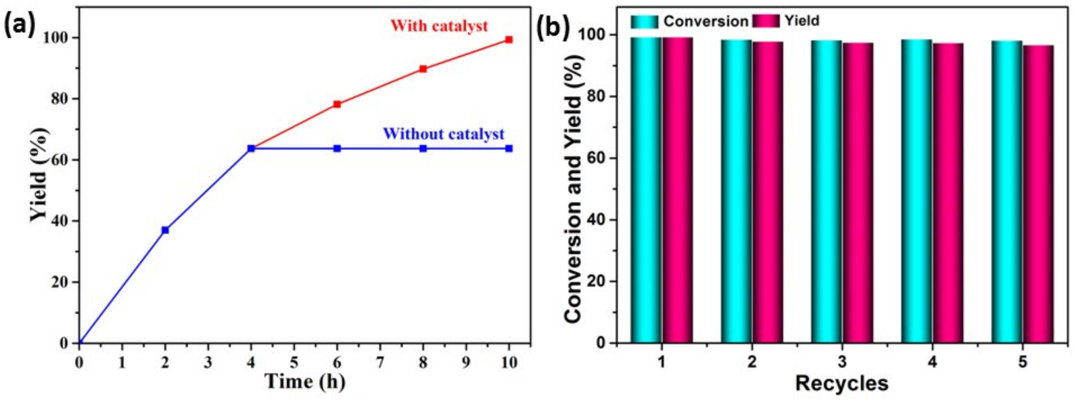


Fig. S8 (a) Hot filtration reactions. (red line) Normal reaction process; (blue line) PCN-222-Co@TpPa-1 was removed from the reaction mixture after 4 h; (b) Recycle capacity tests of PCN-222-Co@TpPa-1 for the cascade deacetalization-Knoevenagel reaction.

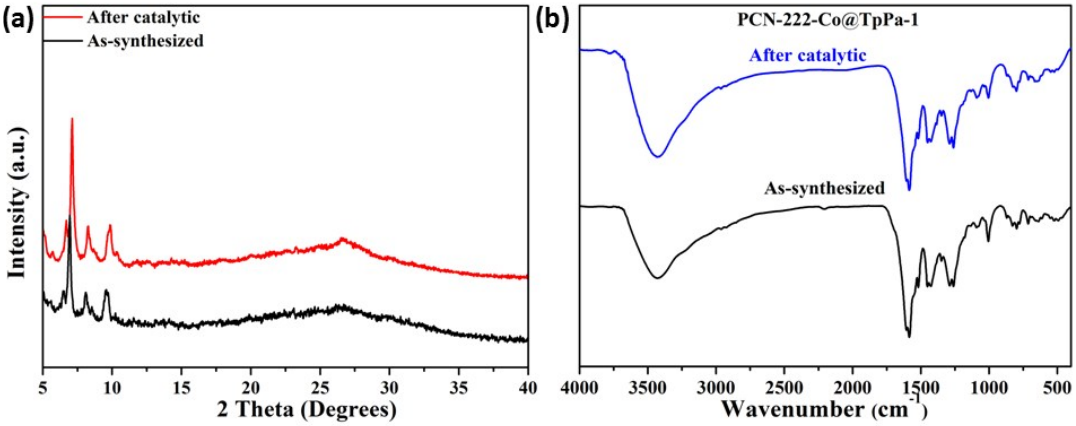


Fig. S9 (a) PXRD spectra of PCN-222-Co@TpPa-1 before and after deacetalization-Knoevenagel condensation reactions; (b) FT-IR spectra of PCN-222-Co@TpPa-1 before and after deacetalization-Knoevenagel condensation reactions.

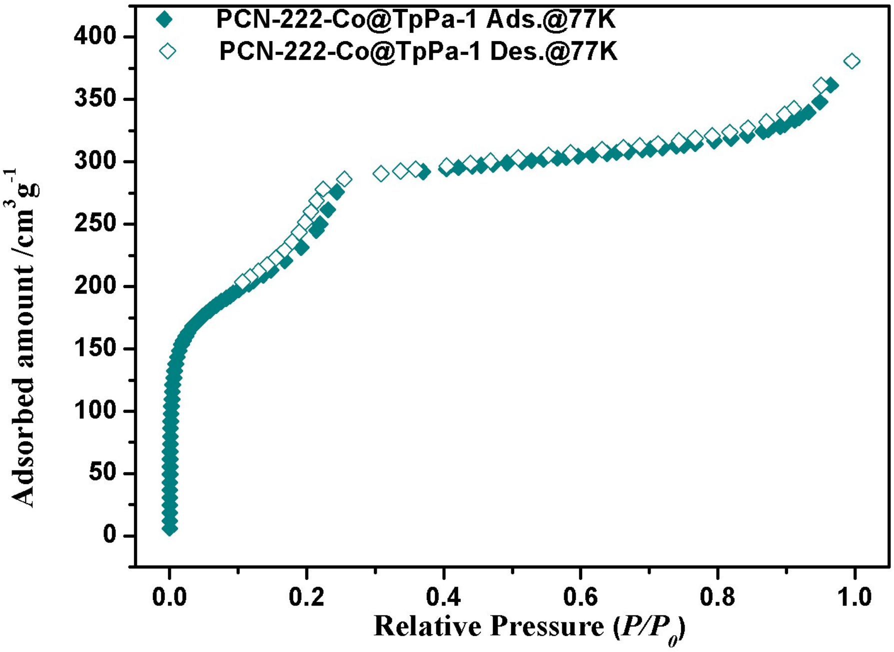


Fig. S10 N_2 sorption isotherms of PCN-222-Co@TpPa-1 after catalytic experiments.

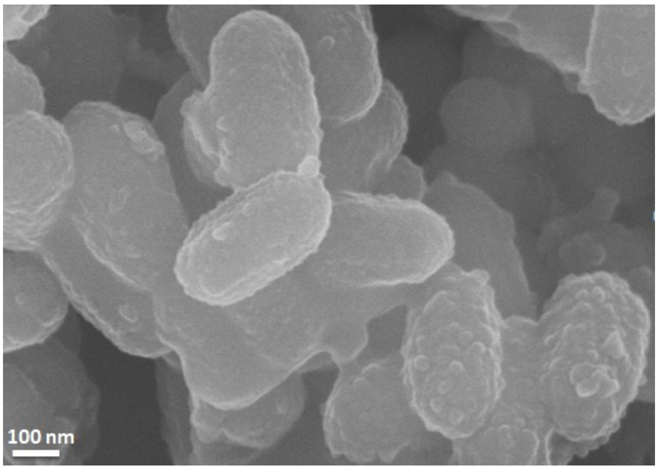


Fig. S11 SEM image of PCN-222-Co@TpPa-1 after deacetalization-Knoevenagel condensation reactions.