Supporting Information for:

Solid-state synthesis of a MOF/polymer composite for hydrodeoxygenation of vanillin

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Materials and methods

All chemicals were obtained from commercial sources (Sigma-Aldrich, Roth) and used without further purification.

Synthesis of Cr-BDC (Cr): In a 1 L Teflon jar containing 660 mL of deionized water, 52.8 g $Cr(NO_3)_3 \cdot 9H_2O$ (0.132 mol) 18.0 g BDC (0.108 mol) was dispersed. Next, 8.56 mL HNO_3 69% was added (0.132 mol, 1 eq respect chromium nitrate). The reaction mixture was stirred for 30 min, and then sealed in an 1 L autoclave that was placed in a preheated oven at 200 ^oC for 16 h. Next, the oven was turned off, and the reaction mixture was allowed to cool in the oven for a period of 12 h whereby the solid settled to the bottom. Next, some of the supernatant was decanted, and the solution was split into six 50 mL falcon tubes. The tubes were centrifuged for 10 min at 7800 rpm, and the remaining supernatant was removed and discarded. The solid after centrifugation in each falcon tube was washed once with 35 mL DMF while shaking for 10 min. Then the solid and liquid was transferred to a 500 mL glass jar, and 200 mL of fresh DMF was added. The mixture was then stirred at 700 rpm for 6 h. The solid was filtered, and the process was repeated 3 more times to ensure the removal of unreacted species. Next, the washing was again carried out, this time with ethanol. For this, 200 mL of fresh ethanol was added to the jar, which was stirred for 6 h. The process was repeated 3 additional times. Afterwards, the solid was filtered and dried in a vacuum oven at room temperature for 24 h. The material was subsequently heated up to 150 ^oC over a 2 h period and then held at this temperature for 12 h under vacuum prior to the N_2 adsorption measurements. Yield of MOF = 10.2 g.

Synthesis of Cr-BDC/PFT (3.2 wt% loading): 100 mg of the as-synthesized Cr-BDC (Cr) was ground in a mortar and pestle with 20 mg of thiourea and 16.4 mg of 2,5-diformylfuran for 15 minutes. The solid mixture was subsequently transferred into a 50 mL single neck round bottom flask and heated at 110^{o}C for 2 hours. The resulting powder underwent Soxhlet filtration with ethanol to remove unreacted monomers and likely short chain oligomers, and the sample was subsequently dried under vacuum for 24 hours at room temperature.

Synthesis of Cr-BDC/PFT (6.1 wt% loading):100 mg of the as-synthesized Cr-BDC (Cr) was ground in a mortar and pestle with 40 mg of thiourea and 32.8 mg of 2,5-diformylfuran for 15 minutes. The solid mixture was subsequently transferred into a 50 mL single neck round bottom flask and heated at 110^{o}C for 2 hours. The resulting powder underwent Soxhlet filtration with ethanol to remove unreacted monomers and likely short chain oligomers, and the sample was subsequently dried under vacuum for 24 hours at room temperature.

Synthesis of Cr-BDC/PFT (10.5 wt% loading): 100 mg of the as-synthesized Cr-BDC (Cr) was ground in a mortar and pestle with 80 mg of thiourea and 65.6 mg of 2,5-diformylfuran for 15 minutes. The solid mixture was subsequently transferred into a 50 mL single neck round bottom flask and heated at 110^{o}C for 2 hours. The resulting powder underwent Soxhlet filtration with ethanol to remove unreacted monomers and likely short chain oligomers, and the sample was subsequently dried under vacuum for 24 hours at room temperature.

Synthesis of Cr-BDC/PFT/Pd: 100 mg of CR-BDC/furan-urea (6.1 wt%) was dispersed in 40 mL of methanol via sonication for 10 minutes. To this dispersion, a solution of 1 mg palladium nitrate in 0.68 mL of MilliQ water was added in a dropwise fashion. Subsequently, 1 mL of 0.5 M $NaBH_4$ solution in methanol was added dropwise under vigorous stirring. The dispersion was subsequently stirred at room temperature for 1 hour, and the powder was isolated by centrifugation and washed with methanol (40 mL, 5 times for 5 minutes) to remove unreacted starting materials. Finally, the powder was dried under vacuum at room temperature.

Synthesis of bulk PFT polymer: In a mortar and pestle, 160 mg of thiourea and 131.2 mg of 2,5-diformylfuran were ground for 15 minutes. The solid mixture was subsequently transferred into a 50 mL single neck round bottom flask and heated at 110^{o}C for 2 hours. The resulting powder was washed with ethanol (6x) and the sample was subsequently dried under vacuum for 24 hours at room temperature.

Catalysis experiments: The catalytic experiments were carried out in a Parr autoclave (series 4600). Vanillin (40 mg), catalyst (5 mg) and ethanol (5 mL) were loaded into a glass test-tube and inserted into the autoclave. The autoclave was sealed and purged with H_2 gas 3 times. Finally, the autoclave was pressurized with 5 bars of H_2 and the reaction was carried out at 80 ^{o}C for 24 hours at a constant stirring speed of 500 rpm. The reaction products were isolated by centrifugation to remove the catalyst and analyzed on an Agilent GC-MS fitted with a HP5 column. The reaction condition optimization was carried out by varying the time, temperature, and pressure of hydrogen gas.

Catalyst cycling experiments: The catalytic experiments were carried out in a Parr autoclave (series 4600). Vanillin (40 mg), catalyst (5 mg) and ethanol (5 mL) were loaded into a glass test-tube and inserted into the autoclave. The autoclave was sealed and purged with H_2 gas 3 times. Finally, the autoclave was pressurized with 5 bars of H_2 and the reaction was carried out at 80 ^{o}C for 24 hours at a constant stirring speed of 500 rpm. The reaction products were isolated by centrifugation to remove the catalyst. The catalyst was further washed thrice with ethanol to remove the reaction products and then was added back to a fresh reaction mixture of vanillin and ethanol. This cycle was repeated up-to 5 times to check the recyclability of the catalytic system.

Characterization methods

Powder X-ray diffraction was performed on a Bruker D8 Discover system with a Cu Kα source (1.54056 Å) at 40 kV and 40 mA. The powder samples were loaded and flattened onto a zero-background silicon sample holder. The scanning range was 1–40° over 2885 steps at a scanning rate of 2 steps per second. The simulated powder diffraction pattern of the MOFs was calculated using Mercury 3.6 crystallography software from the .CIF files of the MOFs.

Nitrogen adsorption measurements were done on a Belsorp Max device. Samples (50–100 mg) were activated at 150 °C under vacuum for 12 hours. Nitrogen isotherms were obtained using incremental exposure of ultra-high purity nitrogen in a liquid nitrogen dewar at 77 K. The specific surface area was calculated by the BET method between a P/P0 range of 0.03–0.3.

X-ray photoelectron spectroscopy measurements were carried out using a Physical Instruments AG PHI VersaProbe II scanning XPS microprobe. Experiments were performed with a beam size of 100 µm using a monochromatic Al Kα X-ray source of 24.8 W power. The spherical capacitor analyzer was set at 45° take-off angle with respect to the sample surface. The pass energy was 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak. The data was analyzed using the CasaXPS software.

Scanning Electron Microscopy (SEM) images were taken using a FEI Teneo. SEM images were acquired using an in-column (Trinity) detector at an accelerating voltage of 1.0 kV. BF-TEM imaging was carried out on a Titan Themis equipped with EDX detectors at an acceleration voltage of 200 kV.

ATR-IR spectra were collected using a PerkinElmer Frontier MIR/FIR spectrometer equipped with a Quest ATR attachment. The sample was pressed on a diamond window and the spectra were recorded between 4000 and 400 cm−1 at a resolution of 4 cm−1 . The thermogravimetric analysis curve was obtained using a TA Q-Series TGA Q500. Samples were loaded onto a tared platinum pan. The balance flow rate was at 10 mL min−1 with nitrogen and the sample flow rate was at 25 mL min−1 with air heating at a rate of 5 °C per minute.

Solution NMR spectra were recorded in deuterated solvents at room temperature on a BRUKER AVIII HD 400 spectrometer. Mestrenova NMR software (version 11.0.1) were used to measure and analyze the data respectively. The catalytic yields, and conversions were determined using NMR and an Agilent 7890B-5977A GC-MS spectrometer equipped with a HP5 column.

Figure S1:

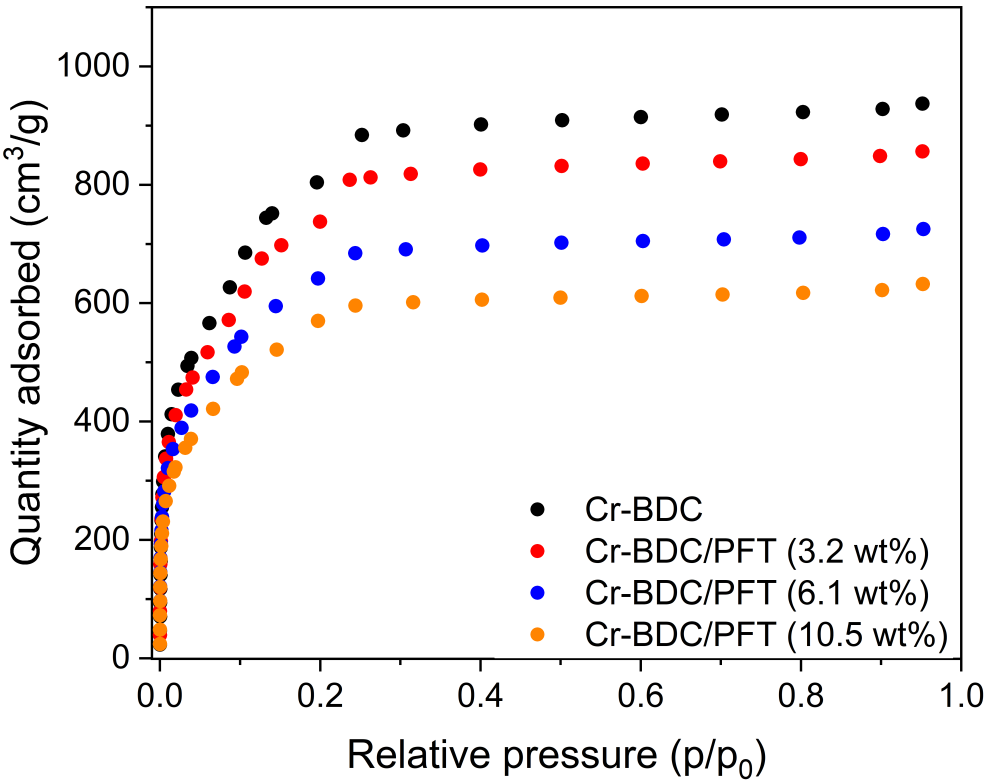


Figure **S1**. N_2 adsorption isotherms measured at 77 K for Cr-BDC and the three composites with successively higher loadings indicating decreased adsorption of N_2 likely due to pore filling by the polymer.

Figure S2:

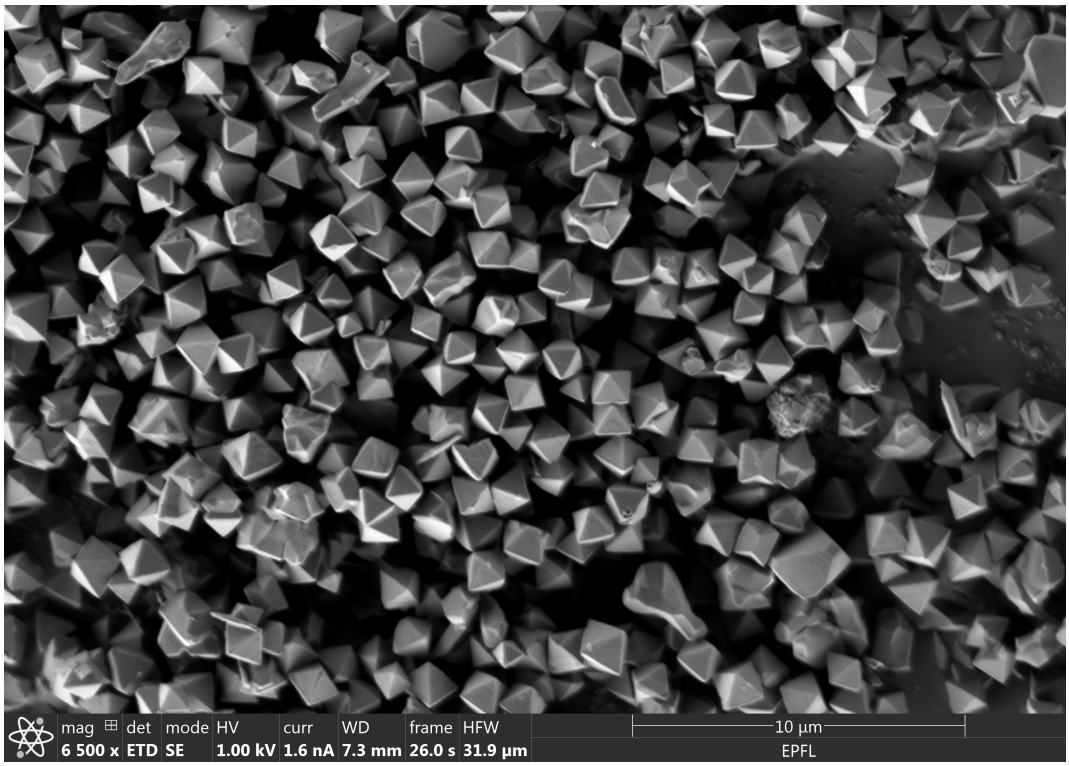


Figure **S2**. SEM image of the Cr-BDC framework indicating its octahedral morphology with an average particle size between 1-3 µm.

Table S3:

Catalyst	C (%)	H(%)	N (%)	S (%)
Cr-BDC	37.09	3.54	1.56	0.42
Cr-BDC/PFT-1	40.92	3.69	3.54	3.18
Cr-BDC/PFT-2	40.66	3.38	4.77	4.63
Cr-BDC/PFT-3	43.26	3.72	7.69	8.43

Table **S3**. Elemental analysis data obtained from the bare framework Cr-BDC and the three polymer loaded samples indicating an increase in the amounts of C, H, N and S elements on introduction of the polymer. The excess CHNS amounts were used to calculate the loading of the polymer within the MOF.

Figure S4:

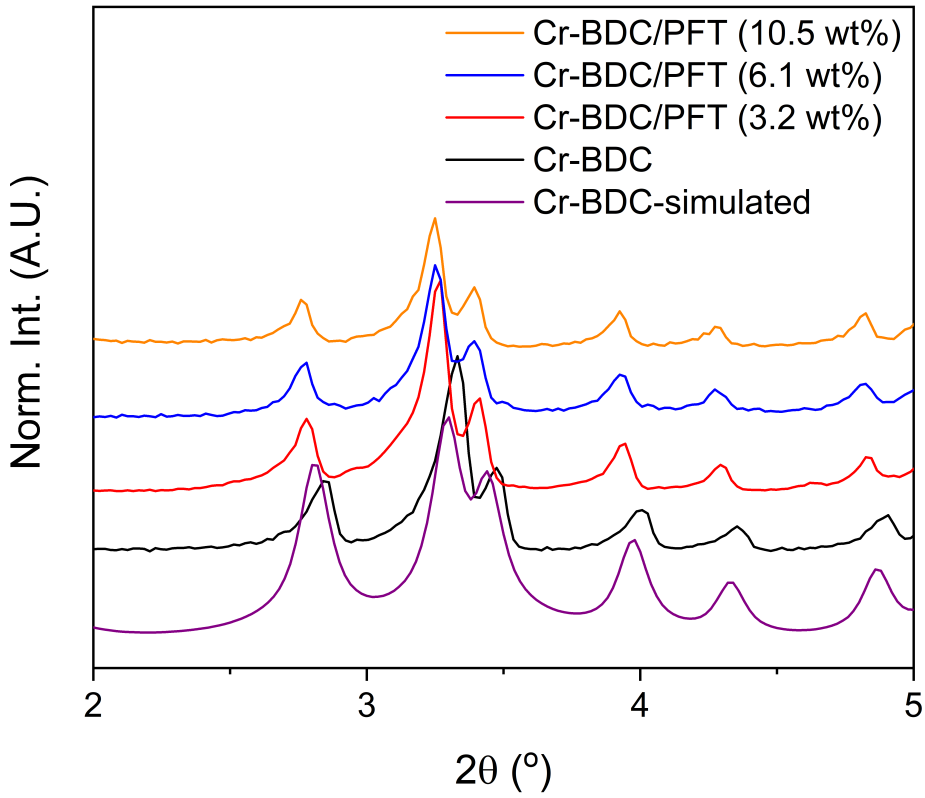


Figure **S4**. Powder X-ray diffractograms for the Cr-BDC (black) and the polymer loaded composites with 3.2 wt% loading (red), c6.1 wt% loading (blue) and 10.5 wt% loading (orange). There is a shift to lower diffraction angles for the peaks indicating an increase in unit cell volume due to polymer inclusion within the MOF pores.

Figure S5:

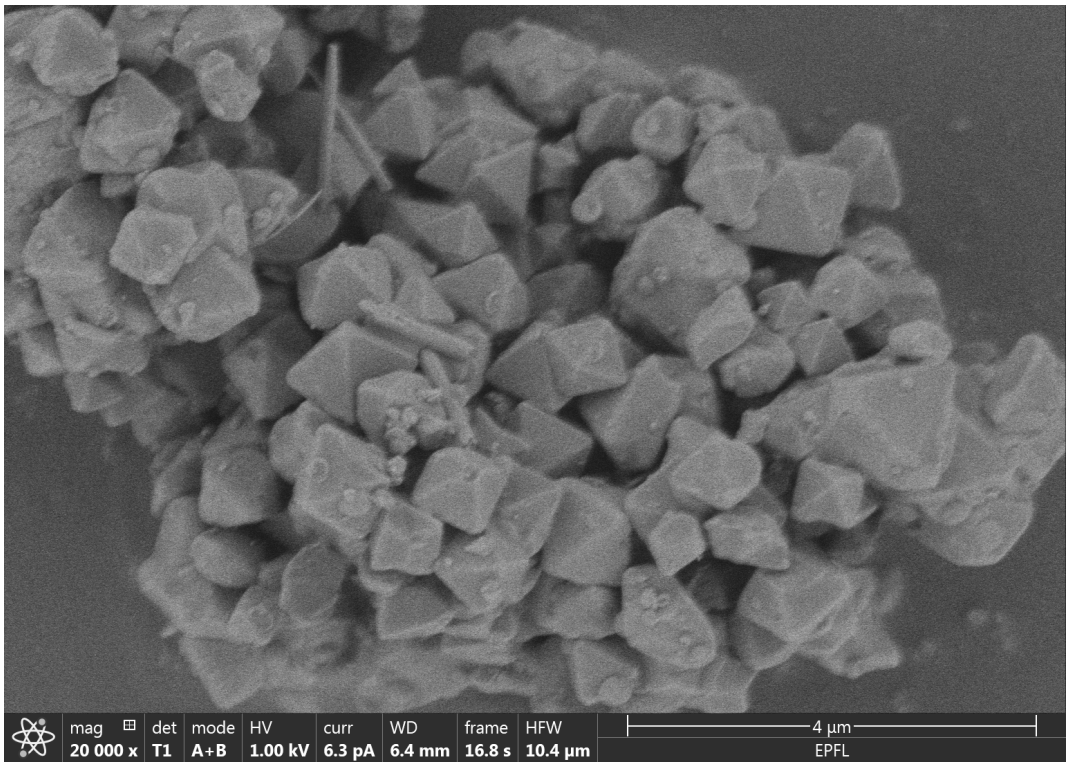


Figure **S5**. SEM image of the Cr-BDC/PFT (6.1 wt%) loaded framework indicating a retention of the octahedral morphology of the original MOF.

Figure S6:

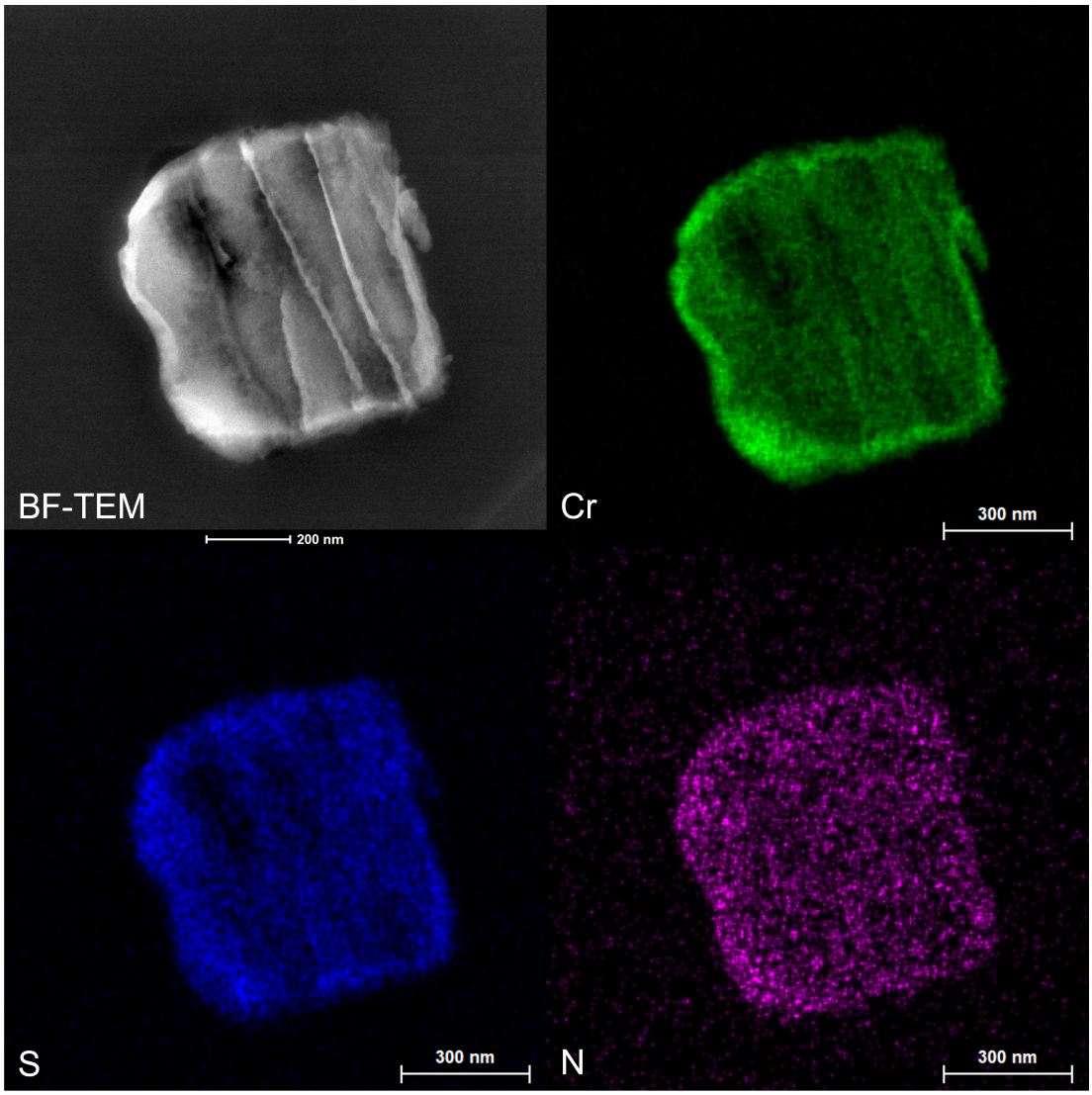


Figure **S6**. Bright-field TEM image and EDX maps for the Cr-BDC/PFT (6.1 wt%) composite indicating uniform distribution of Cr, N and S implying uniform polymer distribution.

Figure S7:

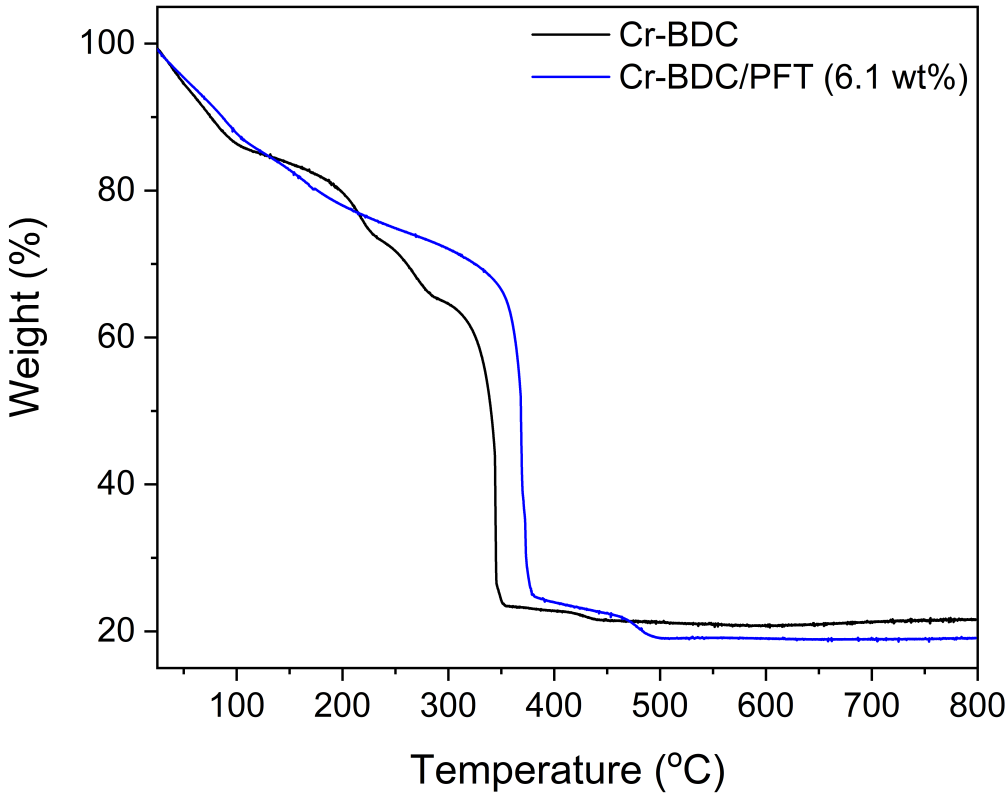


Figure **S7**. Thermogravimetric data for the Cr-BDC (black) and the 6.1 wt% loaded polymer composite indicating a slight enhancement in thermal stability on polymer inclusion due to interactions with the framework walls.

Figure S8:

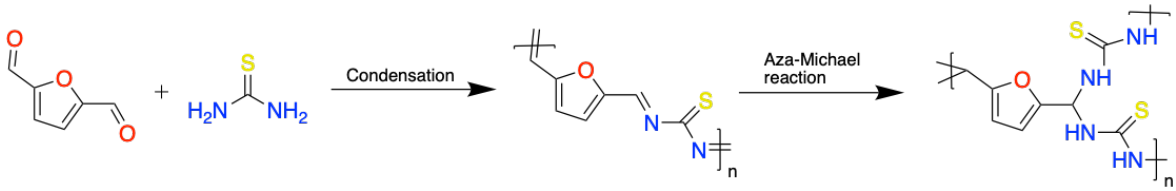


Figure **S8**. Reaction schematic showing the two steps involved in the polymerization process namely, (i) the condensation between the amine groups of thiourea and the aldehyde groups of diformylfuran forming the linear imine bridged polymer and (ii) Aza-Michael addition of the unreacted thiourea molecules on the imine carbon forming the branched secondary amine bridged polymer.

Figure S9:

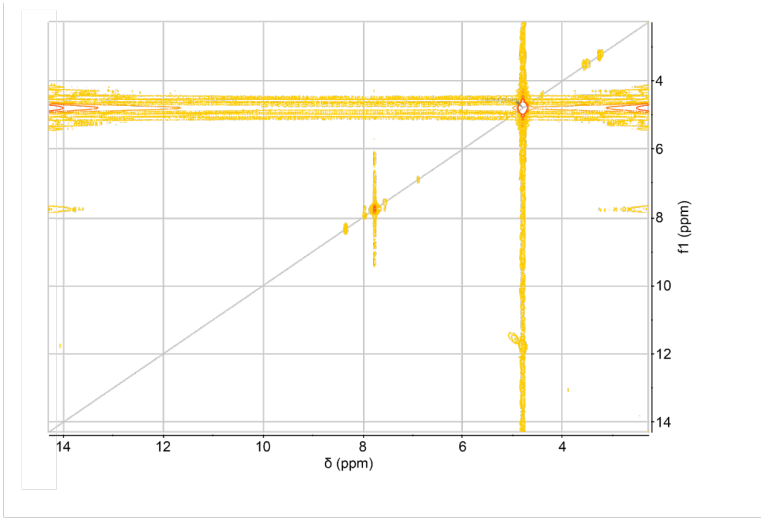


Figure **S9**. 2D COSY NMR spectrum indicating presence of no off-diagonal peaks.

Figure S10:

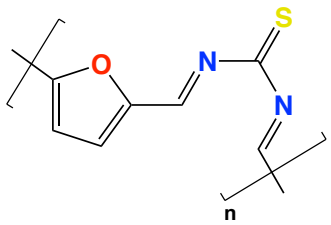


Figure **S10**. Possible structure of the smallest repeating unit of the polymer with a molecular weight of 164 based on the MALDI-TOF-MS data.

Figure S11:

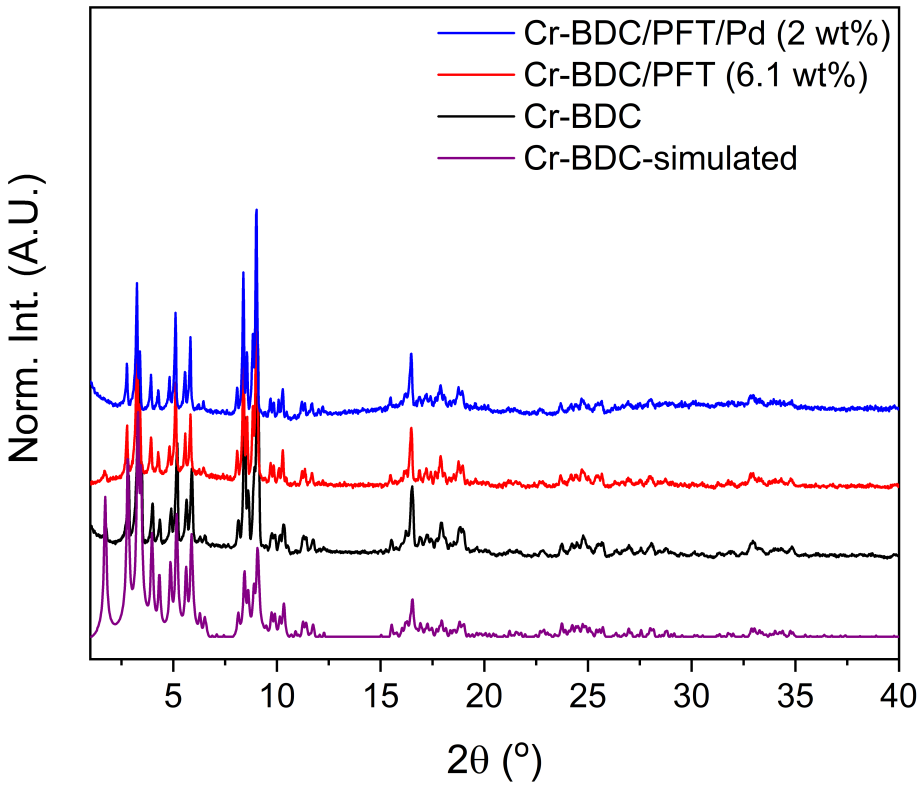


Figure **S11**. Powder XRD patterns for Cr-BDC and the samples modified with the polymer and the Pd nanoparticles.

Figure S12:

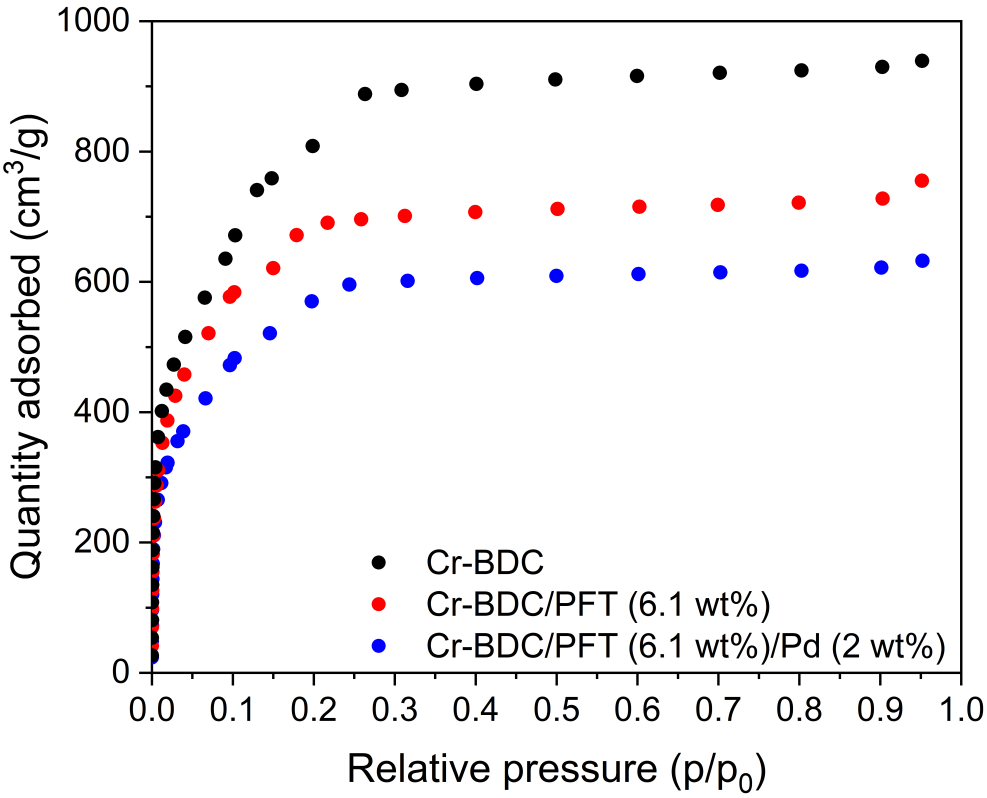


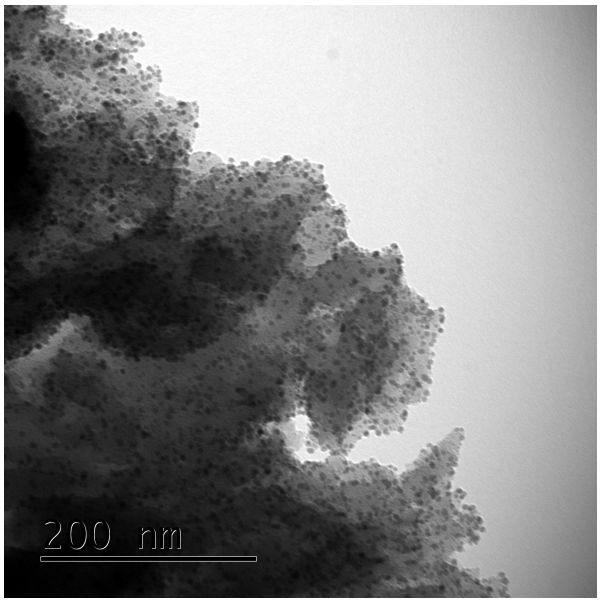
Figure **S12**. N_2 adsorption isotherms measured at 77 K for Cr-BDC and the samples modified with the polymer and the Pd nanoparticles.

Table S13:

Catalyst	Pd (wt %) in catalyst sample	Pd (wt%) in catalyst sample after 5 catalytic cycles
Cr-BDC/Pd	2.11	1.22
PFT/Pd	2.04	0.55
Cr-BDC/PFT/Pd	1.95	1.86
Pd/C	2.01	0.97
Pd weight % calculated by ICP-OES		

Table **S13**. ICP-OES data for the catalyst samples before and after the catalyst cycling indicating significant Pd leaching in case of the Cr-BDC/Pd, PFT/Pd and Pd/C catalysts.

Figure S14:



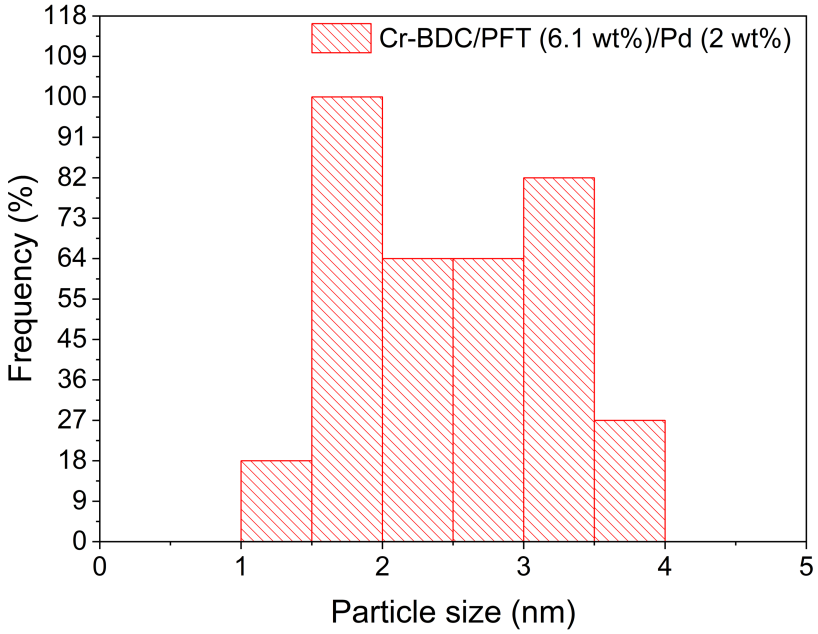


Figure **S14**. TEM image of the pristine Cr-BDC/PFT/Pd catalyst with the corresponding particle size distribution showing an average particle size between 1-4 nm with most being between 1.5 and 3.5.

Figure S15:

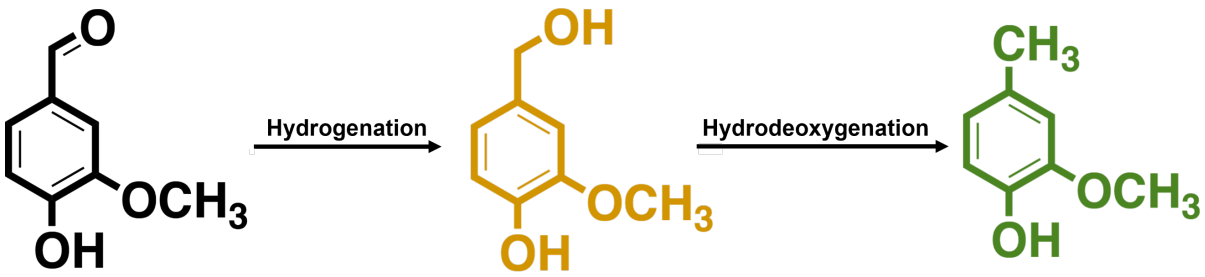


Figure **S15**. Reaction scheme for hydroprocessing of vanillin indicating the 2 reaction steps namely hydrogenation and hydrodeoxygenation.

Figure S16:

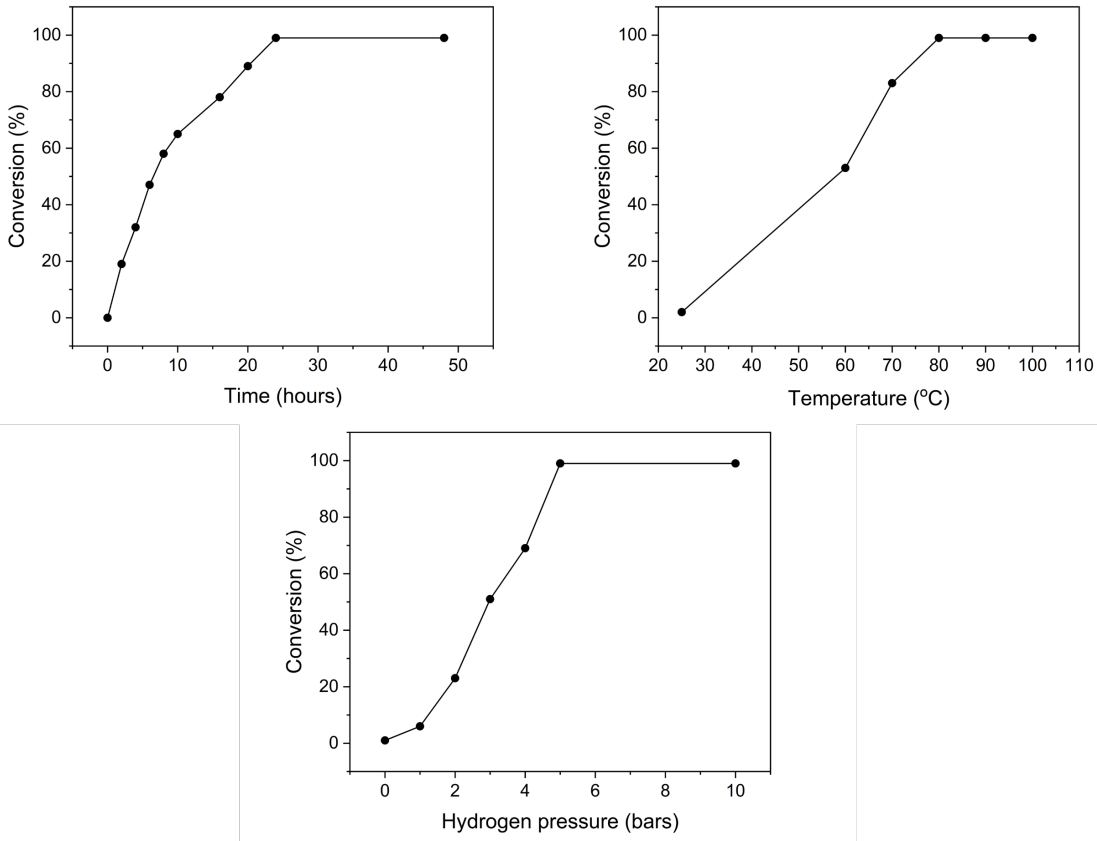


Figure **S16**. Reaction condition optimization for the hydrodeoxygenation of vanillin using the Cr-BDC/PFT/Pd catalyst indicating that the optimal reaction condition seems to be 80 °C, 5 bars of H_2 with a 24-hour reaction time. For all of these experiments the amount of vanillin was 40 mg and the amount of the catalyst was 5 mg. For the time and pressure plots, the temperature was kept constant at 90 °C, while for the pressure and temperature plots the time was kept constant at 30 hours. Finally, for the temperature and time plots the pressure was kept constant at 5 bars of H_2.

Table S17:

Catalyst	Conversion (%)	Selectivity (%)	Time (h)
no catalyst	<1	-	24
Cr-BDC	<1	-	24
Cr-BDC	<1	-	48
Cr-BDC/PFT (6.1 wt%)	<1	-	24
Cr-BDC/PFT (6.1 wt%)	<1	-	48

Table **S17**. Catalytic data for the conversion of vanillin using no catalyst, the bare framework, and the Cr-BDC/PFT composites indicating no activity of the materials without presence of Pd nanoparticles (vanillin (40 mg), catalyst (5 mg), ethanol (5 mL), 80 ^{o}C, 5 bars of H_2.

Figure S18:

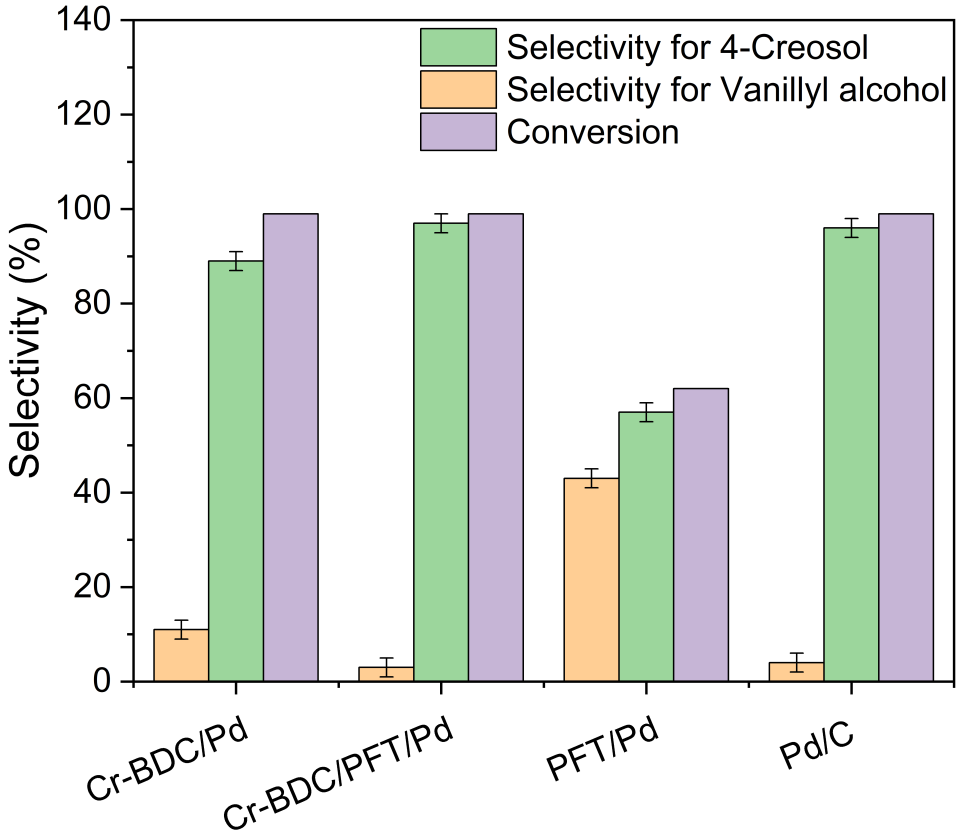


Figure **S18**. Comparison of the three catalysts and Pd/C under the optimized reaction conditions (vanillin (40 mg), catalyst (5 mg), ethanol (5 mL), 80 ^{o}C, 5 bars of H_2, 24 hours.

Figure S19:

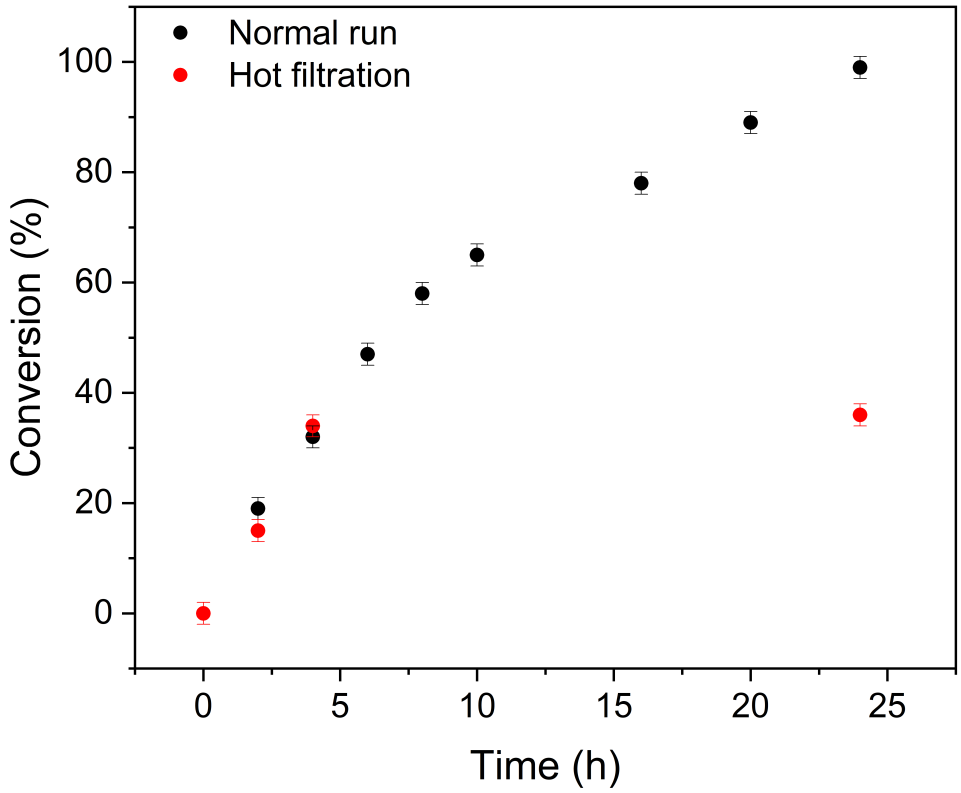
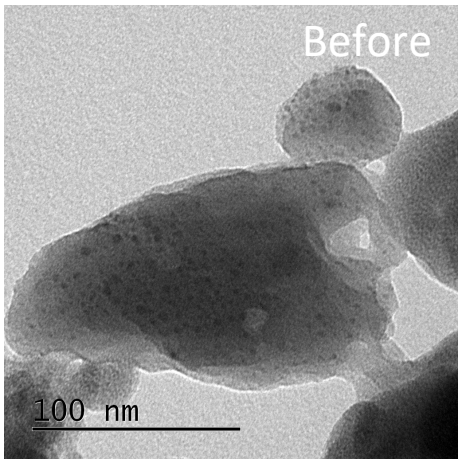
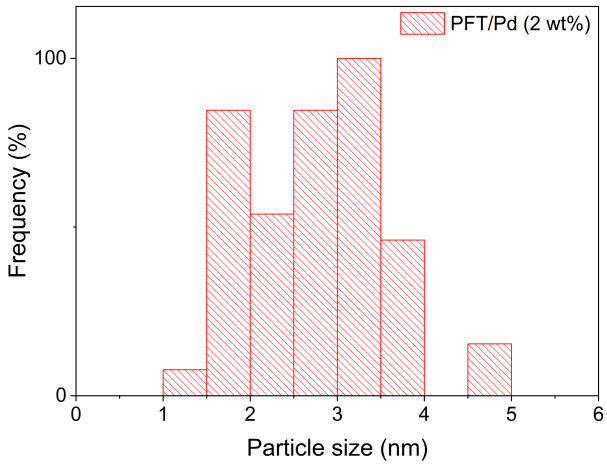
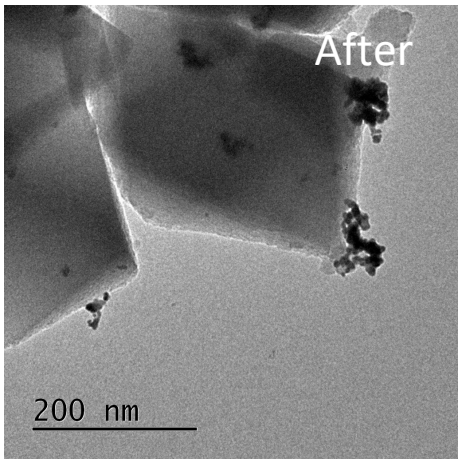


Figure **S19**. Hot filtration experiments indicating the heterogeneity of the catalytic process evidenced by no conversion seen after removal of the catalyst powder at the 5-hour mark.

Figure S20:







cFigure **S20**. TEM image and particle size distribution of the pristine PFT/Pd catalyst before the catalytic cycle and a representative TEM image of the PFT/Pd catalyst after a catalytic reaction showing Pd nanoparticle aggregation.

Figure S21:

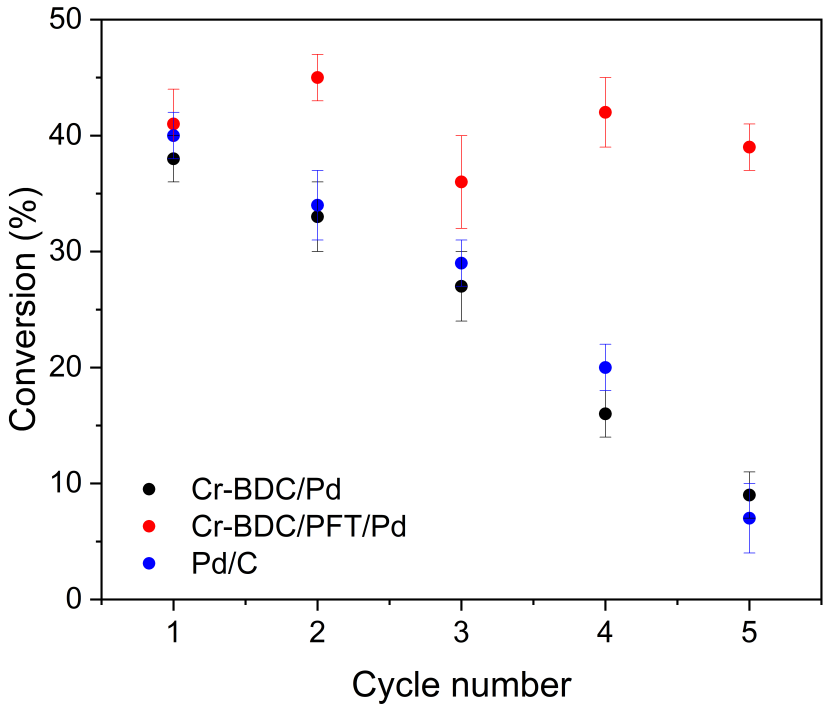


Figure **S21**. Conversion of vanillin with repeated cycling for (A) Cr-BDC/Pd catalyst, (B) Cr-BDC/PFT/Pd and Pd/C. Note, 8 hour cycles were used to ensure that the recyclability was checked at lower conversions.

Figure S22:

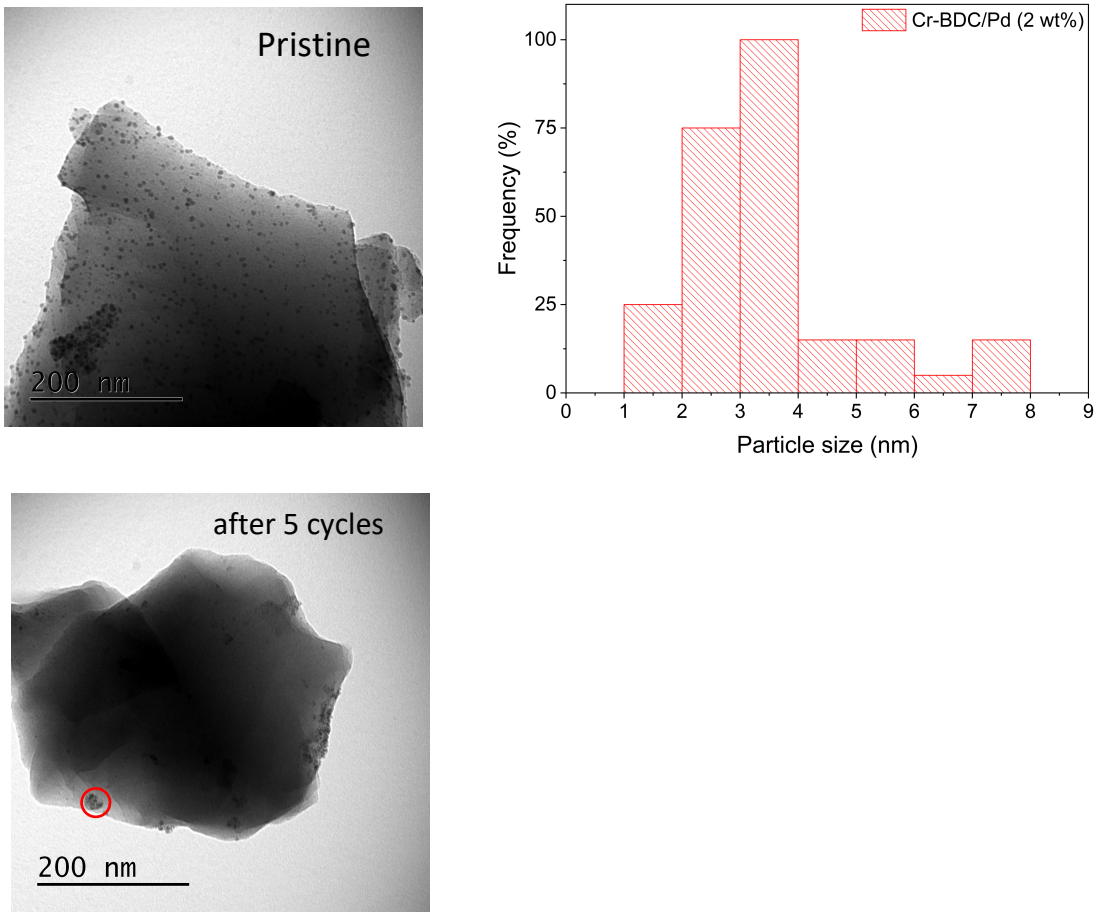


Figure **S22**. TEM image and particle size distribution of the pristine Cr-BDC /Pd catalyst and a TEM image of the catalyst after 5 cycles indicating significant leaching and aggregation (noted with a red circle) due to repeated catalyst use.

Figure S23:

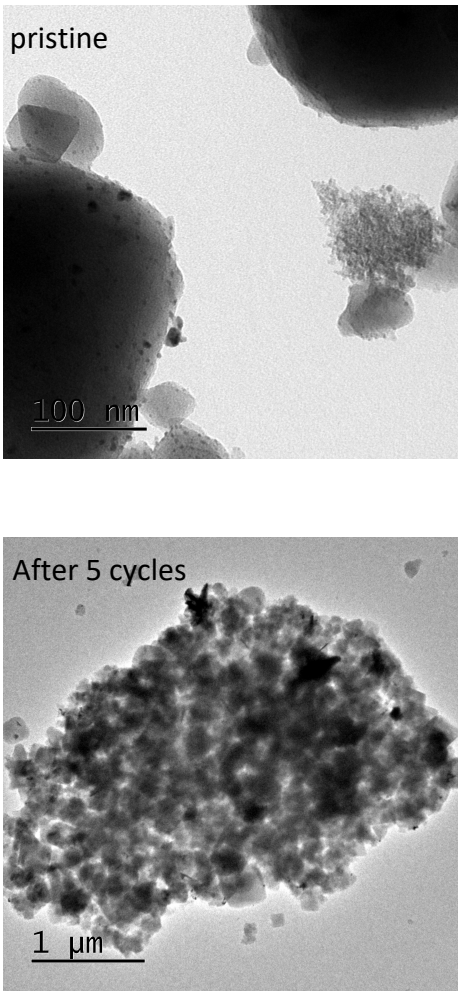


Figure **S23**. TEM images of the pristine Pd/C catalyst and the catalyst after 5 cycles indicating aggregation of the Pd nanoparticles.

Figure S24:

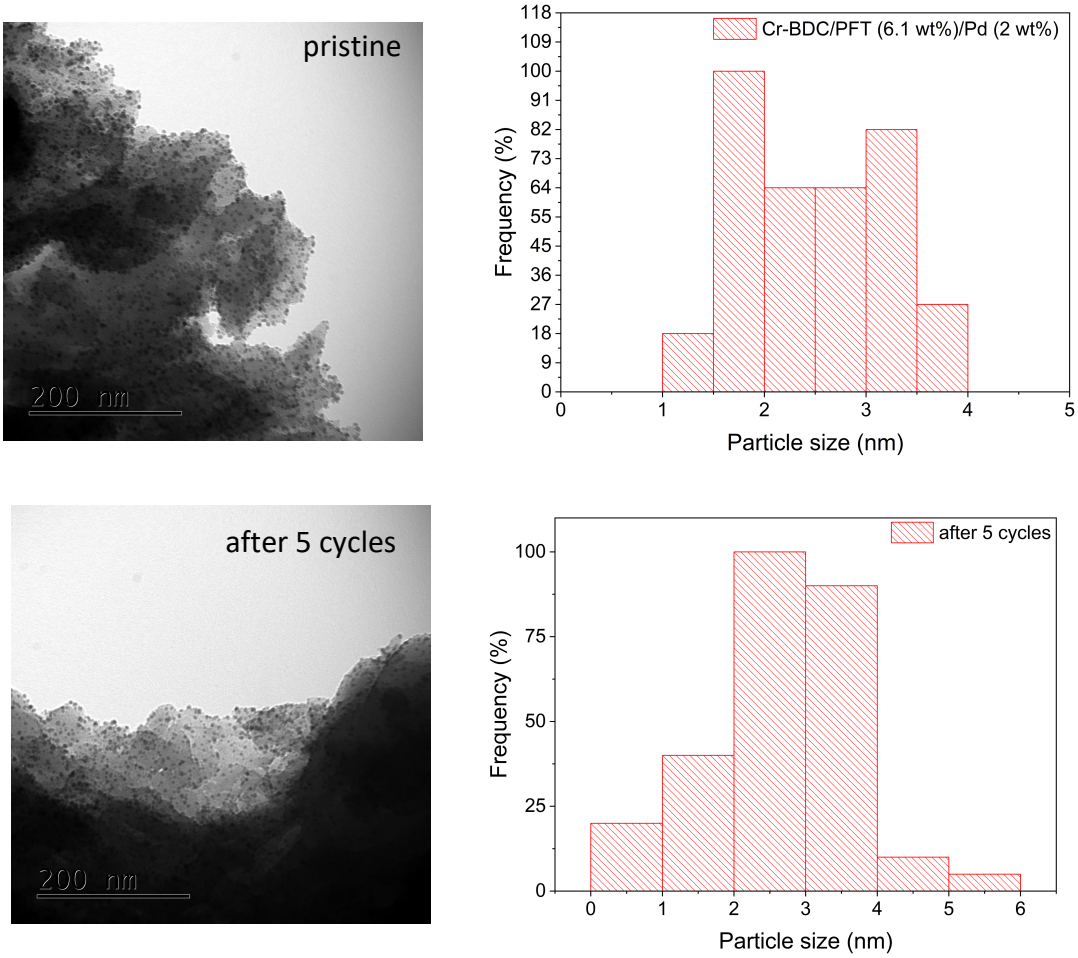


Figure **S24**. TEM images and the corresponding particle size distributions of the pristine Cr-BDC/PFT/Pd catalyst and the catalyst after 5 cycles indicating retention of Pd particle size due to strong binding with the polymer.

Figure S25:

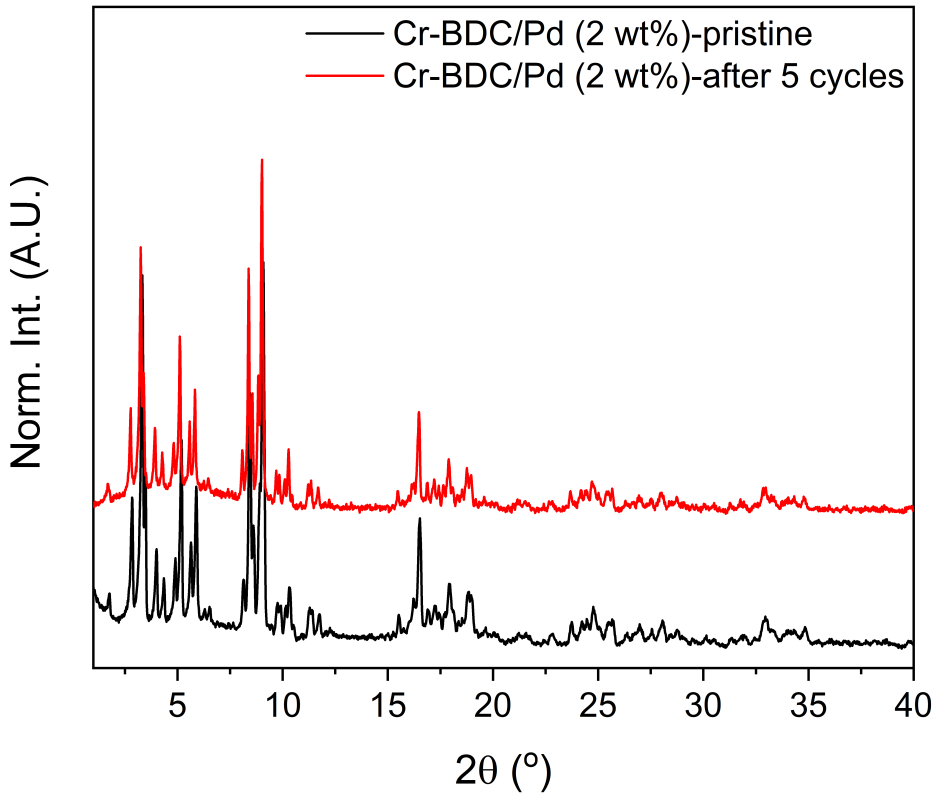


Figure **S25**. PXRD patterns of the pristine Cr-BDC/Pd (2 wt%) (black) and the same catalyst after 5 catalytic cycles (red) showing retention of catalyst crystallinity.

Figure S26:

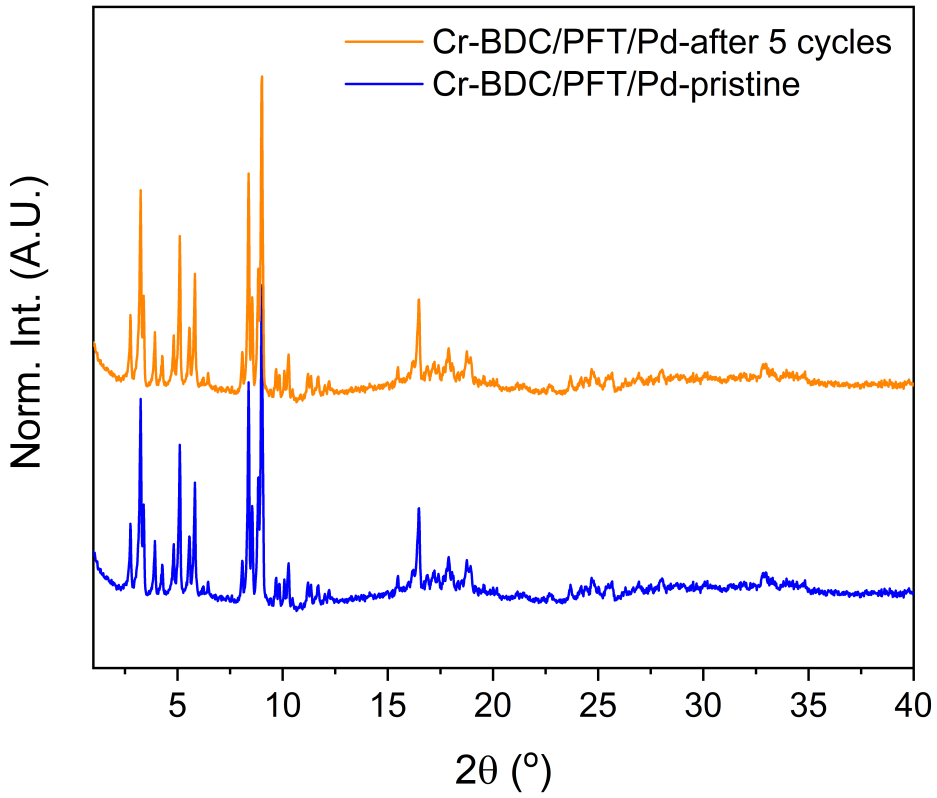


Figure **S26**. PXRD patterns of the pristine Cr-BDC/PFT/Pd (blue) and the same catalyst after 5 catalytic cycles (orange) showing retention of catalyst crystallinity.

Figure S27:

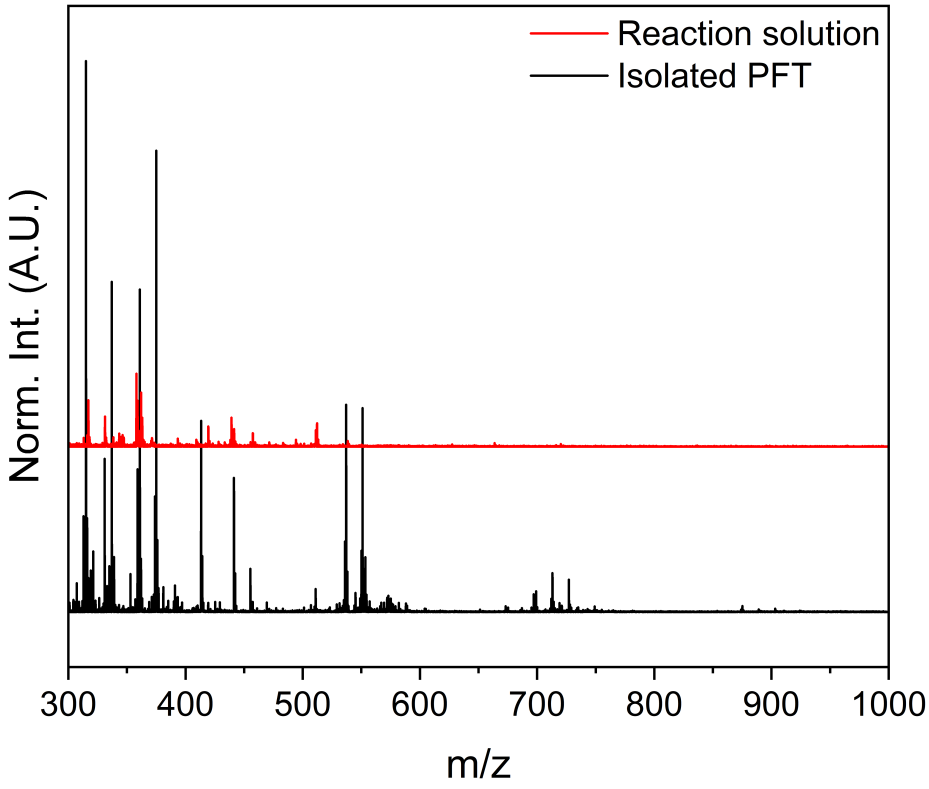


Figure **S27**. MALDI-TOF-MS comparing the mass spectrum of the isolated polymer from the and the reaction solution indicating no polymer leaching evidenced by the absence of the characteristic polymeric peaks between 500-600 and around 700 m/z.

Figure S28:

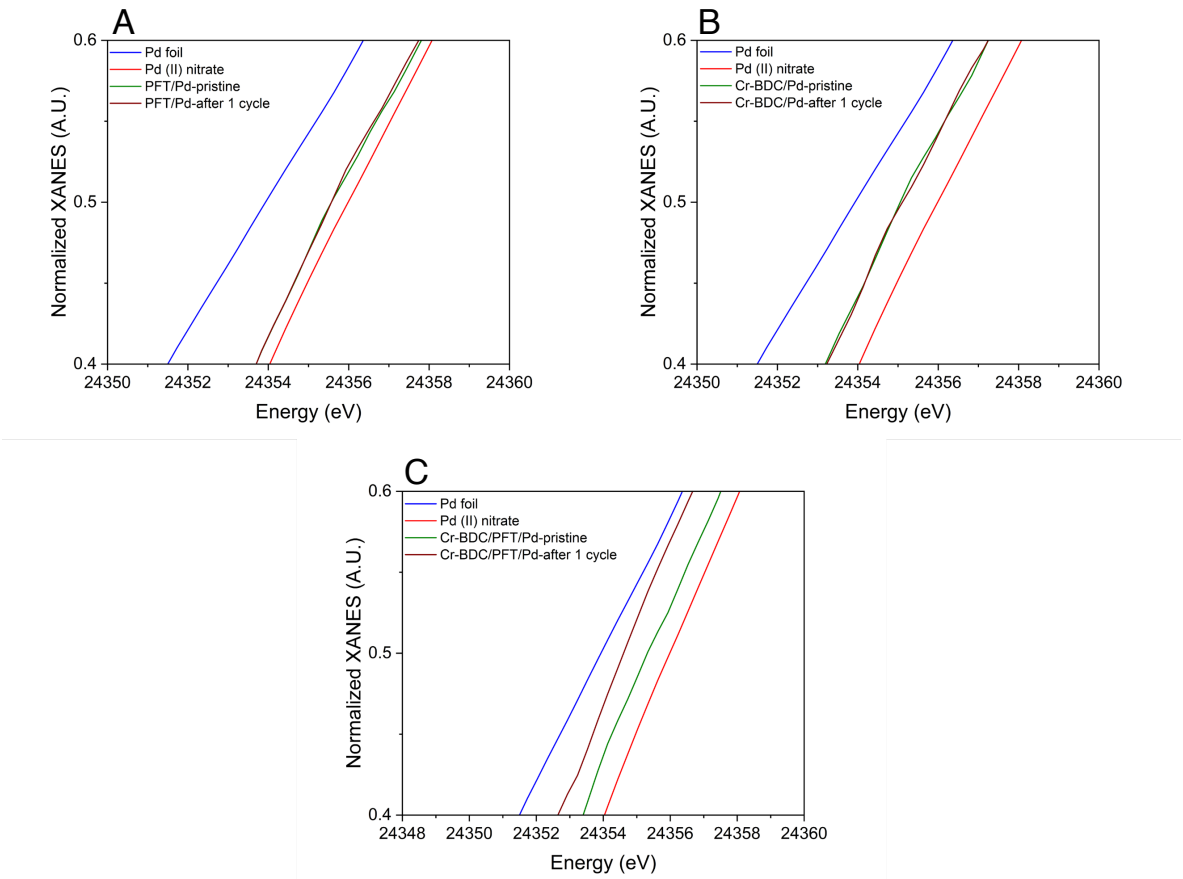


Figure **S28**. XANES spectra for the catalysts after one catalytic cycle indicating that the Pd species show a further reduction during the catalytic process in case of the Cr-BDC/PFT/Pd catalyst (C) only and minimal changes for the Cr-BDC/Pd (B) and PFT/Pd catalysts (A). This indicates that the catalyst state can be altered during the catalytic cycle by the MOF/polymer composite, and this could be another factor which prolongs catalyst lifetime.

Figure S29:

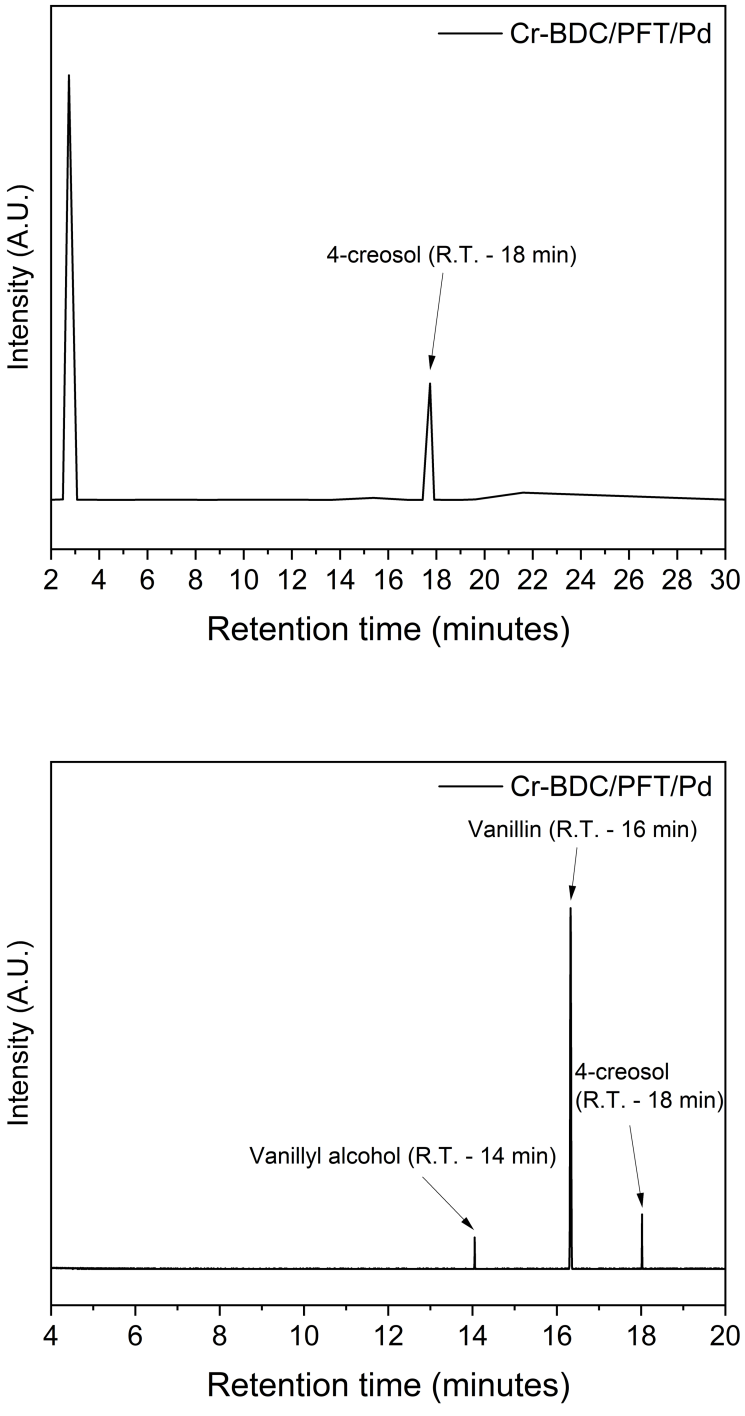


Figure **S29**. Representative GC-MS chromatogram for a catalytic run under the optimized reaction conditions with Cr-BDC/PFT/Pd indicating the presence of only 4-creosol. Expected retention times from standard mixtures: vanillin (R.T. – 16 minutes), vanillyl alcohol (14 minutes), 4-creosol (18 minutes).