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Supplementary Information for

Influence of Nanoscale Structuralisation on the Catalytic Performance of ZIF-8: A Cautionary Surface Catalysis Study

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S1 Synthetic protocols for ZIF-8

ZIF-8 50 nm: Zinc nitrate hexahydrate ($Zn(NO_2)_3 \cdot 6H_2O$, 58.8 mg, 0.197 mmol) was dissolved in methanol (4 mL) and in a separate vial 2-methylimidazole (2-mIM, 64.8 mg, 0.787 mmol) was dissolved in methanol (4 mL) with NaOH (2 M, 0.295 mL, 0.591 mmol). Both solutions were sonicated until the solids dissolved, the zinc nitrate solution added to the solution of 2-mIM, and the mixture was left at room temperature (25 °C) for 24 h in a 20 mL screw cap vial. The resultant white suspension was washed with methanol (5×10 mL) then dried resulting in a colourless micro-crystalline powder (34.4 mg, 76%).

ZIF-8 100 nm: $Zn(NO_2)_3 \cdot 6H_2O$ (58.8 mg, 0.197 mmol) was dissolved in methanol (4 mL) and in a separate vial 2-mIM (64.8 mg, 0.787 mmol) was dissolved in methanol (4 mL). Both solutions were sonicated until the solids dissolved, the zinc nitrate solution added to the solution of 2-mIM and the mixture was left at room temperature (25 °C) for 24 h in a 20 mL screw cap vial. The resultant white suspension was washed with methanol (5×10 mL) then dried resulting in a colourless micro-crystalline powder (10.5 mg, 23%).

ZIF-8 500 nm: Zinc bromide ($ZrBr_2$, 44.4 mg, 0.197 mmol), was dissolved in methanol (4 mL). In a separate vial 2-mIM (64.8 mg, 0.787 mmol) was dissolved in methanol (4 mL). Both solutions were sonicated until the solids dissolved. The solutions were combined, and the mixture was left at room temperature (25 °C) for 24 h in a 20 mL screw cap vial. The resultant white suspension was washed with methanol (5×10 mL) then dried resulting in a colourless micro-crystalline powder (4.2 mg, 9%).

ZIF-8 500 nm cubic: $Zn(NO_2)_3 \cdot 6H_2O$ (29.0 mg, 0.097 mmol) was dissolved in MilliQ water (4 mL). In a separate vial 2-mIM (454.0 mg, 5.530 mmol) was dissolved in MilliQ water (4 mL) and cetyltrimethylammonium bromide (CTAB, 79 µl, 0.01 M). Both solutions were sonicated until the solids were dissolved. The zinc nitrate solution was added to the solution of 2-mIM and CTAB and the mixture was heated at 100 °C for 24 h in a 20 mL screw cap vial. The resultant white suspension was washed with methanol (5×10 mL) then dried resulting in a colourless micro-crystalline powder (16.2 mg, 73%).

ZIF-8 1 µm: $Zn(NO_2)_3\cdot 6H_2O$ (58.8 mg, 0.197 mmol) was dissolved in methanol (4 mL) while in a separate vial 2-mIM (64.8 mg, 0.787 mmol) and 1-methylimidazole (1-mIM, 64.8 µl, 0.787 mmol) were dissolved in methanol (4 mL). Both solutions were sonicated until the solids dissolved. The zinc nitrate solution was added to the solution of 2-mIM and the mixture was left at room temperature (25 °C) for 24 h in a 20 mL screw cap vial. The resultant white suspension was washed with methanol (5×10 mL) then dried resulting in a colourless crystalline powder (3.1 mg, 7%).

ZIF-8 10 µm: $Zn(NO_2)_3\cdot 6H_2O$ (176.4 mg, 0.593 mmol) was dissolved in methanol (4 mL) and in a separate vial 2-mIM (97.2 mg, 1.184 mmol) and sodium formate (HCOONa, 80.7 mg, 0.789 mmol) were dissolved in methanol (4 mL). Both solutions were sonicated until the solids dissolved, the zinc nitrate solution added to the solution of 2-mIM in a 20 mL screw cap vial, and the mixture was heated at 50 °C for 24 h. The resultant clear crystals were washed with methanol (5×10 mL) then dried resulting in a colourless crystalline powder (14.8 mg, 11%).

ZIF-8 100 µm: $Zn(NO_2)_3\cdot 6H_2O$ (134.0 mg, 0.450 mmol) was dissolved in DMF (5 mL). In a separate vial 2-mIM (33.4 mg, 0.407 mmol) was also dissolved in DMF (5 mL). Both solutions were sonicated until the solids dissolved, the zinc nitrate solution added to the solution of 2-mIM in a 20 mL screw cap vial and the mixture was heated at 140 °C for 24 h. The resultant clear crystals were washed with DMF (2×10 mL) methanol (5×10 mL) then dried resulting in a colourless crystalline powder (46.9 mg, 50%). PXRD indicated a small amount of ZnO contaminant.

ZIF-8 100 µm truncated rhombic dodecahedron (trd): $Zn(NO_2)_3\cdot 6H_2O$ (352.8 mg, 1.186 mmol) was dissolved in methanol (4 mL) and in a separate vial 2-mIM (194.4 mg, 2.368 mmol) and sodium formate (180.7 mg, 2.657 mmol) were dissolved in methanol (4 mL). Both solutions were sonicated until the solids dissolved. The solutions were combined in a 20 mL screw cap vial and the mixture was heated at 50 °C for 24 h. The colourless crystals were washed with methanol (5×10 mL) then dried resulting in a colourless crystalline powder (17.3 mg, 6%).

Activation procedure: The as-synthesised samples were washed with methanol (×5), dried under a nitrogen flow, and stored under vacuum in a desiccator for 1 h prior to use. For gas adsorption activation the “dried” sample was then heated under a high vacuum at 100 °C for 3 h. Activation yielded colourless microcrystalline powders.

S2 Transesterification catalytic control experimentals

S2-1 Stirred agitation

2-mIM (14.42 mg, 0.176 mmol) was dissolved in hexanol (20 ml), the solution was stirred under an atmosphere of nitrogen for 1 h at 65 °C. Vinyl acetate (3.3 ml, 35.79 mmol) was added to the reaction mixture, which was then heated at 65 °C for 6 h. The progress of the reaction was followed via GC-MS, as outlined in the experimental.

A blank was run with just hexanol and vinyl acetate, a zinc control was run with a molar equivalent of $Zn(NO_3)_2$ to ZIF-8 (26.14 mg, 0.088 mmol) in place of 2-mIM and a mixed control of $Zn(NO_3)_2$ (26.14 mg, 0.088 mmol) and 2-mIM (14.42 mg, 0.175 mmol) was also done. All reagents were fully dissolved in hexanol prior to heating or addition of vinylacetate.

S2-2 Shaking agitation

2-mIM (7.21 mg, 0.088 mmol) was dissolved in hexanol (10 ml), the solution was dispersed via shaking at 165 rpm for 1 h at 60 °C. Vinyl acetate (1.65 ml, 17.89 mmol) was added to the reaction mixture, which was then heated at 60 °C for 6 h. The progress of the reaction was followed via GC-MS, as outlined in the experimental.

A blank was run with just hexanol and vinyl acetate, a zinc control was run with a molar equivalent of $Zn(NO_3)_2$ to ZIF-8 (13.07 mg, 0.044 mmol) in place of 2-mIM and a mixed control of $Zn(NO_3)_2$ (13.07 mg, 0.044 mmol) and 2-mIM (7.21 mg, 0.088 mmol) was also done. All reagents were fully dissolved in hexanol prior to heating or addition of vinylacetate.

An additional control was run to assess the activity of leached Zn^{2+} in solution, whereby a standard reaction was set up with **ZIF-8 50 nm** (10 mg, 0.044 mmol) dispersed in hexanol (10 ml) via shaking at 165 rpm for 1 h at 60 °C. Vinyl acetate (1.65 ml, 17.89 mmol) was added to the reaction mixture, which was then heated at 60 °C for 6 h. At the 3 h time point the ZIF-8 catalyst was removed by centrifugation at 10000 rpm and the supernatant was then heated for a further 3 h. The progress of the reaction was followed via GC-MS, as outlined in the experimental. See Figure 3c for GC-MS results for catalytic controls.

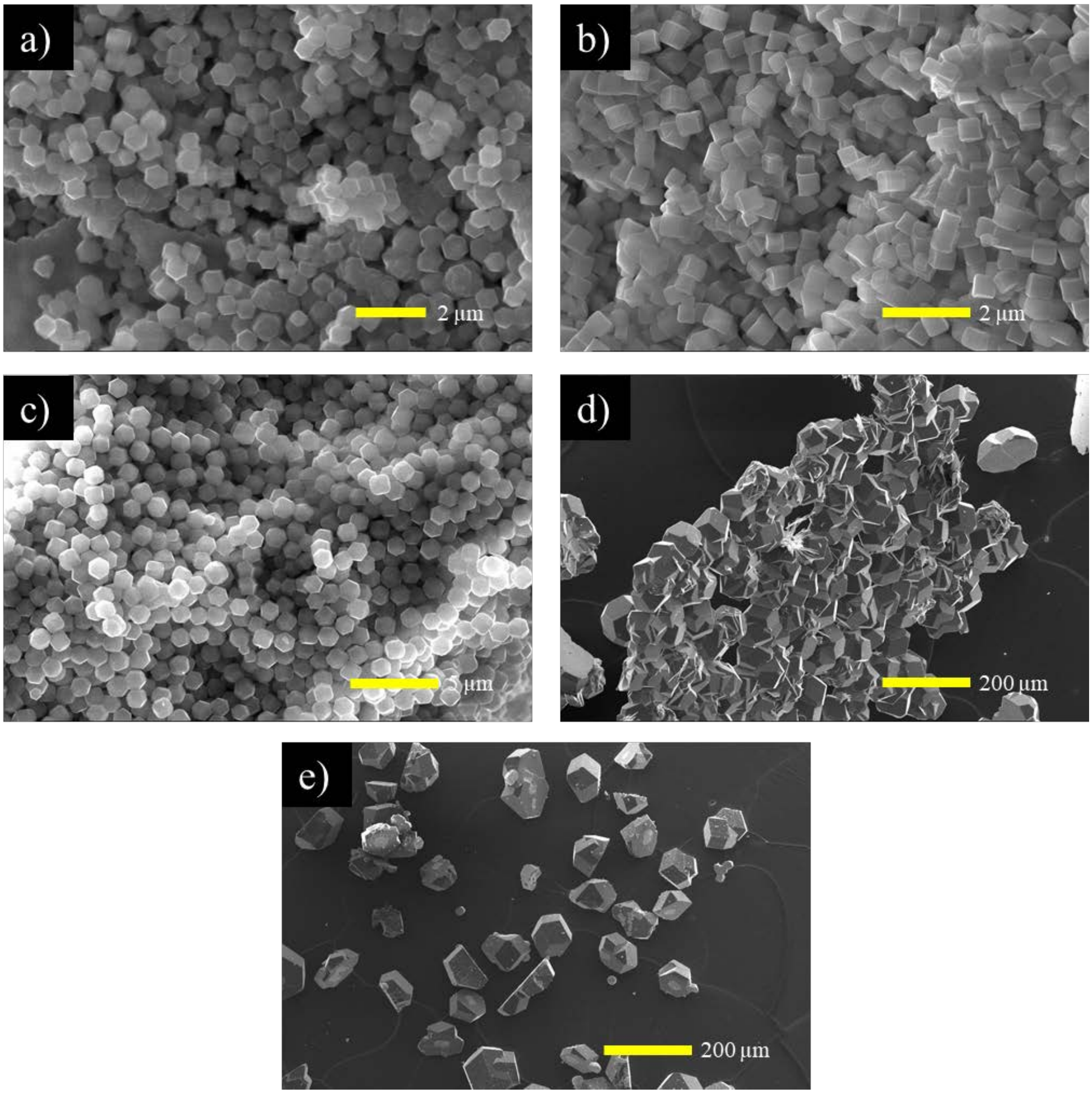

Figure S1: Scanning electron microscope images of ZIF-8 samples for particle size distribution analysis for a) **ZIF-8 500 nm**, b) **ZIF-8 500 nm Cubic**, c) **ZIF-8 1 µm**, d) **ZIF-8 100 µm**, e) **ZIF-8 100 µm Truncated Rhombic Dodecahedra**.

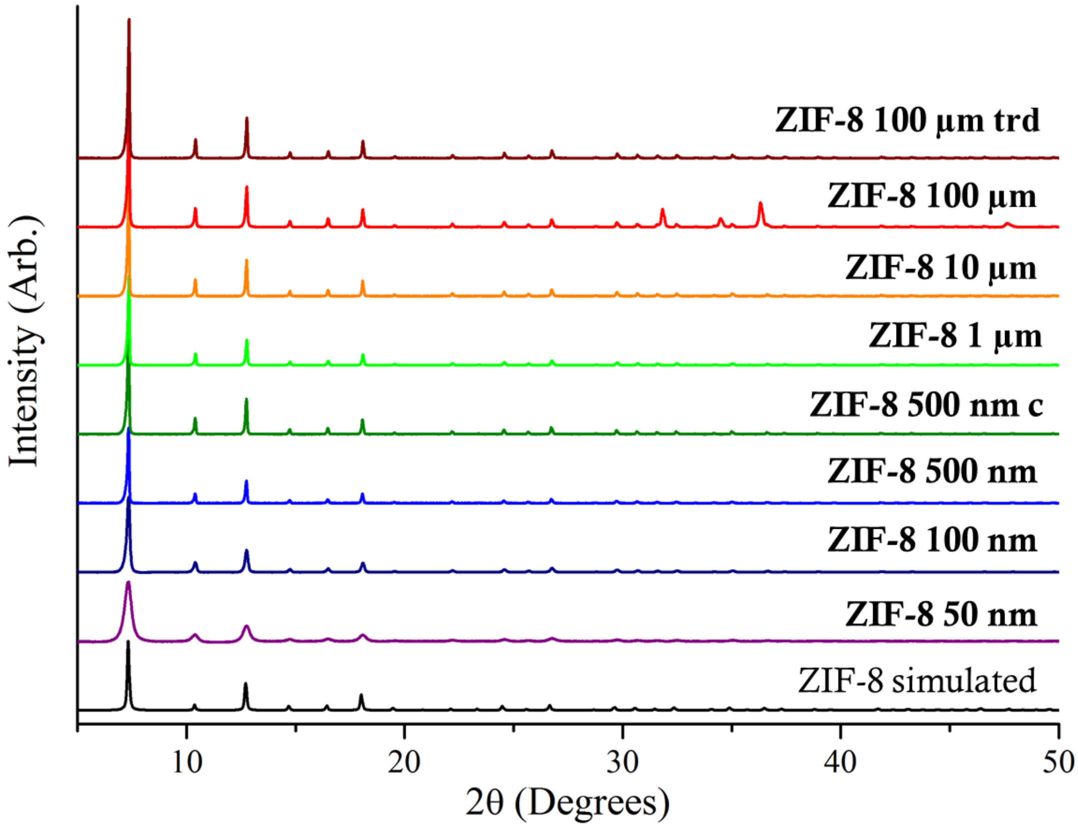

Figure S2: Powder X-ray diffraction patterns of ZIF-8 samples; simulated, **ZIF-8 50 nm**, **ZIF-8 100 nm**, **ZIF-8 500 nm**, **ZIF-8 500 nm c** (cubic), **ZIF-8 1 µm**, **ZIF-8 10 µm**, **ZIF-8 100 µm**, **ZIF-8 100 µm trd** (truncated rhombic dodecahedra). Note all morphologies of ZIF-8 were rhombic dodecahedra unless otherwise specified. The conditions used to form **ZIF-8 100 µm** led to the formation of ZnO, seen in the PXRD trace.

S3 Development of catalysis testing conditions

Preliminary testing showed that the progress of the reaction between vinylacetate and MeOH-d_4, catalysed by ZIF-8, could be followed by ^{1}H NMR spectroscopy, with an increased production of methyl acetate observed with increasing temperature from 25 to 55 °C, (See S3-1, Figure S3). PXRD analysis demonstrated that the crystallinity of the ZIF-8 catalyst was retained post catalysis after 24 h (Figure S4). To facilitate analysis by GC-MS methods, hexanol was used in place of methanol to ensure accurate product quantification (hexyl-acetate is easily distinguished from hexanol and the chosen internal standard propyl-propionate), see Figures S5 & S6.

S3-1 ^{1}H NMR analysis of the transesterification of vinyl acetate with d_4MeOH

Dried **ZIF-8 1 µm** (5 mg, 0.022 mmol) was dispersed in d_4MeOH (1 ml) at room temperature into 4 identical 2.5 ml vials. To these solutions vinyl acetate (82.5 µl, 0.895 mmol) was added and the solution was heated at 25, 35, 45 and 55 °C for 24 h. The solutions were then centrifuged at 10,000 rpm, the ZIF-8 catalyst was separated from the supernatant which was then analysed via ^{1}H NMR (see Figure S3). The ^{1}H NMR signals corresponding to methyl acetate, vinyl acetate, acetaldehyde and the hemiacetal, that were detected after the reaction in d_4MeOH, were as follows: methyl acetate ^{1}H NMR (500 MHz/d_4MeOH): δ 2.03 (3H, s, CH_3); vinyl acetate ^{1}H NMR (500 MHz/d_4MeOH): δ 2.12 (s, 3H, CH_3), 4.58 (dd, J = 6.3, 1.5 Hz, 1H), 4.87 (dd, J = 14.0, 1.5 Hz, 1H), 7.27 (dd, J = 14, 6.3 Hz, 1H); acetaldehyde ^{1}H NMR (500 MHz/d_4MeOH): δ 9.71 (m, 3H); hemiacetal ^{1}H NMR (500 MHz/d_4MeOH): δ 1.26 (m), 4.69 (t, 3H), 4.79 (s, 1H).

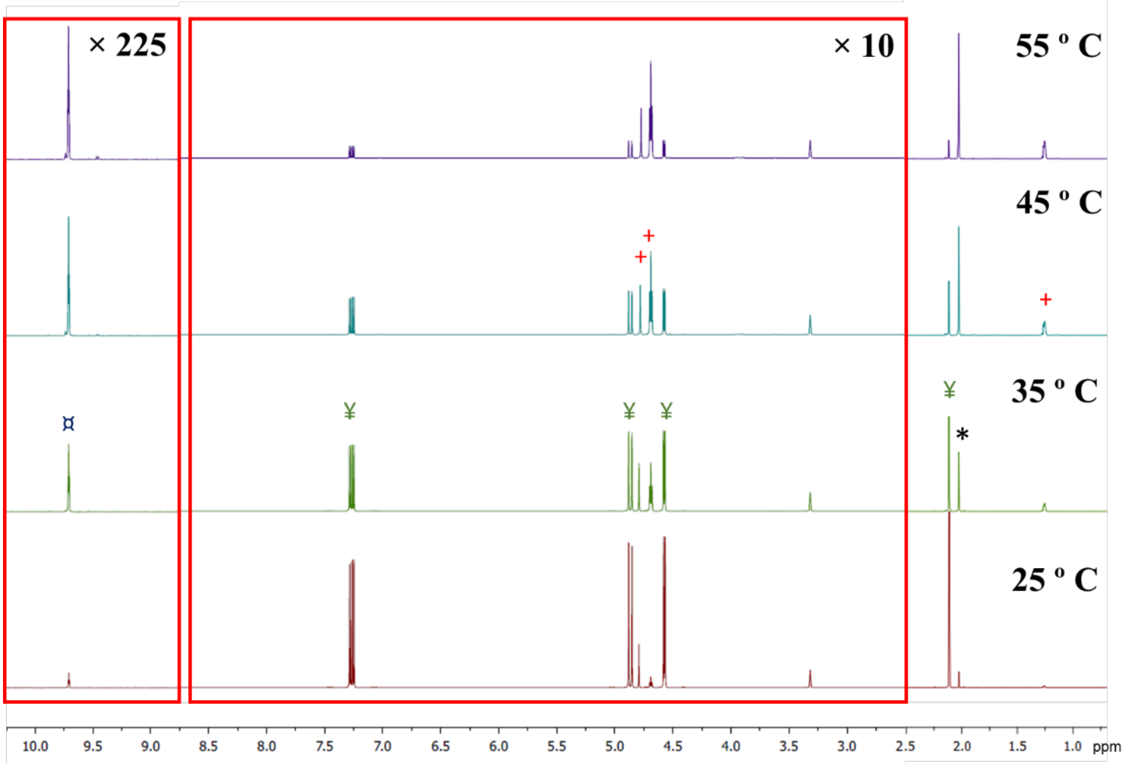

Figure S3: ^{1}H NMR spectra of the transesterification reaction between d$_4$MeOH and vinyl acetate catalysed by **ZIF-8 1 µm**, where *, ¥, + and ¤ correspond to peaks associated with methyl acetate, vinyl acetate, the hemiacetal and acetaldehyde respectively. For clarity the sections between 2.5-8.75 ppm and 8.75-10.25 ppm are displayed at ×10 and × 225 magnification respectively.

S3-2 60 ºC ^{1}H NMR control reaction with catalyst removal at 3 h

Dried **ZIF-8 50 nm** (5 mg, 0.022 mmol) was dispersed in d_4MeOH (1 ml) at room temperature into 2 identical 2.5 ml vials. To these solutions vinyl acetate (82.5 µl, 0.895 mmol) was added and the solution was heated at 60 °C for 6 h. For one vial at the 3 and 6 h time points 50 µl aliquot of each solution was taken and centrifuged at 10,000 rpm, the ZIF-8 catalyst was separated from the supernatant which was then analysed via ^{1}H NMR in 0.65 ml d_4MeOH. For the other vial at the 3 h time point, after the 50 µl aliquot was taken, the ZIF-8 catalyst was separated from the supernatant by centrifugation and the supernatant was heated for a further 3 h at which point the supernatant was analysed via ^{1}HNMR. The ^{1}H NMR signals corresponding to methyl acetate, vinyl acetate, acetaldehyde and the hemiacetal, that were detected after the reaction in d_4MeOH were as follows: methyl acetate ^{1}H NMR (500 MHz/d_4MeOH): δ 2.03 (3H, s, CH_3); vinyl acetate ^{1}H NMR (500 MHz/d_4MeOH): δ 2.12 (s, 3H, CH_3), 4.58 (dd, J = 6.3, 1.5 Hz, 1H), 4.87 (dd, J = 14.0, 1.5 Hz, 1H), 7.27 (dd, J = 14, 6.3 Hz, 1H); acetaldehyde ^{1}H NMR (500 MHz/d_4MeOH): δ 9.71 (m, 3H); hemiacetal ^{1}H NMR (500 MHz/d_4MeOH): δ 1.26 (m), 4.69 (t, 3H), 4.79 (s, 1H).

Table S1: ^{1}HNMR analysis of controls for the transesterification of vinyl acetate with d_4MeOH catalysed by **ZIF-8 50 nm**

Sample	Integration of vinyl acetate CH_3 (δ 2.12)	Integration of methyl acetate CH_3 (δ 2.03)	Conversion (%)
3 h with **ZIF-8 50 nm** (1)	1	2.43	70
3 h with **ZIF-8 50 nm** (2)	1	2.08	67
6 h with **ZIF-8 50 nm** (1)	1	9.60	90
6 h with **ZIF-8 50 nm** removed at 3 h (2)	1	4.34	81

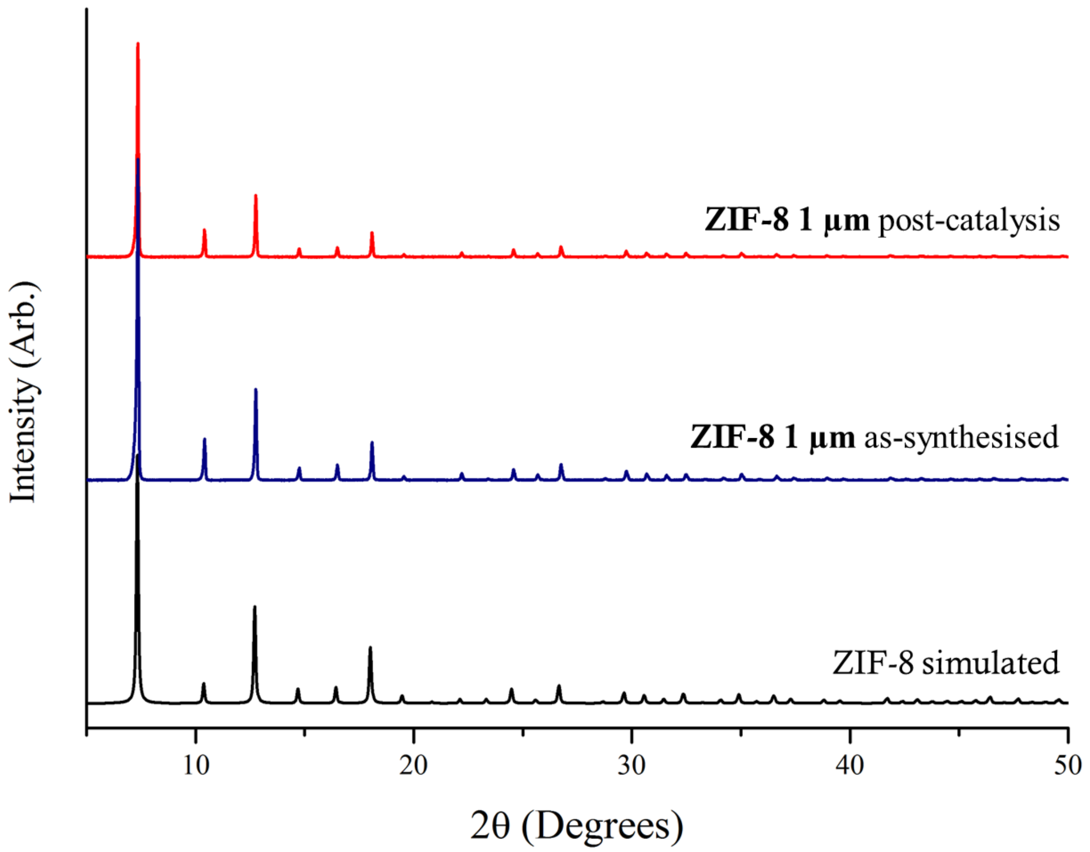

Figure S4: Powder X-ray Diffraction patterns of ZIF-8; simulated, **ZIF-8 1 µm** as-synthesised and **ZIF-8 1 µm** post-catalysis at 55 °C in methanol, catalysing the transesterification of vinyl acetate with d_4MeOH.

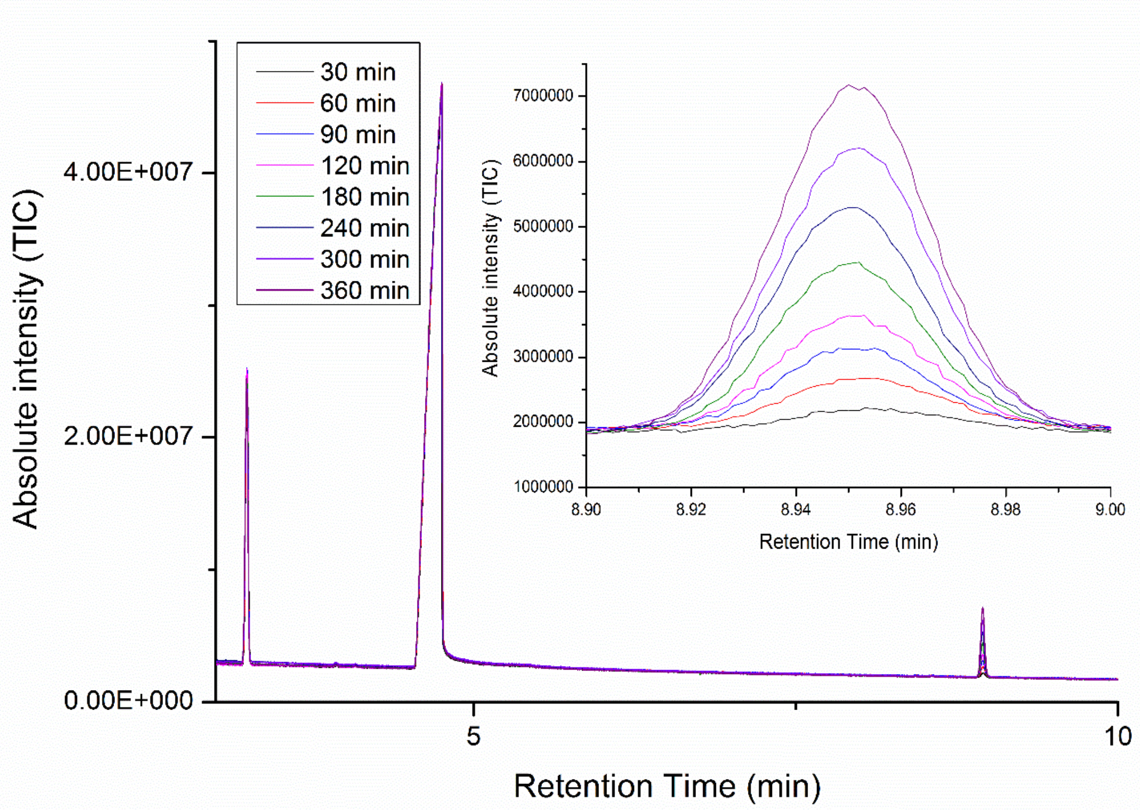

Figure S5: GC-MS traces for the transesterification of hexanol with vinyl acetate, catalysed at 65 °C by **ZIF-8 1 µm** agitated by stirring, with peaks at retention times 3.10, 4.81 and 8.95 min corresponding to propyl propionate, hexanol and hexyl acetate respectively. The inset is an expansion of the hexyl acetate peak at 8.95 min.

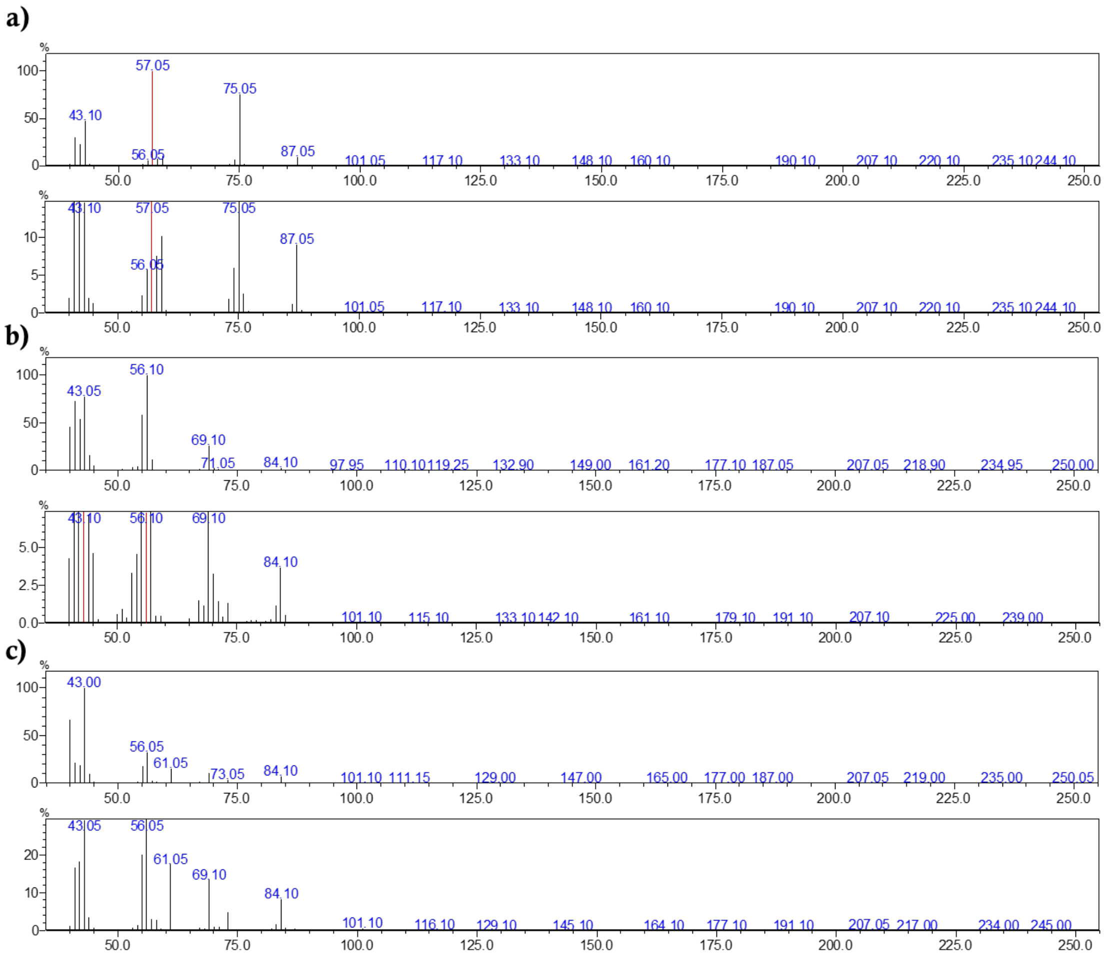

Figure S6: Mass Spectra corresponding to peaks in the GC-MS trace in Figure S5 for a) propyl propionate, b) hexanol and c) hexyl acetate, which correspond to mass spectra in the NIST data base.[1]

S4 Transesterification catalytic activity and crystal degradation analyses

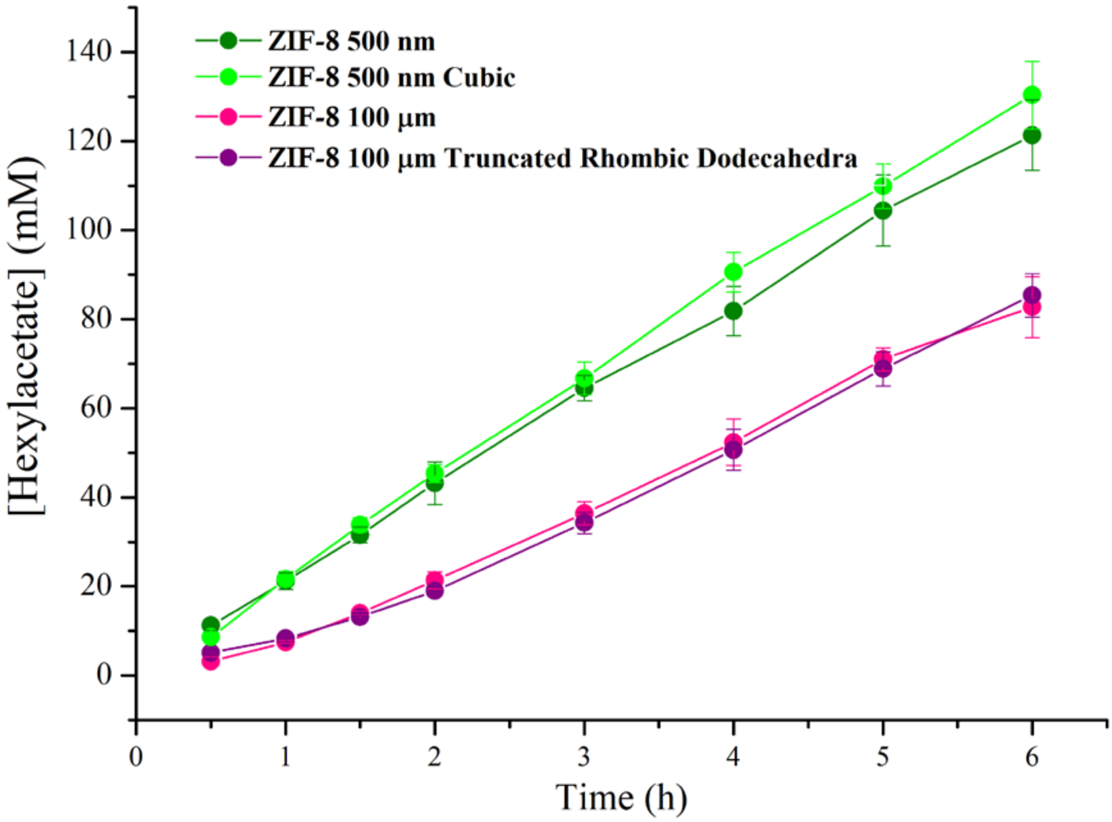

Figure S7: Comparison of hexyl acetate production from the transesterification of hexanol with vinyl acetate catalysed by ZIF-8 samples of different morphology under stirring agitation.

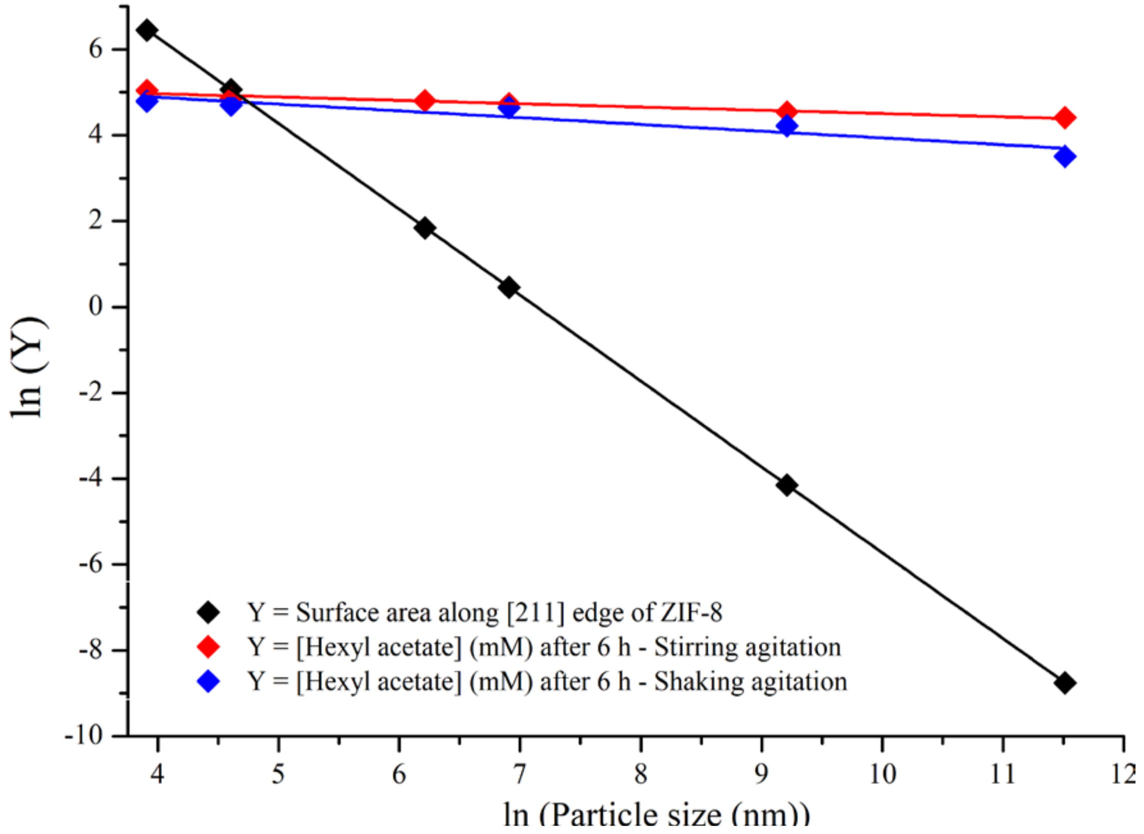

Figure S8: Ln/Ln plots of Ln (Y) vs Ln (Particle size (nm)), where Y = the surface area along the [211] edge (assuming a width of 0.1 nm) of rhombic dodecahedra ZIF-8 (black) (these values were calculated as shown in S5), Y = [Hexyl acetate] (mM) after 6 h with stirring agitation (red) and Y = [Hexyl acetate] (mM) after 6 h with shaking agitation (blue).

Table S2: Values for the line of best fit plots for Figure S8 to the equation y = a + b × x for the ln/ln plot.

Y	**Intercept (a)**	**Std. Error in Intercept**	**Slope (b)**	**Std. Error in slope**	**R^2**
Surface area	14.2752	1.73027E-14	-2.0000	2.29776E-15	1.00000
[Hexyl acetate] mM: Stirring	5.2728	0.0593	-0.0768	0.0079	0.94941
[Hexyl acetate] mM: Shaking	5.5144	0.2482	-0.1577	0.0319	0.85381

S5 Calculations for Figure S8

The catalytically active surface area for 20 mg of ZIF-8 (along the [211] edge, assuming an edge thickness of 0.1 nm) was calculated as follows. The crystal size was assigned as the midsphere of the rhombic dodecahedra crystals (d) and the radius of the midsphere ($r = d/2$) was then used to determine the side length of the crystal (l, where $l = \frac{\left(\frac{3r}{2}\right)}{2\sqrt{2}}$). The surface area along the edges corresponding to the [211] plane in one crystal of ZIF-8 assuming a thickness of 0.1 nm (SA_{edge}) was determined by multiplying the edge length (l) by 0.1 nm. Rhombic dodecahedra have 24 edges that correspond to the [211] plane, therefore SA_{edge} was multiplied by 24 to give the catalytically active surface area for 1 crystal ($SA_{all\ edges}$). The mass of one crystallite was calculated by multiplying the volume of one crystal (given by $\frac{16\sqrt{3}}{9}l^3$) by the bulk density of ZIF-8 (0.35 g/cm^3). The number of crystallites in a 20 mg sample of ZIF-8 (N) was determined by dividing 20 mg by the mass of one crystallite. The catalytically active surface area for a 20 mg sample of ZIF-8 (SA_{active}) could then be determined by multiplying N by $SA_{all\ edges}$. Figure S8 was then generated by plotting ln (SA_{active} (cm^2)) vs ln (Particle size (nm)).

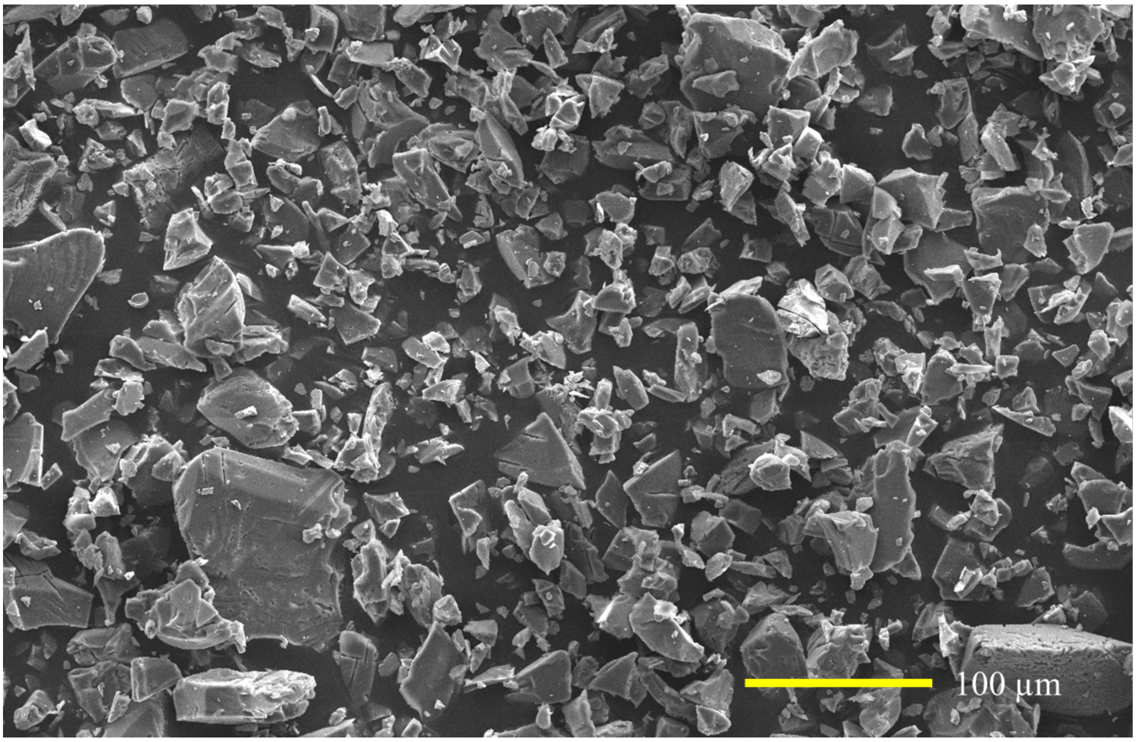

Figure S9: SEM image of **ZIF-8 100 µm** post-catalysis for the transesterification of hexanol with vinylacetate at 65 °C, demonstrating mechanical degradation of crystals arising from stirring.

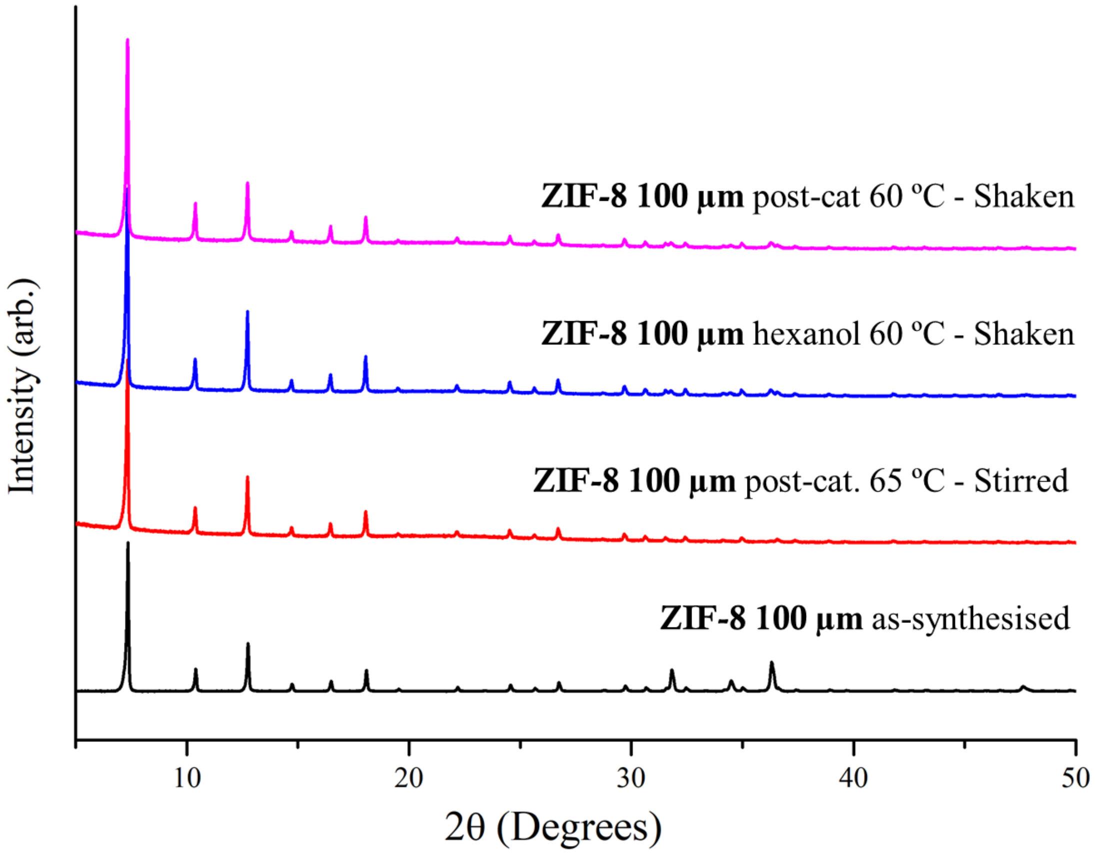

Figure S10: Powder X-ray diffraction patterns of **ZIF-8 100 µm**; as-synthesised, post-catalysis at 65 °C with stirring agitation, hexanol soaked at 60 °C with shaking agitation and post-catalysis at 60 °C with shaking agitation.

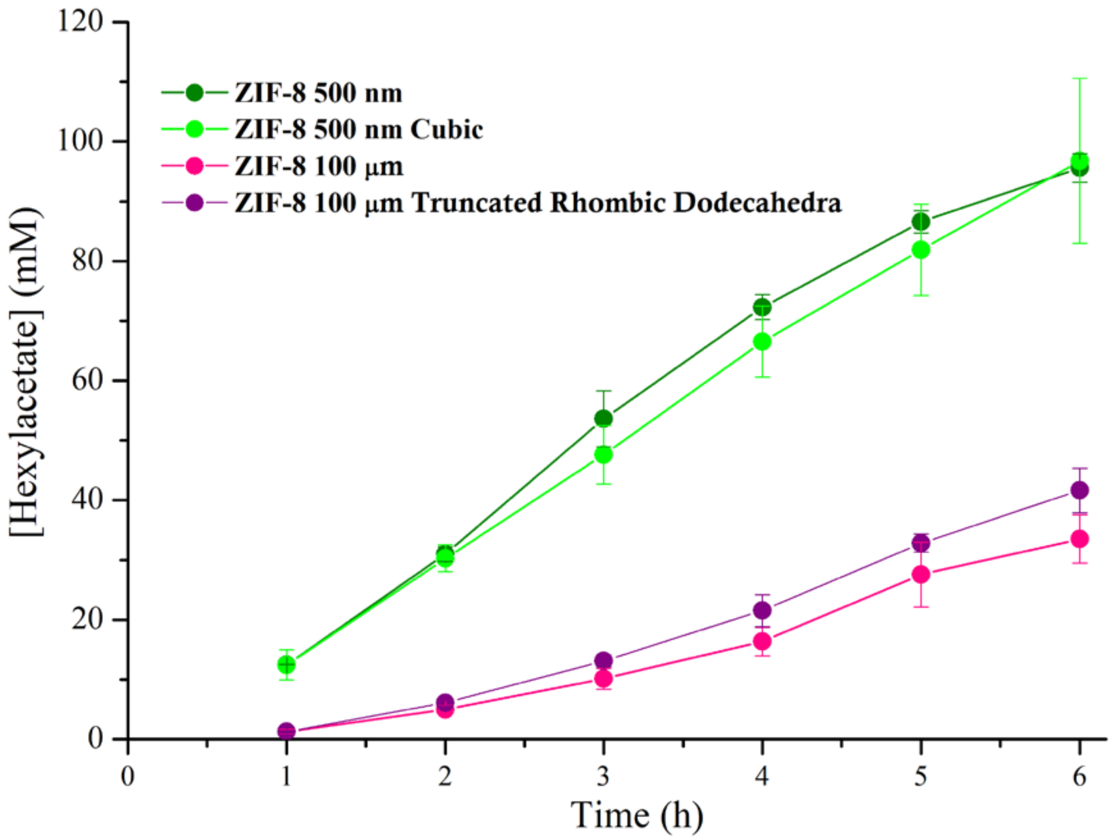

Figure S11: Comparison of hexyl acetate production from the transesterification of hexanol with vinyl acetate catalysed by ZIF-8 samples of different morphology under shaking agitation.

S6 Surface etching investigation with SEM, N_2 77 K adsorption, pore size analysis and PXRD analysis of ZIF-8 crystallinity under Knoevenagel condensation conditions

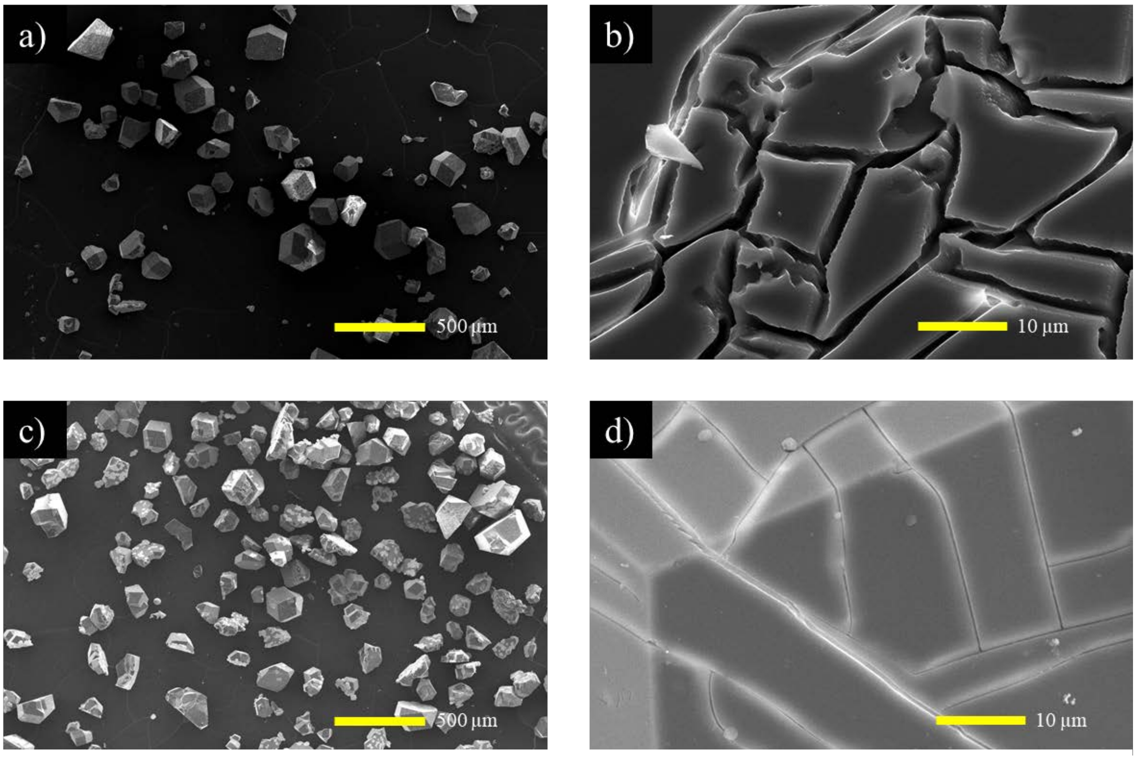

Figure S12: SEM images of **ZIF-8 100 µm**, a) & b) post-catalysis at 60 °C with shaking agitation, c) & d) hexanol at 60 °C with shaking agitation, demonstrating increased etching under catalytic conditions.

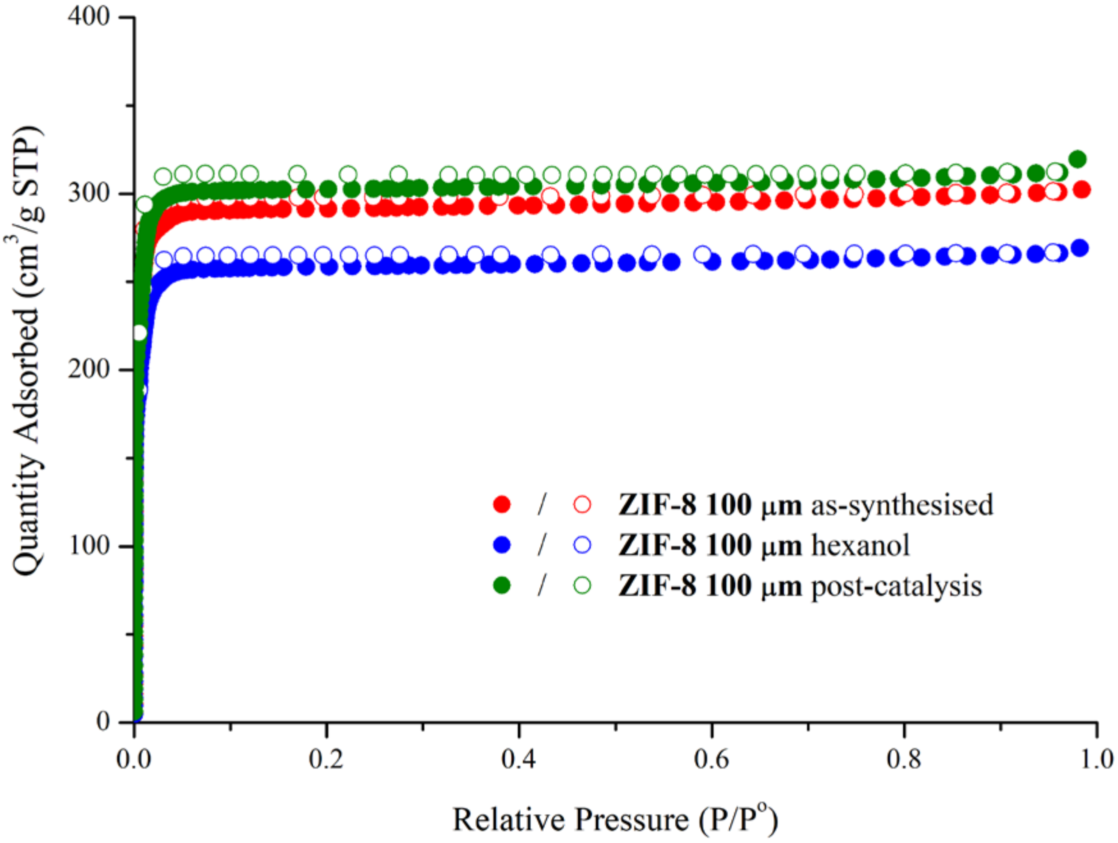

Figure S13: N_2 77 K isotherms of **ZIF-8 100 µm** as-synthesised (red), heated in hexanol for 6 h (blue) and post-catalysis (green).

Table S3: Brunauer-Emmett-Teller (BET) surface areas of **ZIF-8 100 µm**

Sample	**BET (m^2/g)**
ZIF-8 100 µm as-synthesised	1164.1143 ± 17.5396
ZIF-8 100 µm hexanol	881.9513 ± 5.7647
ZIF-8 100 µm post-catalysis	1036.0673 ± 8.2199

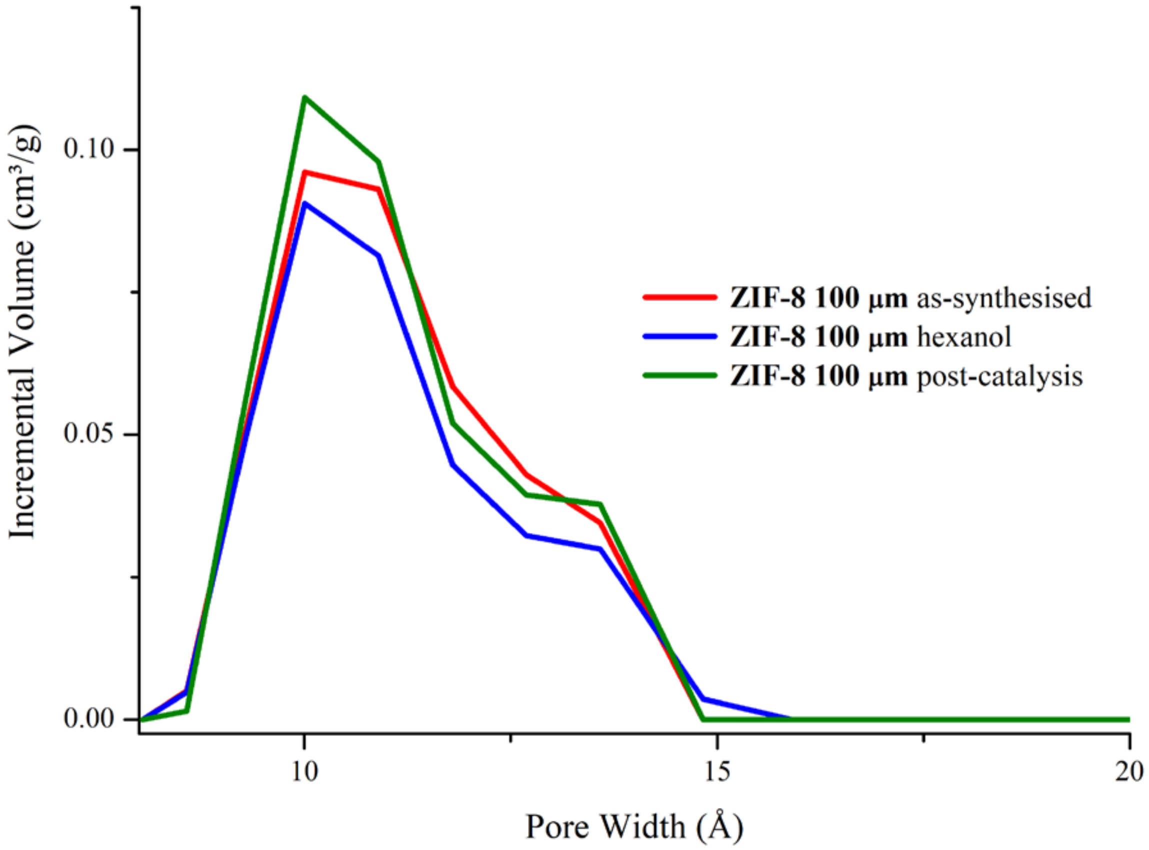

Figure S14: Pore size distributions of **ZIF-8 100 µm** as-synthesised (red), heated in hexanol for 6 h (blue) and post-catalysis (green).

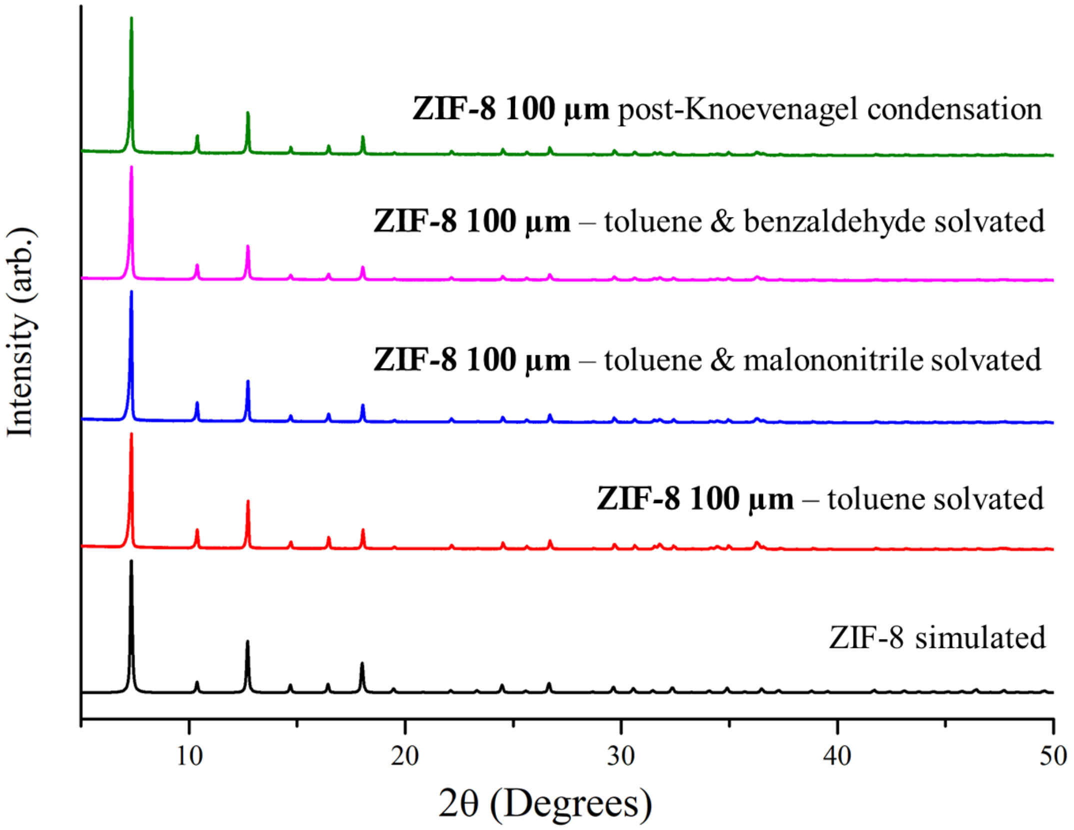

Figure S15: Powder X-ray diffraction patterns of **ZIF-8 100 µm**; simulated, toluene solvated 6 h, toluene & malononitrile solvated 6 h, toluene & benzaldehyde solvated 6 h and post-Knoevenagel condensation conditions 6 h.

References

1. P.J. Linstrom and W.G. Mallard, Eds., **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, (retrieved April 30, 2018).