Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Designing of a novel heterogeneous nanocatalyst ZIF-4@HAp for solvent free base catalyzed esterification reaction

Linkon Bharali, Debarati Chakraborty, Triveni, Juri Kalita, Siddhartha Sankar Dhar* [a]

[a] Department of Chemistry, National Institute of Technology Silchar, Cachar, Assam- 788010, India.

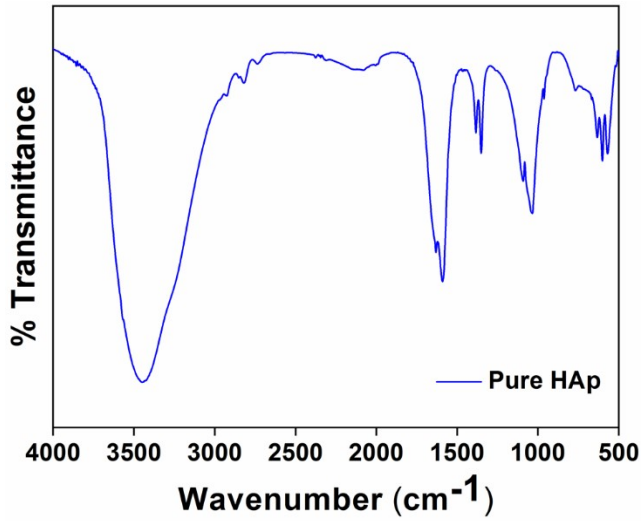
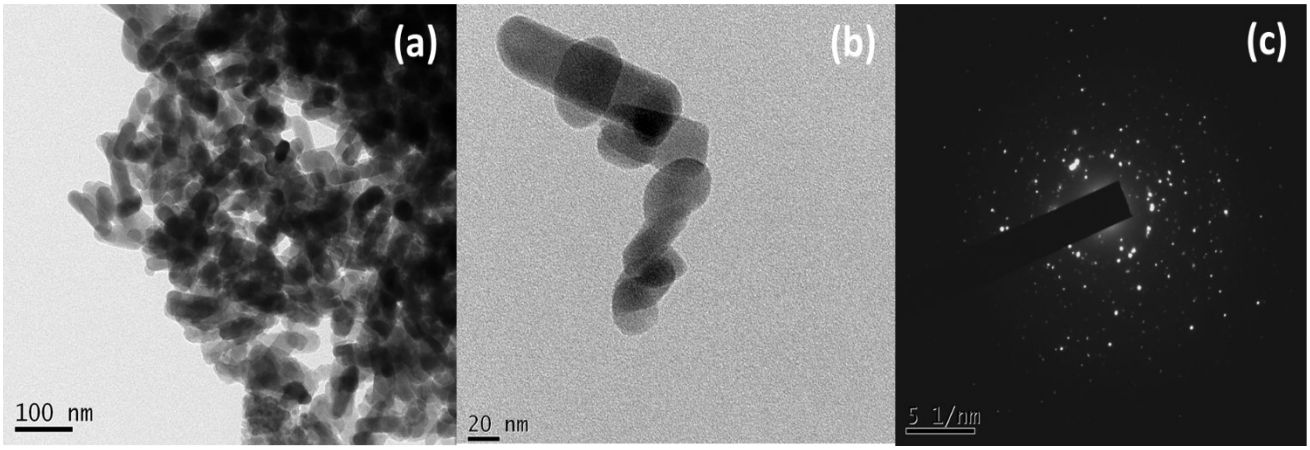


Figure S1. FT-IR Spectrum of Pure HAp



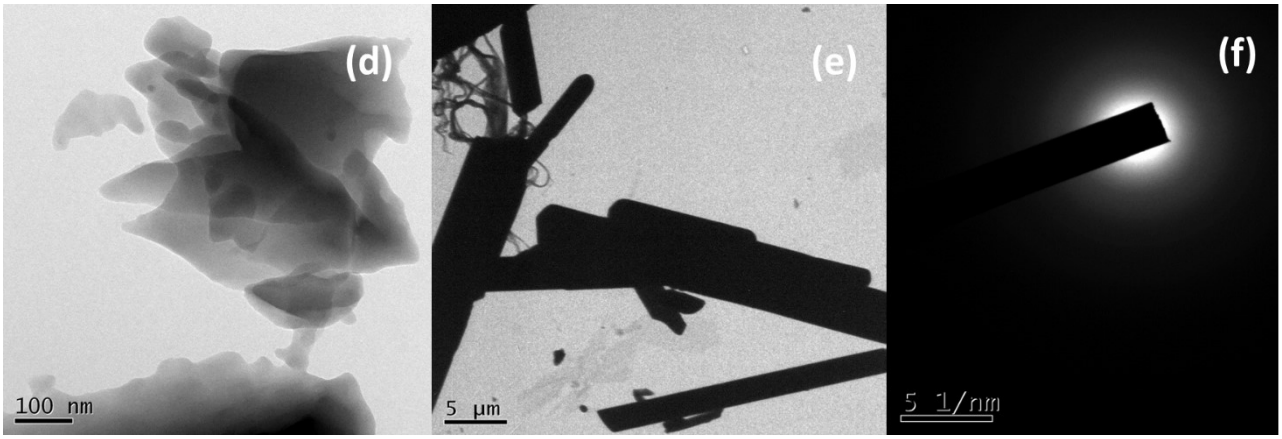


Figure S2. HR-TEM Images (a, b) Pure HAp and (d, e) ZIF-4 and SAED pattern of (c) pure HAp and (f) ZIF-4

Table S1: Values of surface area, pore volume, and pore diameter of pure HAp and as-synthesized catalyst:

Sl No.	Photocatalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
1	HAp	48.90	0.091	18.240
2	ZIF-4@HAp	60.36	0.102	30.610

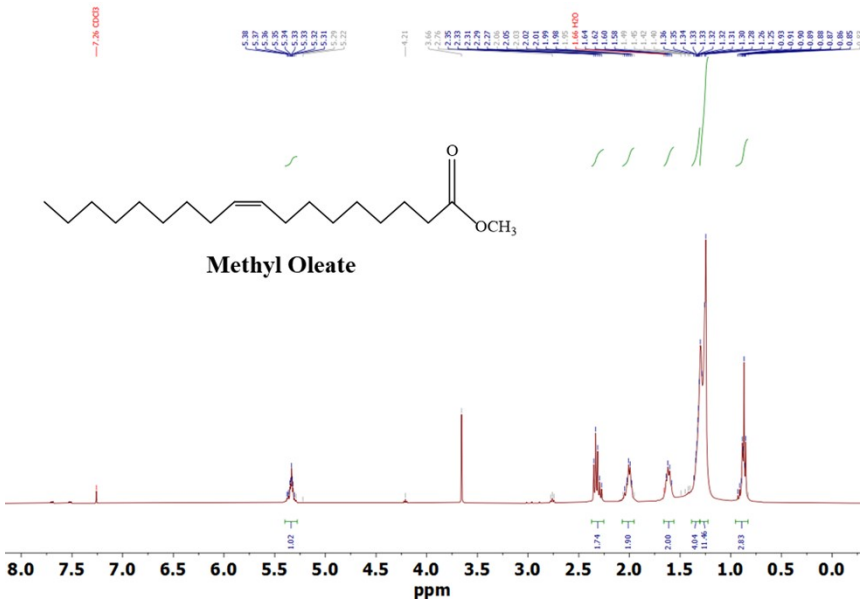


Figure S3. ^{1}H NMR Spectrum of Methyl Oleate

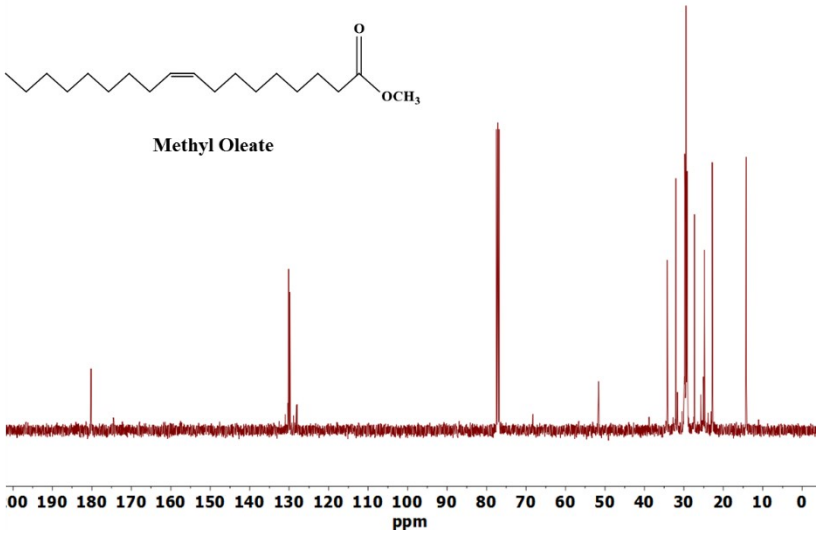


Figure S4. ^{13}C NMR Spectrum of Methyl Oleate

^{1}H NMR ($CHCl_3$, 400 MHz, δ ppm): 3.66 (s, 3H), 1.27- 2.70 (m, 14H), 2.31 (t, 2H), 0.87 (t, 3H), 5.34 (d, 1H) and ^{13}C NMR ($CHCl_3$, 100 MHz, δ ppm): 180.2, 130.13, 77.48, 51.59, 34.27, 32.09, 29.51, 27.33, 25.15, 24.77, 22.91, 14.21.

Table S2: Optimization of Methyl Oleate formation

Entry	Catalyst Amount (mg)	Reactants		Product	Temperature (°C)	Time (h)	% Yield
		Acid	Alcohol				
1	20	Oleic Acid	Methanol	Methyl Oleate	RT	7	-
2	40	Oleic Acid	Methanol	Methyl Oleate	40	2	40.8
3	40	Oleic Acid	Methanol	Methyl Oleate	50	2	72.5
4	40	Oleic Acid	Methanol	Methyl Oleate	60	2	90.4

(Optimum Reaction Condition: ZIF-4@HAp catalyst: 40 mg, acid: 10 mmol, alcohol: 60 mmol, Reaction Temperature: 60 °C, Reaction Time: 2 h)

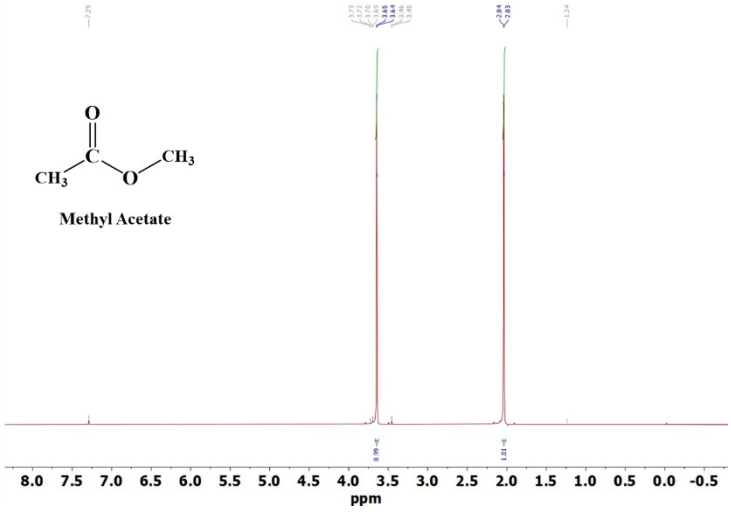


Figure S5. ^{1}H NMR Spectrum of Methyl Acetate

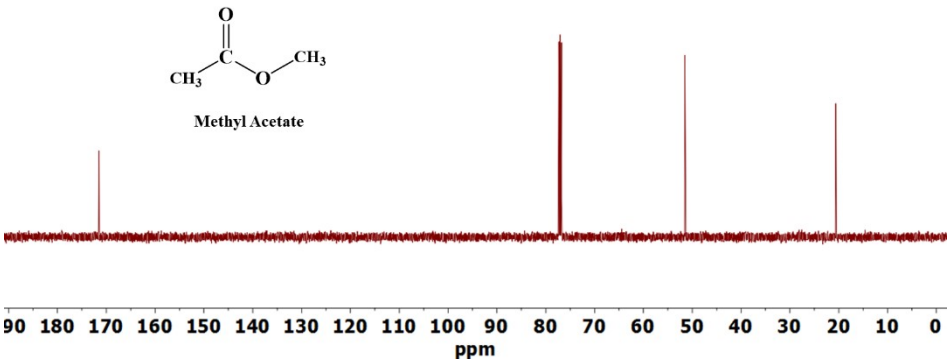


Figure S6. ^{13}C NMR Spectrum of Methyl Acetate

^{1}H NMR ($CHCl_3$, 500 MHz, δ ppm): 3.64 (s, 1H), 2.04 (s, 1H) and ^{13}C NMR ($CHCl_3$, 125 MHz, δ ppm): 171.5, 77.06, 51.53, and 20.6.

Table S3: Optimization of Methyl Acetate formation

Entry	Catalyst Amount (mg)	Reactants		Product	Temperature (°C)	Time (h)	% Yield
		Acid	Alcohol				
1	20	Acetic Acid	Methanol	Methyl Acetate	RT	7	-
2	40	Acetic Acid	Methanol	Methyl Acetate	40	2	33.6
3	40	Acetic Acid	Methanol	Methyl Acetate	50	2	67.2
4	40	Acetic Acid	Methanol	Methyl Acetate	60	2	91.7

(Optimum Reaction Condition: ZIF-4@HAp catalyst: 40 mg, acid: 10 mmol, alcohol: 60 mmol, Reaction Temperature: 60 °C, Reaction Time: 2 h)

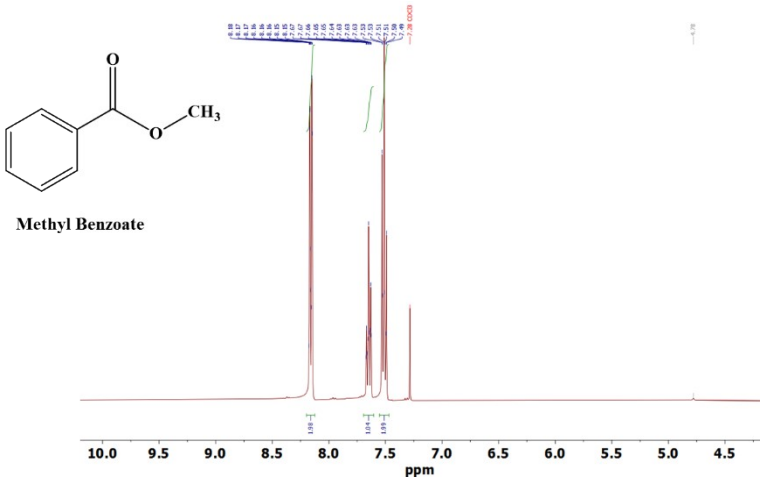


Figure S7. ^{1}H NMR Spectrum of Methyl Benzoate

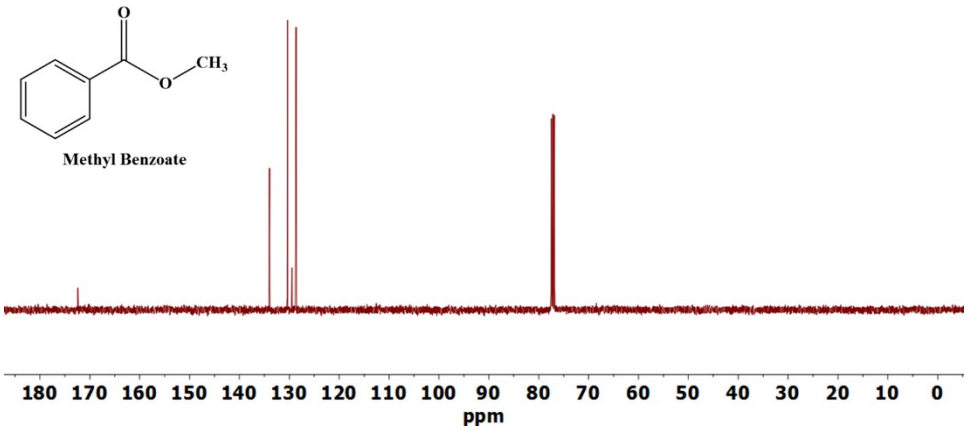


Figure S8. ^{13}C NMR Spectrum of Methyl Benzoate

^{1}H NMR ($CHCl_3$, 400 MHz, δ ppm): 8.16 (d, 2H), 7.64 (t, 1H). 7.51 (t, 2H), 4.78 (s, 3H) and ^{13}C NMR ($CHCl_3$, 100 MHz, δ ppm): 172.39, 133.96, 130.37, 128.9, 76.84.

Table S4: Optimization of Methyl Benzoate formation

Entry	Catalyst Amount (mg)	Reactants		Product	Temperature (°C)	Time (h)	% Yield
		Acid	Alcohol				
1	20	Benzoic Acid	Methanol	Methyl Benzoate	RT	7	-
2	30	Benzoic Acid	Methanol	Methyl Benzoate	40	2	42.6
3	35	Benzoic Acid	Methanol	Methyl Benzoate	45	2	78.3
4	35	Benzoic Acid	Methanol	Methyl Benzoate	50	2	94.5

(Optimum Reaction Condition: ZIF-4@HAp catalyst: 35 mg, acid: 10 mmol, alcohol: 60 mmol, Reaction Temperature: 50 °C, Reaction Time: 2 h)

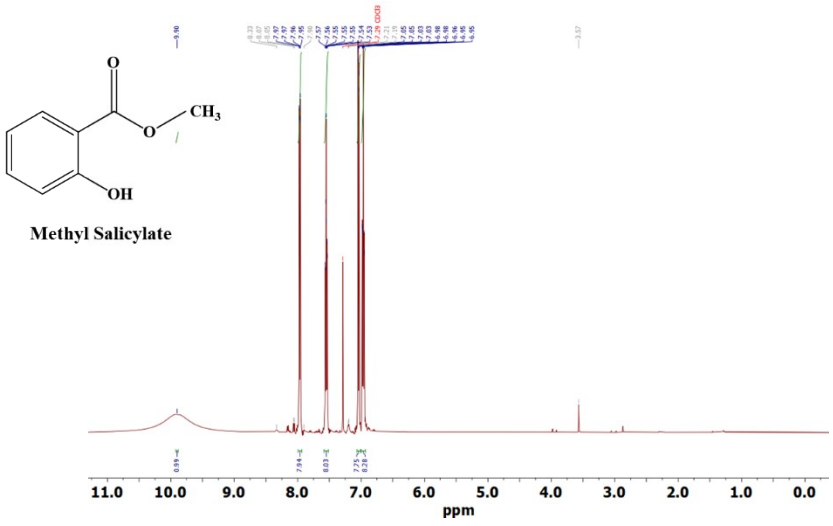
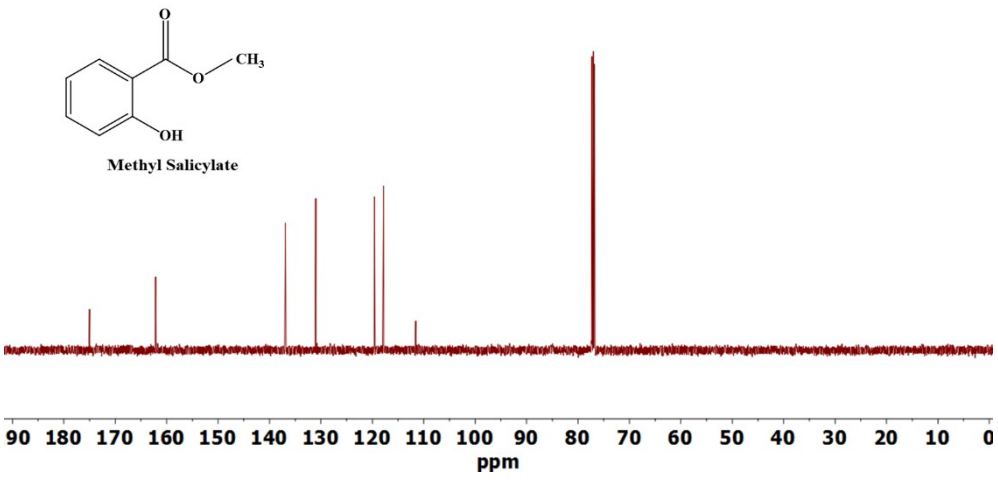


Figure S9. ^{1}H NMR Spectrum of Methyl Salicylate



`

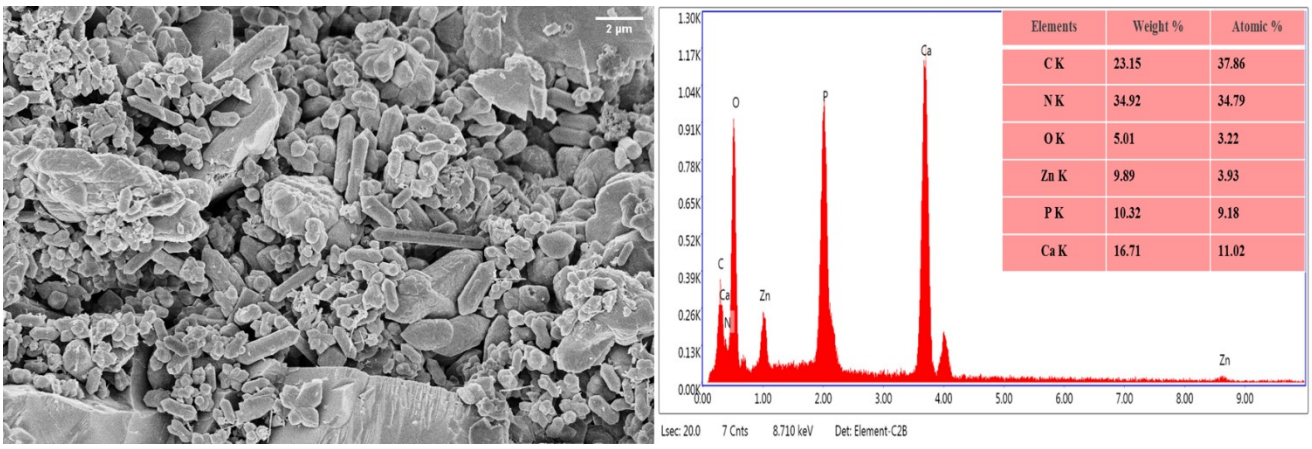
Figure S10. ^{13}C NMR Spectrum of Methyl Salicylate

^{1}H NMR ($CHCl_3$, 400 MHz, δ ppm): 3.57 (s, 3H), 7.96 (d, 1H), 7.55 (t, 1H) 7.04 (d, 1H), 6.97 (t, 1H), 3.57 (s, 3H), 9.90 (s, 1H) and ^{13}C NMR ($CHCl_3$, 100 MHz, δ ppm): 175, 162.14, 136.91, 131.1, 119.61, 117.82, 77.29.

Table S5: Optimization of Methyl Salicylate formation

Entry	Catalyst Amount (mg)	Reactants		Product	Temperature (°C)	Time (h)	% Yield
		Acid	Alcohol				
1	20	Salicylic Acid	Methanol	Methyl Salicylate	RT	7	-
2	30	Salicylic Acid	Methanol	Methyl Salicylate	40	2	44.8
3	35	Salicylic Acid	Methanol	Methyl Salicylate	45	2	83.7
4	35	Salicylic Acid	Methanol	Methyl Salicylate	50	2	95.8

(Optimum Reaction Condition: ZIF-4@HAp catalyst: 35 mg, acid: 10 mmol, alcohol: 60 mmol, Reaction Temperature: 50 °C, Reaction Time: 2 h)



Elements	Weight %	Atomic %
C K	23.15	37.86
N K	34.92	34.79
O K	5.01	3.22
Zn K	9.89	3.93
P K	10.32	9.18
Ca K	16.71	11.02

Figure S11. SEM-Image and EDS Spectrum of Reused Catalyst

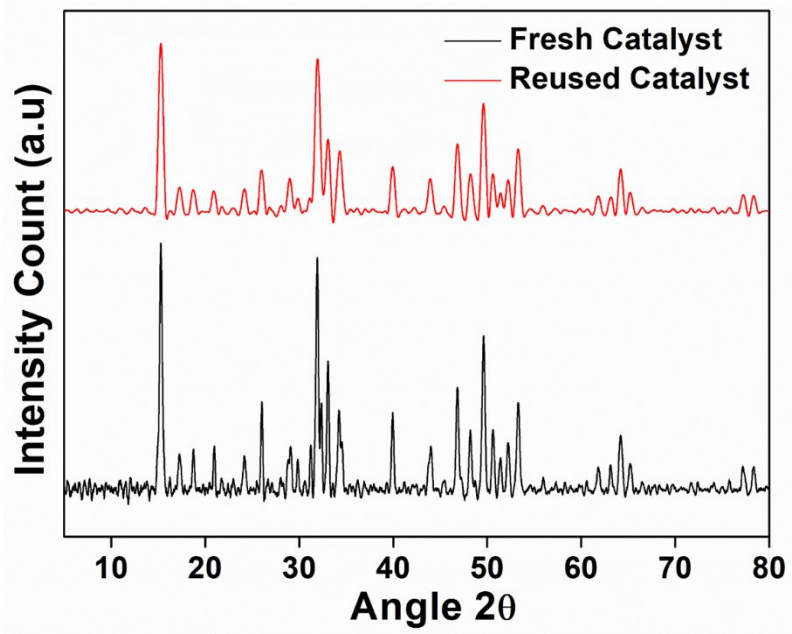


Figure S12. PXRD Spectra of fresh and reused catalyst, ZIF-4@HAp