Supplementary Material (ESI) for Journal of Materials Chemistry

Synthesis optimisation of nanoparticles of the flexible porous iron fumarate MIL-88A

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Supporting information

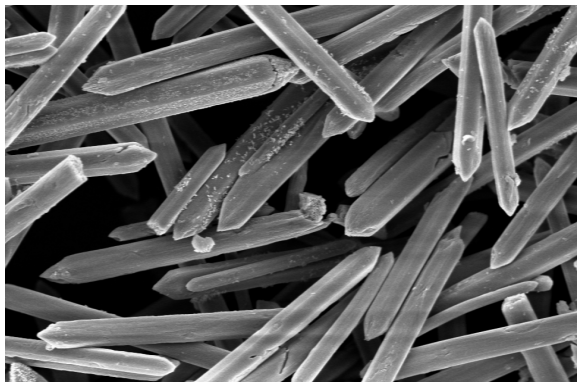

Figure S1. SEM image of MIL-88A synthesised by solvothermal method in methanol at 100°C for 3 days.

Table S1: Particle size and yield of the MIL-88A solids synthesised under solvothermal conditions in DMF, MeOH or water.

Solvent	Presence of NaOH (2M)	2h	6h	24h
		Particle size (nm) (Yield %)	Particle size (nm) (Yield %)	Particle size (nm) (Yield %)
DMF	0	NP	430±15 (11,9±1,2)	>1200 (83,0±3,7)
	0,4	255±25 (38,6±2,0)	855±35 (56,4±2,9)	>1200 (91,7±2,1)
MeOH	0	NP		
	0,4	390±30 (24,4±1,5)	960±70 (37,3±1,6)	>1200* (51,2±1,9)
Water	0	360±35 (59,9±2,1)	915±65 (60,1±2,4)	>1200 (60,8±2,8)
	0,4	550±55 (71,2±3,3)	1050±135 (71,3±3,1)	>1200 * (72,7±3,0)

NP= No significant precipitation

* presence of iron oxides

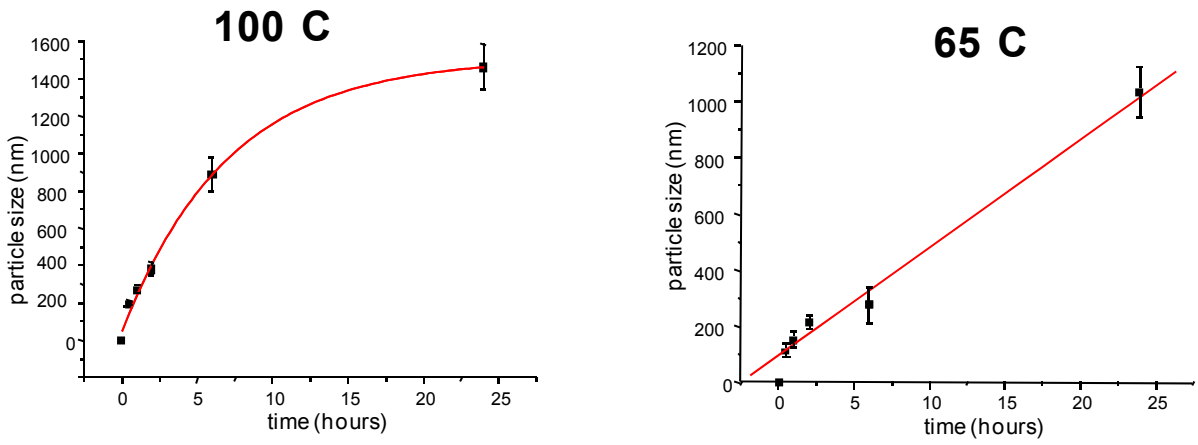

Figure S2. Fitting curves for the synthesis performed at 100 and 65°C under autogenous pressure

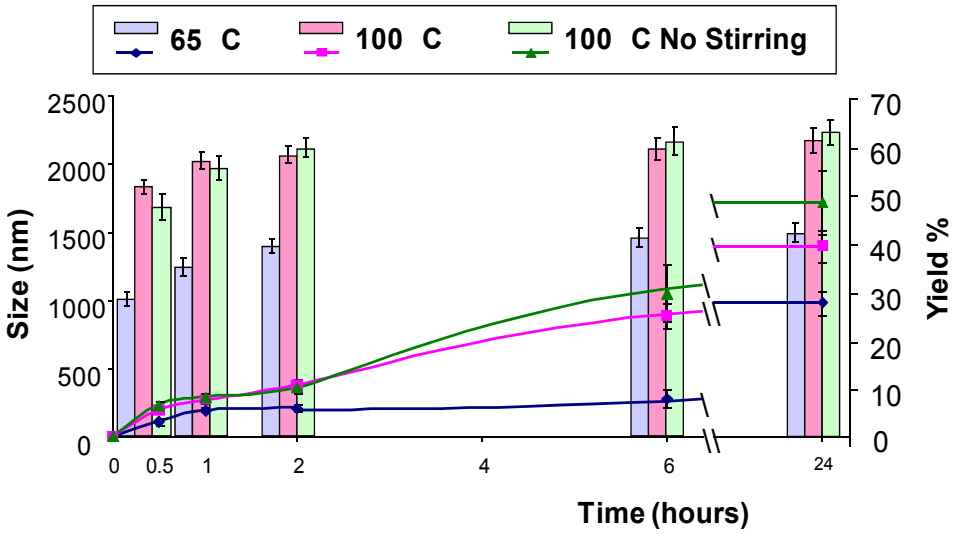

Figure S3. Yields and particle sizes as function of time of the synthesis performed at 100 and 65°C under autogenous pressure

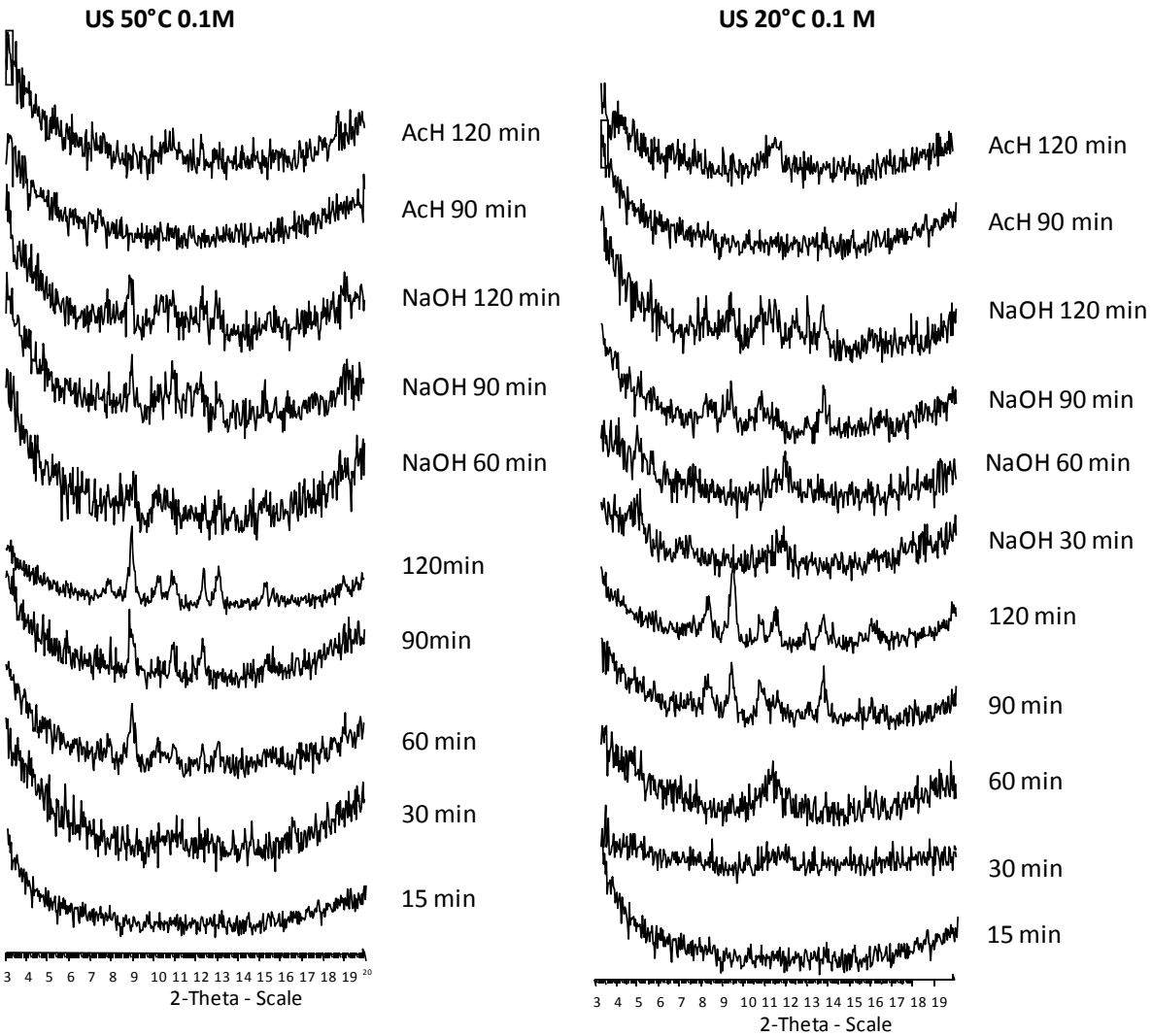

Figure S4. XRD patterns of powders obtained from ultrasonic route using 0.1 M concentrations at 50°C (left) and 20°C (right)

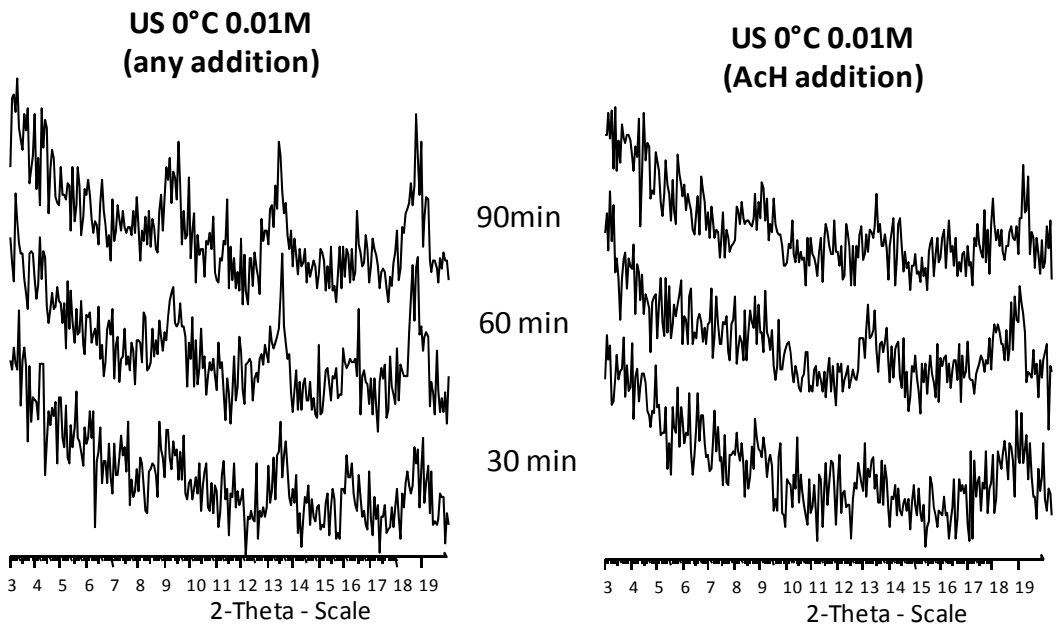

Figure S5. XRD patterns of powders obtained from ultrasonic route using 0.01 M concentrations at 0°C without (left) and with the addition of acetic acid (right).

Table S2. Particle size and yield of the MIL-88A solids synthesised under ultrasonic method

			Reaction time (min)				
Temp. (°C)	**Conc. (M)**	**Additives**	**15**	**30**	60	90	120
			Size(nm) (Yield %)				
50°C	**0.1**	**No additive**	720±75 (16,2±1,2)	1040±95 (16,5±1,2)	>1200(16, 9±1,4)	>1200 (17,3±1,7)	>1200 (18,1±1,8)
		NaOH	>1200 (22,5±1,3)	>1200 (22,9±1,5)	>1200 (23,3±1,8)	>1200 (24,1±2,1)	>1200 (25,1±2,2)
		AcH	380±35 (4,4±0,4)	590±45 (4,7±0,4)	890±70 (5,1±0,7)	>1200 (5,7±0,9)	>1200 (5,9±1,3)
20°C	**0.1**	**-**	480±45 (9,0±0,9)	740±65 (9,3±1,3)	1150±105 (9,9±1,4)	>1200 (10,3±1,3)	>1200 (10,3±1,6)
		NaOH	>1200 (13,3±1,1)	>1200 (13,6±1,6)	>1200 (14,1±1,8)	>1200 (14,0±2,1)	>1200 (14,6±2,0)
		AcH	180±15 (2,4±0,2)	260±25 (2,7±0,4)	450±30 (3,1±0,4)	850±55 (3,2±0,5)	1080±95 (3,3±0,7)
	0,05	**-**	240±15 (8,4±0,7)	385±15 (8,7±0,9)	620±30 (9,6±0,9)	890±35 (9,9±1,7)	>1200 (10,1±1,9)
		NaOH	390±25 (12,9±0,8)	615±35 (13,2±0,7)	830±45 (13,5±0,8)	>1200 (13,8±0,9)	>1200 (14,1±1,4)
		AcH	95±15 (2,4±0,2)	155±15 (2,6±0,2)	235±25 (2,6±0,3)	320±35 (2,8±0,2)	410±40 (2,9±0,3)
	0,01	**-**	75±10 (7,6±0,9)	120±15 (7,9±1,1)	190±20 (9,1±0,7)	275±25 (9,7±0,6)	350±25 (10,3±0,8)
		NaOH	190±20 (12,5±1)	320±30 (12,7±1,1)	480±35 (13,4±1,3)	625±45 (13,9±0,9)	835±50 (14,3±1,1)
		AcH	60±10 (1,8±0,1)	75±10 (2,1±0,1)	95±10 (2,3±0,3)	110±15 (2,7±0,3)	120±15 (2,7±0,3)
	0,008	**-**	70±10 (5,3±0,3)	110±10 (6,2±0,3)	185±15 (7,3±0,5)	260±20 (8,4±0,6)	330±20 (8,9±0,5)

		NaOH	180±15 (9,4±0,6)	300±15 (9,8±0,8)	465±20 (11,1±0,6)	610±20 (11,8±0,9)	810±25 (13,1±1,4)
		AcH	No significant precipitation				115±15 (2,0±0,2)
0°C	**0,01**	-	70±10 (3,8±0,1)	95±10 (4,0±0,1)	135±15 (4,2±0,3)	185±15 (4,2±0,5)	225±15 (4,9±0,6)
		AcH	No significant precipitation		75±5 (0,4±0,1)	90±10 (1,2±0,1)	110±10 (1,3±0,2)
	0,008	-	60±5 (2,5±0,2)	80±10 (2,8±0,3)	125±15 (3,6±0,5)	165±15 (3,9±0,5)	200±10 (4,1±0,7)
		AcH	No significant precipitation				80±5 (0,8±0,2)

Table S3. Particle size and yield of the MIL-88A solids synthesised under microwave route

Conditions	**Yield %**	**Particle size (nm)**
Temperature (°C)		
50	39,1±1,2	85 ± 8
65	48,3± 1,4	110 ±10
80	58,7 ± 1,7	160 ± 10
100	60,8 ± 2,4	270 ± 23
120	61,1± 1,1	350 ± 55*
Time of reaction (min)		
1	56,6±1,4	87 ± 15
2	58,7 ± 1,7	110 ± 10
3	60,3±1,9	380±35
5	61,2±2,3	635±40
10	61,9±2,6	>1200*
Concentration(mM)		
25	54,1±2,1	98± 15
50	55,4 ± 1,8	106± 12
100	58,7 ± 1,7	110 ± 10
200	58,4± 1,9	280± 45
400	56,9±1,7	575±85
Pressure (Pa)		
15	58,7 ± 1,7	110 ± 10
45	56,3 ± 2,1	185 ± 25*
80	55,6 ±1,9	275 ± 25*

* Presence of Iron Oxides