Electronic Supplementary Information

Size- and Morphology-Controlled NH_2-MIL-53(Al) Prepared in DMF-Water Mixed Solvents

Xinquan Cheng,[a] *Anfeng Zhang,*[a] *Keke Hou,*[a] *Min Liu,**[a] *Yingxia Wang,*[b] *Chunshan Song,*[a,c,d]

Guoliang Zhang,[e] *Xinwen Guo**[a]

[a] State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China. Fax: +86-0411-84986134; Tel: +86-0411-84986133, +86-0411-84986134; E-mail: guoxw@dlut.edu.cn, lium@dlut.edu.cn

[b] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China. Fax: +86 10 62753541; Tel: +86 10 62755538; E-mail: wangyx@pku.edu.cn

[c] EMS Energy Institute, PSU-DUT Joint Center for Energy Research and Department of Energy & Mineral Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States. Fax: 814-865-3573; Tel: 814-863-4466; E-mail:csong@psu.edu

[d] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

[e] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China. Fax: +86-0571-88320863; Tel: +86-0571-88320863; E-mail: guoliangz@zjut.edu.cn

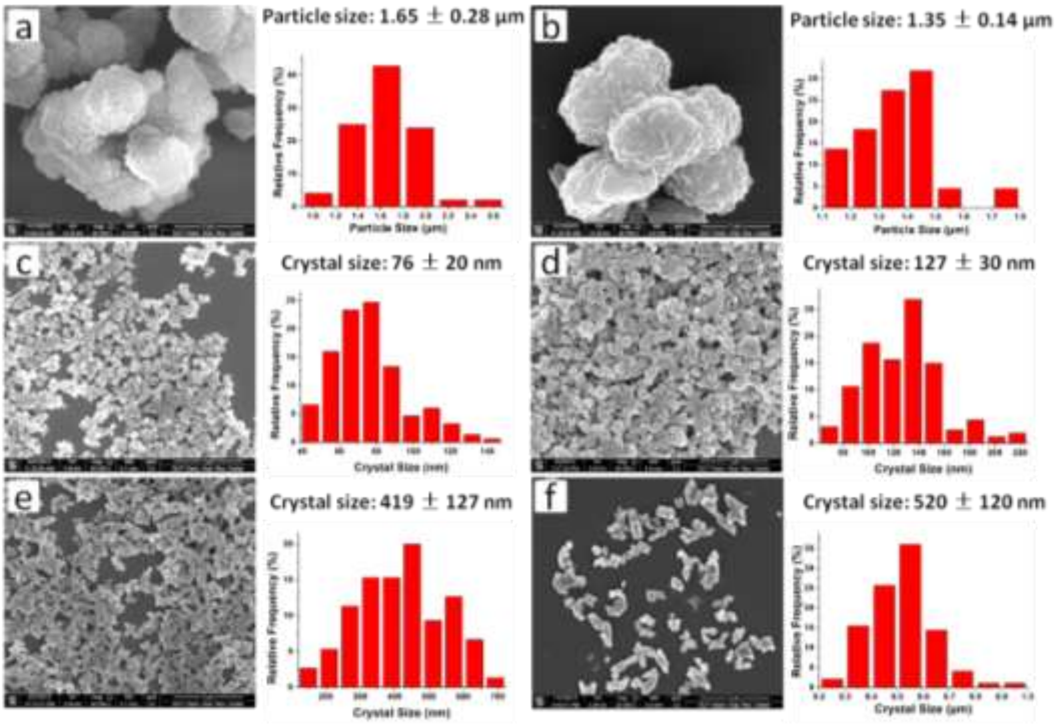

Fig. S1 Particle or crystal size distributions of NH_2-MIL-53(Al) synthesized with different volume ratios of water in DMF-water mixed solvents: (a) 0 vol%, (b) 3.3 vol%, (c) 25 vol%, (d) 50 vol%, (e) 75 vol%, and (f) 100 vol%.

All these particle and crystal sizes were calculated from the SEM images by counting over 100 particles or crystals and obtaining the average and standard deviation of them, except for the crystal sizes of (a) and (b) were estimated from the strongest diffraction peak (110) by using Scherrer equation, but the small crystals' length of (b) was obtained from the above SEM image. From Fig. S1, we could know that, with the increasing ratio of water as the mixed solvent, the resulting products had a significant change in particle size and crystal size. First of all, from (a) to (b), the particle size of the crystal aggregate was slightly reduced, and those small crystals placed on its surface became longer and narrower. Second, these crystal aggregates were dispersed to monocrystals, and then these monocrystals were gradually increased their crystal sizes.

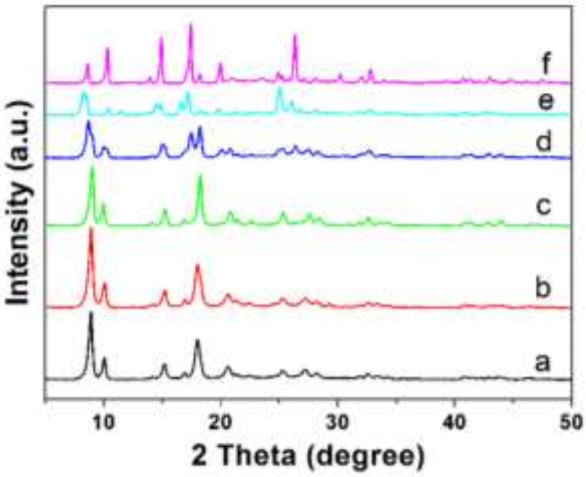

Fig. S2 XRD patterns of NH_2-MIL-53(Al) crystals before boiled in DMF.

Fig. S2 shows that there has minor change in the XRD patterns of some samples such as (d), (e), and (f) with the others. It is because that, with the increasing ratio of water in the mixed solvents, there has a lot of water molecules remained in the pores of (d) and (e) after crystallization, and the pores of (f) mainly contain unreacted NH_2-BDC. NH_2-MIL-53(Al) has flexible structure, which means its unit cell parameters can vary significantly when different guests are adsorbed within its pores, so that it will lead to this kind of change in the XRD patterns. However, those molecules can be replaced by DMF under reflux, after that the patterns of all products became very similar with each other (Fig. 2).

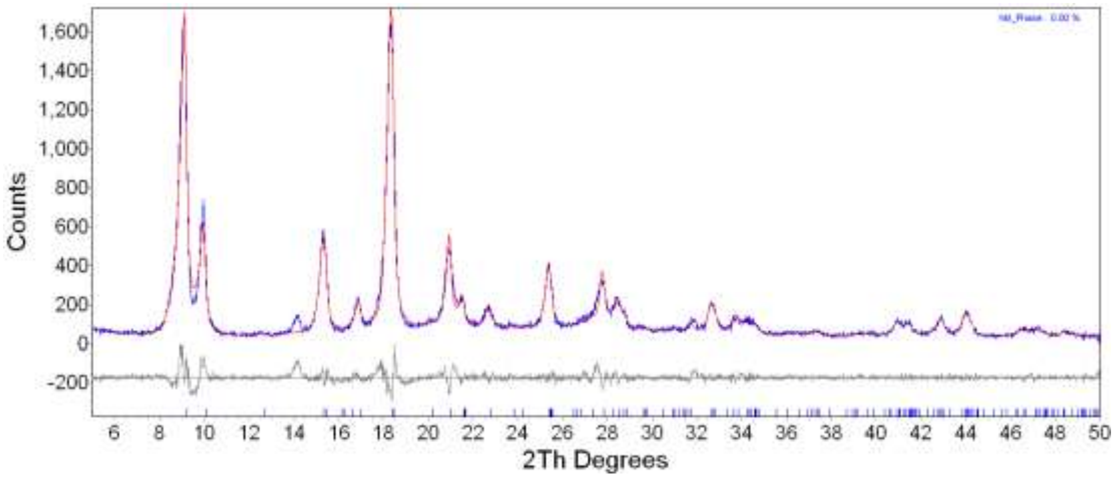

Fig. S3 Pawley fit of the XRD pattern of NH_2-MIL-53(Al).

Taking the sample (c) as an example, and its structure has been determined by means of powder X-ray diffraction analysis. Crystal data for NH_2-MIL-53(Al) are as follows[1]: *Pnam* (no. 62), R_{wp} = 12.8 %, a=17.587(7) Å, b=11.460(3) Å, c=6.686(2) Å. Profile fitting by Pawley method[2] and qualitative analysis confirmed that the peak at $2\theta = 9.2°$ corresponds to the (110) reflection. The peak at $2\theta = 18.2°$ has nearly twice the 2θ value of the first peak, but it consists of two overlapping peaks: the (211) reflection at $2\theta = 18.37°$, and the (220) reflection at $2\theta = 18.47°$. The reflections were listed below:

hkl	m	d	2Th
110	4	9.602	9.203
200	2	8.793	10.051
210	4	6.976	12.679
011	4	5.775	15.331
020	2	5.730	15.451
111	8	5.487	16.141
120	4	5.448	16.256
201	4	5.322	16.644
310	4	5.219	16.975
211	8	4.827	18.365
220	4	4.801	18.466
400	2	4.397	20.181
121	8	4.223	21.017
311	8	4.114	21.583
410	4	4.105	21.632
320	4	4.098	21.670
221	8	3.900	22.785
130	4	3.733	23.816
401	4	3.673	24.208
230	4	3.504	25.400
411	8	3.498	25.442
321	8	3.494	25.475
420	4	3.488	25.516
510	4	3.362	26.486
002	2	3.343	26.645
031	4	3.317	26.858
131	8	3.259	27.340
330	4	3.200	27.853
112	8	3.157	28.245
202	4	3.125	28.543
231	8	3.103	28.743
421	8	3.092	28.846
212	8	3.015	29.609
511	8	3.004	29.716
520	4	2.998	29.781
600	2	2.931	30.473
022	4	2.887	30.945
331	8	2.887	30.952
430	4	2.884	30.986
040	2	2.865	31.193

122	8	2.849	31.370
610	4	2.840	31.479
140	4	2.828	31.614
312	8	2.815	31.763
222	8	2.743	32.615
521	8	2.735	32.713
240	4	2.724	32.851
601	4	2.684	33.351
402	4	2.661	33.653
431	8	2.648	33.825
611	8	2.614	34.281
620	4	2.610	34.338
141	8	2.604	34.407
412	8	2.592	34.576
322	8	2.590	34.601
530	4	2.588	34.638
340	4	2.574	34.825
241	8	2.523	35.557
132	8	2.490	36.036
710	4	2.454	36.587
621	8	2.431	36.948
232	8	2.419	37.142
422	8	2.413	37.225
531	8	2.413	37.231
341	8	2.402	37.406
440	4	2.400	37.435
512	8	2.371	37.922
630	4	2.325	38.689
332	8	2.312	38.927
711	8	2.304	39.068
720	4	2.301	39.118
150	4	2.273	39.622
441	8	2.259	39.871
522	8	2.232	40.382
540	4	2.221	40.580
250	4	2.218	40.645
602	4	2.204	40.916
800	2	2.198	41.024
631	8	2.196	41.062
013	4	2.188	41.234
432	8	2.184	41.315
721	8	2.176	41.470
042	4	2.175	41.476
113	8	2.171	41.566
051	4	2.168	41.620
612	8	2.164	41.700
203	4	2.160	41.780
810	4	2.159	41.807

142	8	2.159	41.807
151	8	2.152	41.950
350	4	2.135	42.304
213	8	2.123	42.551
242	8	2.112	42.787
541	8	2.108	42.865
251	8	2.105	42.928
730	4	2.099	43.058
801	4	2.088	43.291
123	8	2.063	43.856
622	8	2.057	43.984
811	8	2.054	44.040
820	4	2.052	44.086
313	8	2.050	44.152
640	4	2.049	44.168
532	8	2.046	44.229
342	8	2.040	44.381
351	8	2.034	44.518
450	4	2.032	44.543
223	8	2.021	44.800
731	8	2.003	45.242
403	4	1.988	45.600
712	8	1.978	45.833
821	8	1.962	46.232
641	8	1.959	46.310
413	8	1.958	46.320
323	8	1.958	46.340
442	8	1.950	46.540
451	8	1.944	46.672
910	4	1.926	47.143
033	4	1.925	47.177
550	4	1.920	47.298
133	8	1.914	47.476
060	2	1.910	47.568
632	8	1.909	47.596
830	4	1.905	47.692
160	4	1.899	47.865
722	8	1.895	47.960
740	4	1.889	48.132
233	8	1.880	48.364
152	8	1.880	48.388
423	8	1.878	48.431
260	4	1.866	48.748
513	8	1.858	48.997
911	8	1.851	49.185
542	8	1.850	49.208
920	4	1.849	49.227
252	8	1.848	49.265

551	8	1.846	49.335
802	4	1.837	49.591
831	8	1.832	49.717
333	8	1.829	49.819
161	8	1.827	49.884
741	8	1.818	50.143
360	4	1.816	50.194

Fig. S4 Color changing properties of the reaction mixtures.

When the ratio of water less than 50 vol% such as (a), (b), and (c), all the reaction mixtures shown transparent faint yellow. However, stated from (d), NH_2-BDC was gradually precipitated from the solution and led to yellow suspension liquid just like the color of NH_2-BDC. This is based on the fact that NH_2-BDC is particularly soluble in DMF, but almost insoluble in water. Even raising the temperature to 150 °C, it is still partly dissolved in water. Hence, the already dissolved NH_2-BDC in DMF would precipitate when too much water was added to the solution. In conclusion, in the DMF-water mixed solvent system, NH_2-BDC will gradually precipitate from the solution with increased water content in the mixed solvent.

1. J. M. Chin, E. Y. Chen, A. G. Menon, H. Y. Tan, A. T. S. Hor, M. K. Schreyer and J. Xu, *CrystEngComm*, 2013, **15**, 654-657.
2. G. S. Pawley, *J. Appl. Cryst.*, 1981, **14**, 357-361.