Supporting Information:

Syntheses of metal-organic frameworks and aluminophosphates under microwave heating: A quantitative analysis of accelerations

Enamul Haque,[†] *Nazmul Abedin Khan,*[†] *Chang Min Kim,*[†] *and Sung Hwa Jhung*[†]*

[†] Department of Chemistry and Green-Nano Materials Center, Kyungpook National University

Daegu 702-701, Korea, Fax: (+)82-53-950-6330; E-mail: sung@knu.ac.kr

Synthesis procedure:

The MOFs were synthesized using the mixture of metal chlorides ($AlCl_3 \cdot 6H_2O$, 99%; $CrCl_3 \cdot 6H_2O$, 96%; VCl_3, 97%), terephthalic acid (TPA or H_2BDC, C_6H_4-1,4-$(CO_2H)_2$, 98%) and deionized water with the molar ratio of 1$MeCl_3$: 0.5 TPA: 80 H_2O (Me = Al, Cr or V). All chlorides and TPA were purchased from Sigma-Aldrich and were used without further purification. The reaction mixtures containing TPA, metal chlorides and water were stirred for 5 min. The AlPOs were synthesized similarly from phosphoric acid (85 %), pseudoboehmite (74.2 %, Catapal A, Vista Chemical Co.) and templates (triethyl amine (TEA) for AlPO-5 and di-n-propyl amine (DPA) for AlPO-11). The reactant compositions were Al_2O_3: 1.0P_2O_5: 1.5TEA: 100H_2O and Al_2O_3: 1.0P_2O_5: 1.5DPA: 100H_2O for AlPO-5 and AlPO-11, respectively. The resulting reactant mixture (30 g) was loaded into a Teflon-lined autoclave, sealed and placed in a preheated electric oven or in a microwave oven (MARS-5, CEM, USA, maximum power of 1200 W) for a fixed time. The temperature of the reactant mixture was increased rapidly up to the reaction temperature in about 1.5 min and 1 h for the MW and CE syntheses, respectively. The reaction temperature was relatively low (125 – 185 ^oC for MOFs and 130 – 150 ^oC for AlPOs) in order to compare the kinetics precisely to take advantage of low reaction rates at low temperature. The measured temperature was regarded as the actual reaction temperature of the system to calculate thermodynamic parameters even though the instantaneous temperature may be different to the bulk temperature.[1] The dimensions of the MW and CE reactors were nearly same each other (ID: 33-35 mm, height: 110-115 mm), and wide CE reactors were also used to check the effect of reactor dimension on the CE syntheses. After completion of the reactions for a predetermined time, the produced porous materials were collected by cooling (in air, natural cooling), centrifugation, washing with water and drying for 12 hours at 110 °C.

In the synthesis using microwave heating, the reaction temperature was controlled/measured using EST-300 Plus system (Electronic Sensor – Temperature) that monitored and controlled temperature conditions inside sample vessels. In this system, a microwave transparent fiberoptic temperature probe was inserted into a thermowell of a sample vessel. The temperature sensor was a phosphor located at the

tip of the probe. The decay rate of fluorescent light emitted from the phosphor is temperature dependent, allowing a precise determination of temperature. For safety, the temperature of the reaction vessel in the microwave oven was measured using an optional TempGuard^{TM}system. An infrared lens and sensor were located in the microwave oven and the temperature of each vessel was measured as the vessels rotated over the sensor. If the temperature in any vessel was higher than the maximum pre-set temperature, the TempGuard^{TM} stopped microwave generation.

The nitrogen adsorption was carried out using Micromeritics Tristar II 3020 surface area and porosity analyzer at liquid nitrogen temperature (-196 °C) after evacuation at 150 °C for 15 h. Surface area and micropore volume were calculated with the BET equation and t-plot, respectively, using the nitrogen adsorption isotherms.

[1.] Gharibeh, M.; Tompsett, G.; Lu, F.; Auerbach, S. M.; Yngvesson, K. S.; Conner, W. C. *J. Phys. Chem. B* **2009**, *113*, 12506–12520.

Calculation procedure for relative crystallinity:

After synthesis of the porous materials, the materials were analyzed with XRD. The XRD crystallinity of the materials were calculated by the relative intensity of a specific diffraction peak of as-synthesized materials, compared with the fully crystallized samples under a selected condition. The (2 0 0) (2theta=about 10.3), (1 0 0) (2theta=about 7.5) and (0 0 2) (2theta=about 21.0) diffraction peaks of MOFs, AlPO-5 and AlPO-11 were used to calculate the XRD intensity. The XRD intensity increases and saturates at a certain time, and this plateau was regarded as 100% crystallinity of the materials at the specific synthesis conditions. The XRD intensity may be changed with heating methods (such as CE and MW because of crystal size), temperatures and crystal structures (MOFs and AlPOs); however, the saturated intensity at the specific condition was used as pure crystalline materials at that condition for various reaction times. The XRD crystallinity was also evaluated after purification to remove organics in the pore structures and with 3 major XRD diffractions; however, there is little change in the crystallization curves. The syntheses were carried out for various times (at least 8 points) to derive smooth crystallization curves.

Supporting Table S1. Reaction conditions and textural properties of fully crystallized porous materials

Reaction condition				Textural properties		
Porous materials	Heating Method [a]	Temp. (^{o}C)	Time	S_{BET} [b] (m^2/g)	S_{Lang} [c] (m^2/g)	PV_{micro} [d] (cc/g)
MIL-53(Al)	CE	150	4d	1282	1365	0.47
	MW	150	5.5h	1307	1391	0.48
MIL-53(Cr)	CE	175	4d	1419	1518	0.50
	MW	175	7h	1436	1533	0.52
MIL-47(V)	CE	135	5d	1049	1118	0.36
	MW	135	3h	1087	1170	0.38
AlPO-5	CE	140	4d	281.3	412.8	0.15
	MW	140	3h	297.5	432.3	0.15
AlPO-11	CE	140	3d	204.7	318.4	0.10
	MW	140	2.5h	219.3	297.0	0.11

[a] CE: conventional electric heating, MW: microwave heating. [b] S_{BET}: BET surface area. [c] S_{Lang}: Langmuir surface area. [d] PV_{micro}: microporevolume calculated with t-plot.

Supporting Table S2. Nucleation and crystal growth rates of porous materials at various temperatures and calculated pre-exponential factors (A) and activation energies (E_a) of the Arrhenius equation with syntheses methods.

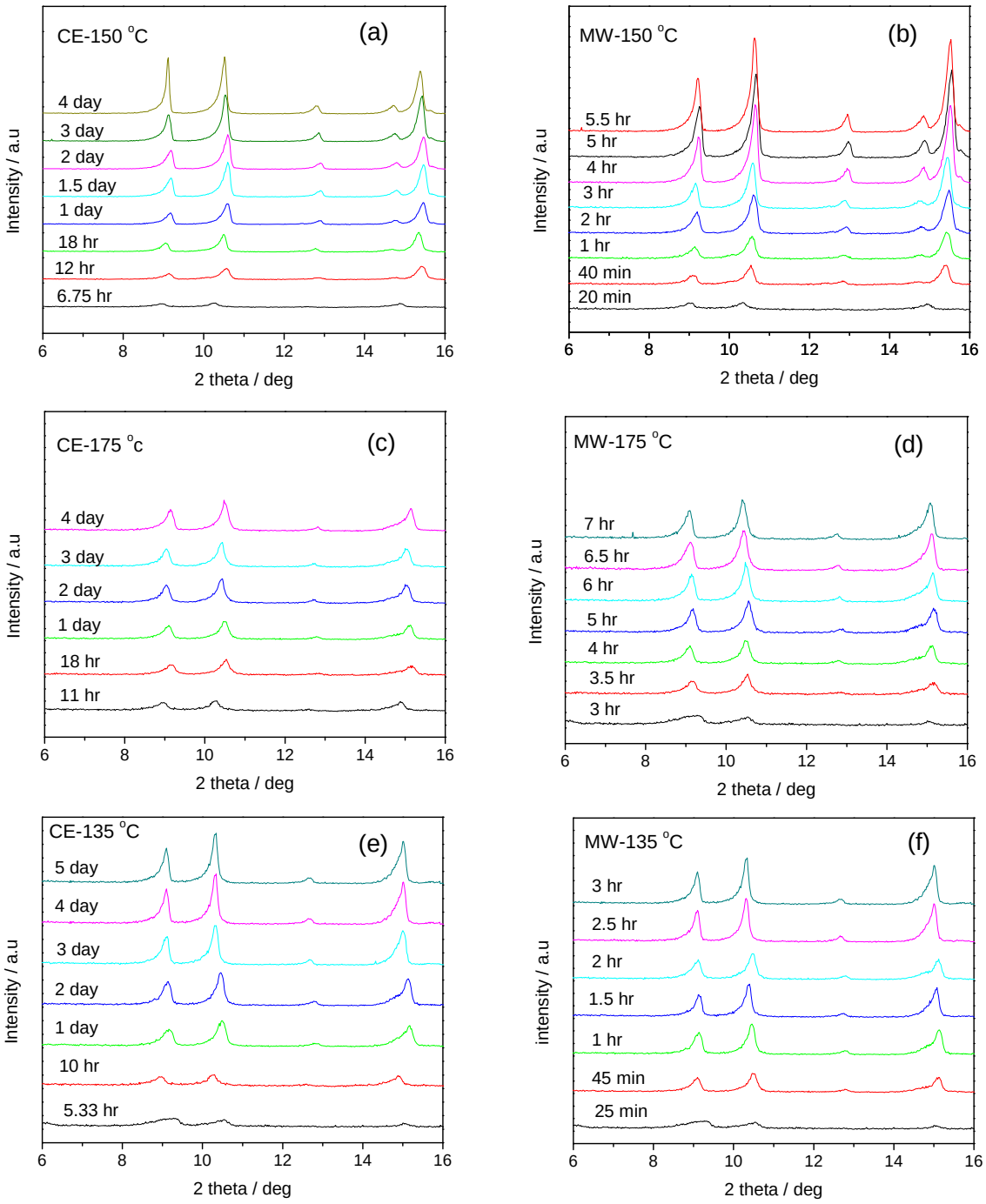
Porous materials	Methods[a]	Temp. (°C)	Nucleation					Crystal growth			
			Nucleation time (min)	Nucleation rate (/min)[b]	A (/min)[c]	E_a (kJ/mol)[c]	Relative rate[d]	Crystal growth rate (/min)[e]	A (/min)[c]	E_a (kJ/mol)[c]	Relative rate[d]
MIL-53(Al)	CE	140	660	1.52×10^{-3}			20.3	1.32×10^{-4}			20.5
		150	405	2.47×10^{-3}	4.78×10^{6}	75.2		2.17×10^{-4}	1.40×10^{8}	95.3	
		160	240	4.18×10^{-3}				4.76×10^{-4}			
	MW	140	40	2.50×10^{-2}				1.94×10^{-3}			
		150	20	5.00×10^{-2}	2.68×10^{11}	103		5.51×10^{-3}	2.63×10^{13}	127	
		160	10	1.00×10^{-1}				1.11×10^{-2}			
MIL-53(Cr)	CE	165	2520	3.97×10^{-4}			4.9	8.40×10^{-5}			21.1
		175	660	1.52×10^{-3}	2.28×10^{17}	174		2.71×10^{-4}	1.57×10^{18}	187	
		185	315	3.18×10^{-3}				7.89×10^{-4}			
	MW	165	545	1.84×10^{-3}				1.20×10^{-3}			
		175	180	5.56×10^{-3}	1.04×10^{22}	208		6.28×10^{-3}	3.09×10^{24}	230	
		185	45	2.22×10^{-2}				1.88×10^{-2}			
MIL-47(V)	CE	125	525	1.91×10^{-3}			14.4	1.41×10^{-4}			31.8
		135	320	3.13×10^{-3}	2.48×10^{5}	61.8		3.02×10^{-4}	1.75×10^{7}	84.4	
		145	215	4.65×10^{-3}				4.76×10^{-4}			
	MW	125	40	2.50×10^{-2}				4.29×10^{-3}			
		135	25	4.00×10^{-2}	1.91×10^{9}	83.1		7.90×10^{-3}	9.69×10^{10}	102	
		145	12	8.33×10^{-2}				1.88×10^{-2}			
AlPO-5	CE	130	285	3.51×10^{-3}			28.1	1.71×10^{-4}			35.9
		140	210	4.76×10^{-3}	3.74×10^{2}	38.8		2.45×10^{-4}	8.12×10^{3}	59.3	
		150	165	6.06×10^{-3}				3.95×10^{-4}			
	MW	130	12	8.33×10^{-2}				5.18×10^{-3}			
		140	7.5	1.33×10^{-1}	9.30×10^{6}	62.1		8.33×10^{-3}	7.22×10^{8}	86.1	
		150	5	2.00×10^{-1}				1.75×10^{-2}			
AlPO-11	CE	130	465	2.15×10^{-3}			32.7	2.10×10^{-4}			31.0
		140	375	2.67×10^{-3}	2.27×10^{1}	31.0		3.26×10^{-4}	2.61×10^{3}	54.7	
		150	300	3.33×10^{-3}				4.54×10^{-4}			
	MW	130	18	5.56×10^{-2}				4.45×10^{-3}			
		140	12	8.33×10^{-2}	2.50×10^{7}	66.8		8.53×10^{-3}	1.03×10^{13}	119	
		140	7	1.43×10^{-1}				2.39×10^{-2}			

[a] CE: conventional electric heating; MW: microwave heating. [b] Calculated from the 1/(nucleation time). [c] Pre-exponential factors (A) and activation energies (E_a) are calculated with the Arrhenius equation. [d] Relative rate (r_{MW}/r_{CE}), calculated with the Arrhenius equation at medium temperature. [e] Calculated from the slope of a crystallization curve (between 20% and 80% crystallinity).

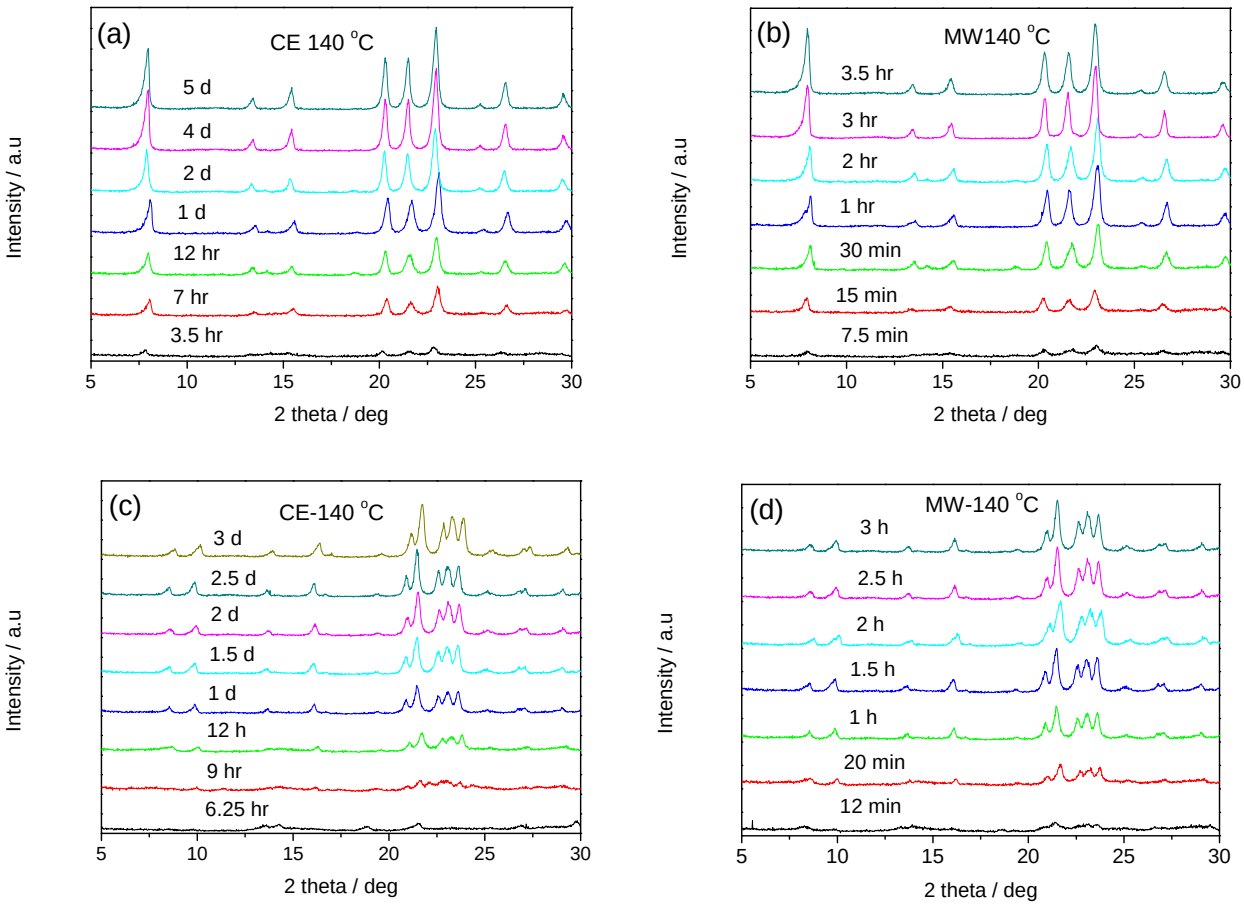
Supporting Table S3. Nucleation and crystal growth rates of Fe-BDC at various temperatures and thermodynamic parameters obtained with the Eyring equation

Porous materials	Methods [a]	Temp. (°C)	Nucleation							Crystal growth					
			Nucleation time (min)	Nucleation rate (/min)[b]	$\Delta G^{\neq}$ (kJ/mol)[c]	$\Delta H^{\neq}$ (kJ/mol)[d]	$\Delta S^{\neq}$ (J/mol·K)[d]	E_a (kJ/mol)[e]	Relative rate[f]	Crystal growth rate (/min)[g]	$\Delta G^{\neq}$ (kJ/mol)[c]	$\Delta H^{\neq}$ (kJ/mol)[d]	$\Delta S^{\neq}$ (J/mol·K)[d]	E_a (kJ/mol)[e]	Relative rate[f]
Fe-BDC	CE	70	310	3.23×10^{-3}					26.1	3.78×10^{-4}					77.1
		75	250	4.00×10^{-3}	114	36.3	-222	39.2		5.16×10^{-4}	119	63.5	-161	66.4	
		80	210	4.76×10^{-3}						7.31×10^{-4}					
	MW	60	44	2.27×10^{-2}						8.01×10^{-3}					
		65	32	3.13×10^{-2}	104	72.0	-95.4	74.8		1.11×10^{-2}	107	87.8	-56.8	90.6	
		70	20	5.00×10^{-2}						2.08×10^{-2}					

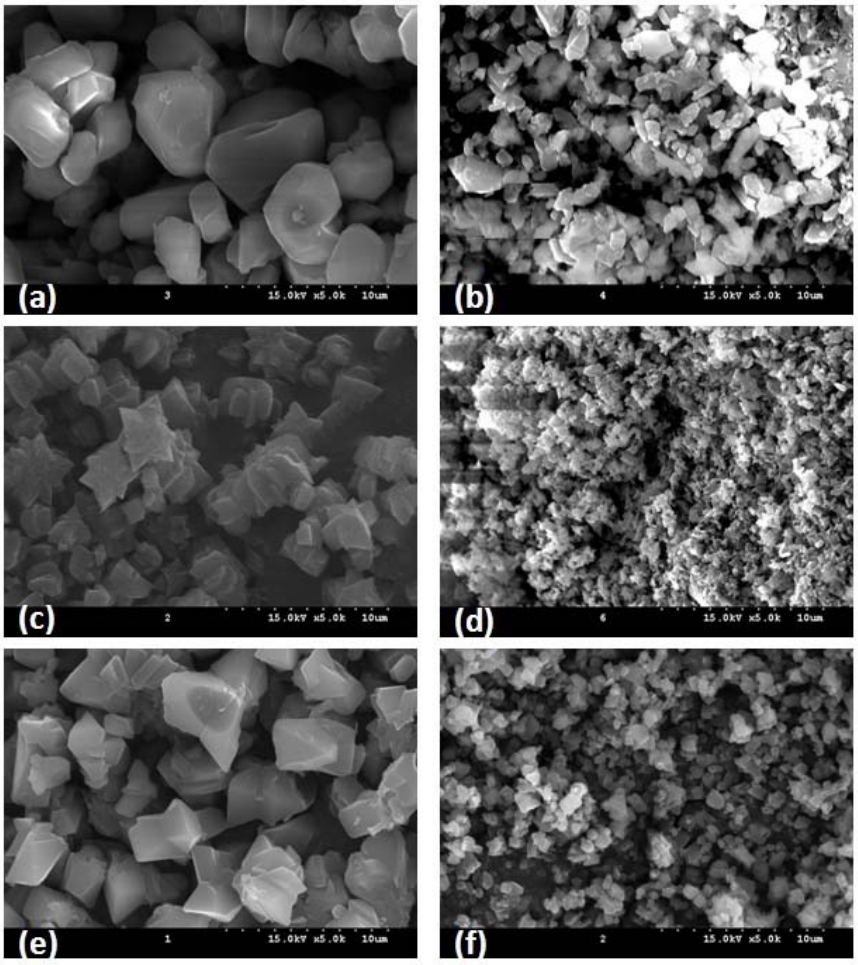
[a] CE: conventional electric heating; MW: microwave heating. [b] Calculated from the value of 1/(nucleation time). [c] Calculated from $\Delta G^{\neq} = \Delta H^{\neq} - T\,\Delta S^{\neq}$. [d] Calculated with the Eyring equation. [e] Calculated from $E_a = \Delta H^{\neq} + RT$. [f] Relative rate ($r_{MW}/r_{CE}$), calculated with the Eyring equation at the medium temperature of the syntheses. [g] Calculated from the slope of a crystallization curve (between 20% and 80% crystallinity).



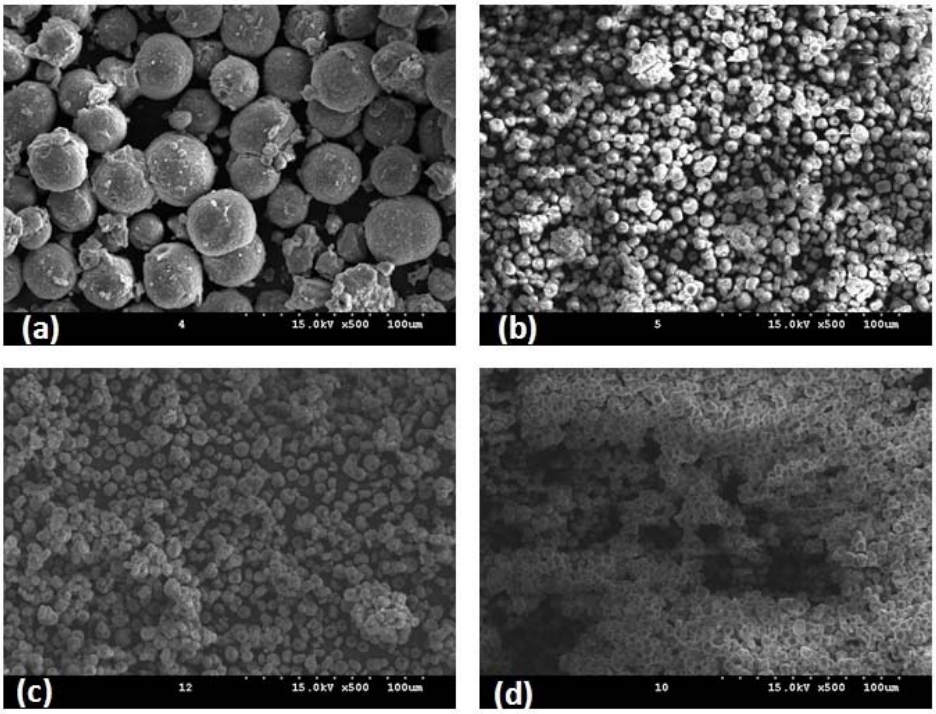
Supporting Figure S1. Typical XRD patterns of MOFs synthesized at various conditions: (a) MIL-53(Al) synthesized at 150 °C under conventional electric heating; (b) MIL-53(Al) synthesized at 150 °C under microwave heating; (c) MIL-53(Cr) synthesized at 175 °C under conventional electric heating; (d) MIL-53(Cr) synthesized at 175 °C under microwave heating; (e) MIL-47(V) synthesized at 135 °C under conventional electric heating; (f) MIL-47(V) synthesized at 135 °C under microwave heating.



Supporting Figure S2. Typical XRD patterns of AlPOs synthesized at various conditions at 140 °C: (a) AlPO-5 synthesized under conventional electric heating; (b) AlPO-5 synthesized under microwave heating; (c) AlPO-11 synthesized under conventional electric heating; (d) AlPO-11 synthesized under microwave heating



Supporting Figure S3. SEM images of fully crystallized MOFs: (a) MIL-53(Al) synthesized at 150 ^{o}C for 4 d under conventional electric heating; (b) MIL-53(Al) synthesized at 150 ^{o}C for 5.5 h under microwave heating; (c) MIL-53(Cr) synthesized at 175 ^{o}C for 4 d under conventional electric heating; (d) MIL-53(Cr) synthesized at 175 ^{o}C for 7 h under microwave heating; (e) MIL-47(V) synthesized at 135 ^{o}C for 5 d under conventional electric heating; (f) MIL-47(V) synthesized at 135 ^{o}C for 3 h under microwave heating. The crystal sizes of (a), (b), (c), (d), (e) and (f) are about 2-6, 0.5-2, 2-3, 0.5, 3-5 and 0.5-1 μm, respectively.



Supporting Figure S4. SEM images of fully crystallized AlPOs: (a) AlPO-5 synthesized at 140 ^{o}C for 4 d under conventional electric heating; (b) AlPO-5 synthesized at 140 ^{o}C for 3 h under microwave heating; (c) AlPO-11 synthesized at 140 ^{o}C for 3 d under conventional electric heating; (d) AlPO-11 synthesized at 140 ^{o}C for 2.5 h under microwave heating. The crystal sizes of (a), (b), (c) and (d) are about 10-40, 5-10, 5-10 and 2-3 μm, respectively.