Electronic Supplementary Information

Unprecedented performance of N-doped activated hydrothermal carbon towards C_2H_6/CH_4, CO_2/CH_4, and CO_2/H_2 separation

Bin Yuan,[†] Jun Wang, [‡] Yingxi Chen,[†] Xiaofei Wu,[§] Hongmei Luo and Shuguang Deng* [‡]

Department of Chemical & Materials Engineering, New Mexico State University, Las Cruces, NM 88003, USA. *E-mail: Shuguang.Deng@asu.edu; Fax: 480-727-9321; Tel: 480-727-7238*

Present address

† Department of Chemical & Biological Engineering, Iowa State University of Science and Technology, Sweeney Hall, Ames, IA 50011, USA

‡ School for Engineering of Matter, Transport, and Energy, Arizona State University, 551 E. Tyler Mall, Tempe, AZ 85287, USA

§ Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Science, 1219 Zhongong West Road, Ningbo, Zhejiang Province, 315201, China

Fitting of adsorption isotherms with Toth model

The pure-component adsorption isotherms of C_2H_6, CO_2, CH_4, and H_2 were well fitted with Toth model:

$$q = \frac{q_m (bP)^t}{(1+(bP)^t)^{1/t}}$$

Here, q is the amount of gas uptake (mmol g^{-1}), q_m is the maximum amount of gas uptake (mmol g^{-1}), P is the equilibrium pressure (kPa), b (kPa^{-1}) and t are constants. The fitting parameters are summarized in Table S3 along with the average relative deviation (*ARD*) defined by the following equation:

$$ARD = \frac{100}{N}\sum_{i}^{N}\left|\frac{q_{\exp} - q_{fit}}{q_{\exp}}\right|,$$

where N is the total number of experimental data points, and q_{exp} and q_{fit} are the experimental and fitted gas uptake at the same equilibrium pressure, respectively.

Selectivity calculation using the ideal adsorbed solution theory (IAST)

The pure-component adsorption isotherms were first fitted with Toth equation (see above information). The selectivity for a binary mixture was calculated using the following equation:

$$S_{1,2} = \frac{x_1 / y_1}{x_2 / y_2}$$

where x_i and y_i are the molar fractions of component i (i = 1, 2) in the adsorbed phase and bulk phase, repectively.

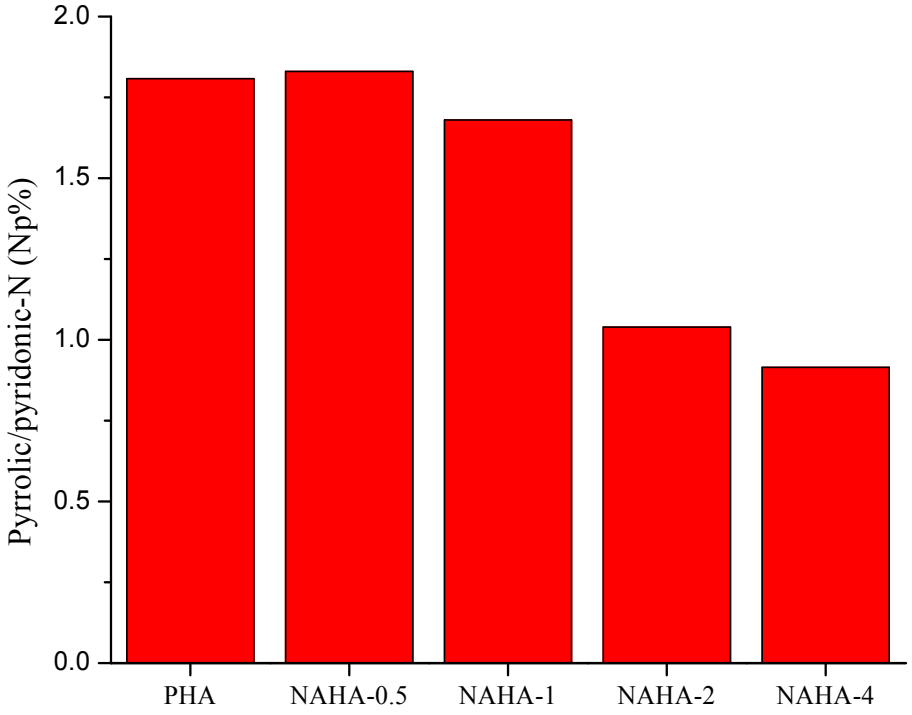

Fig. S1 Pyrrolic/pyridonic-N content by atom, i.e. the percentage of nitrogen atom in the form of pyrrolic/pyridonic-N with respect to all the atoms (C, O, and N) determined by XPS. This value is denoted as Np%.

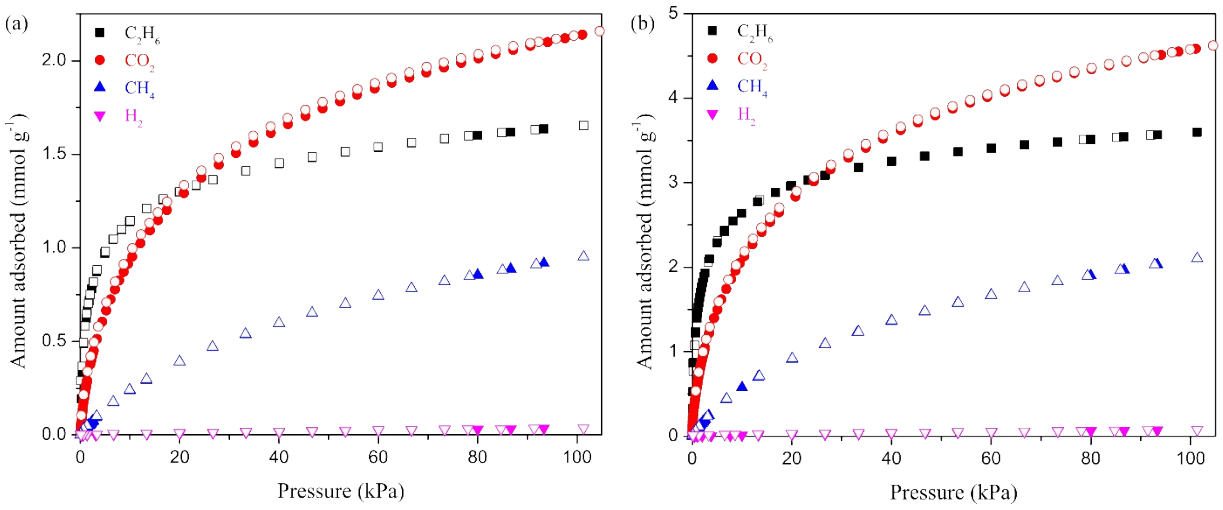

Fig. S2 Representative adsorption and desorption isotherms of CO_2, C_2H_6, CH_4, and H_2 on (a) pyrolyzed carbon (PHA) and (b) activated carbon (NAHA-0.5).

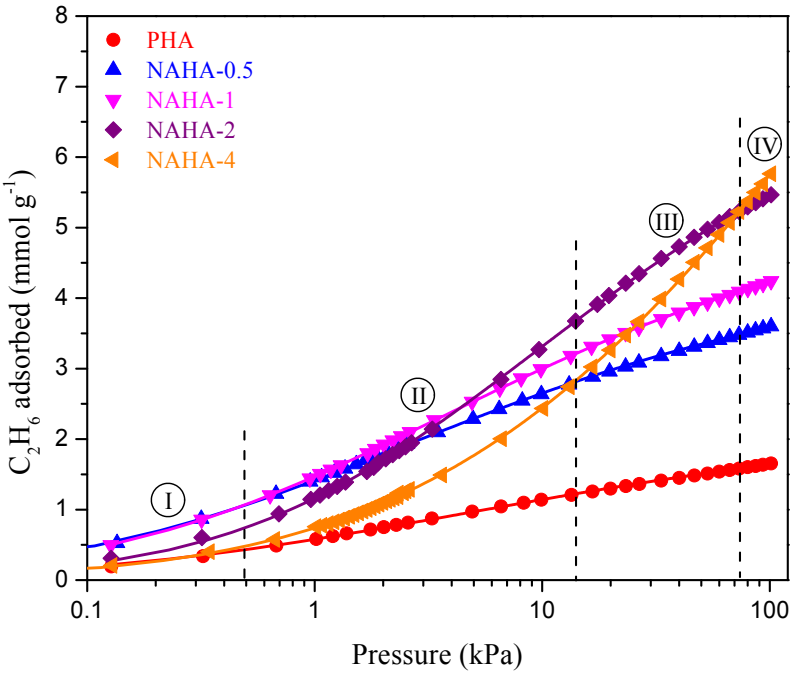

Fig. S3 C_2H_6 adsorption isotherms of the investigated carbons at 273 K. The lines represent Toth isotherm fitting.

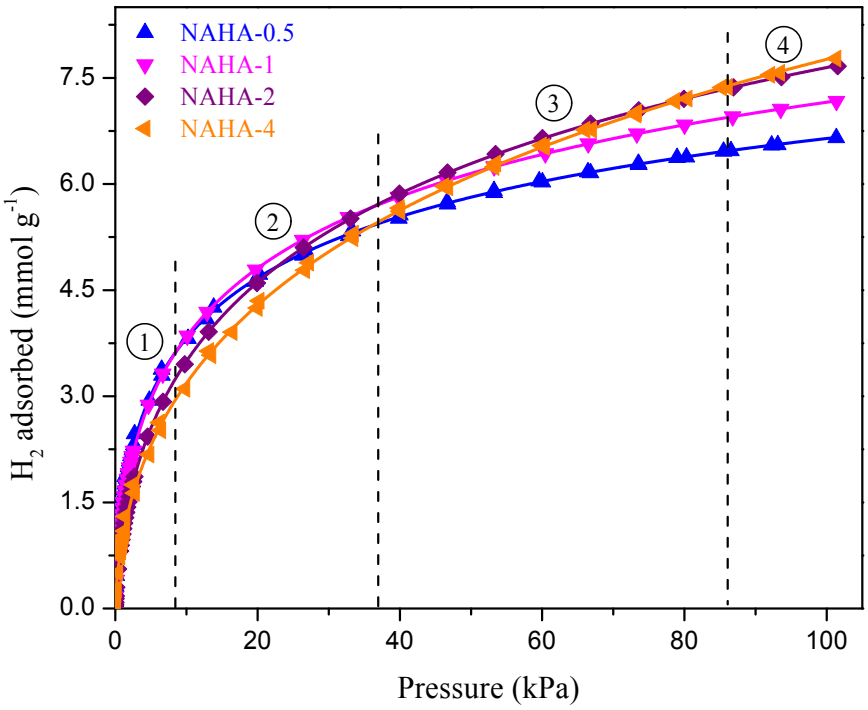

Fig. S4 H_2 adsorption isotherms of the investigated carbons at 87 K. The lines represent Toth isotherm fitting.

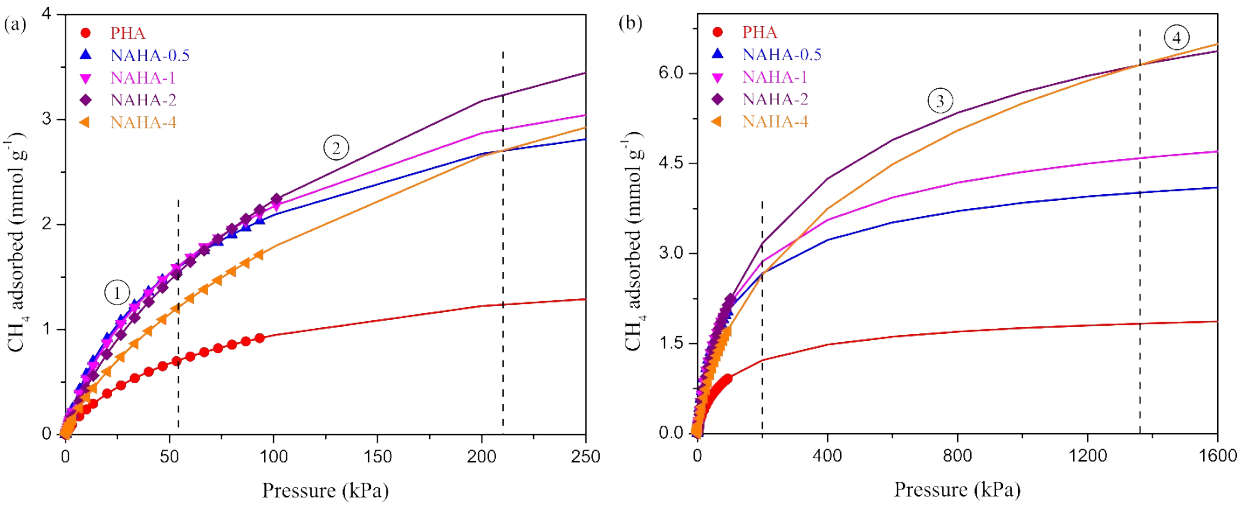

Fig. S5 CH_4 adsorption isotherms of the investigated carbons at 273 K. The lines represent Toth isotherm fitting.

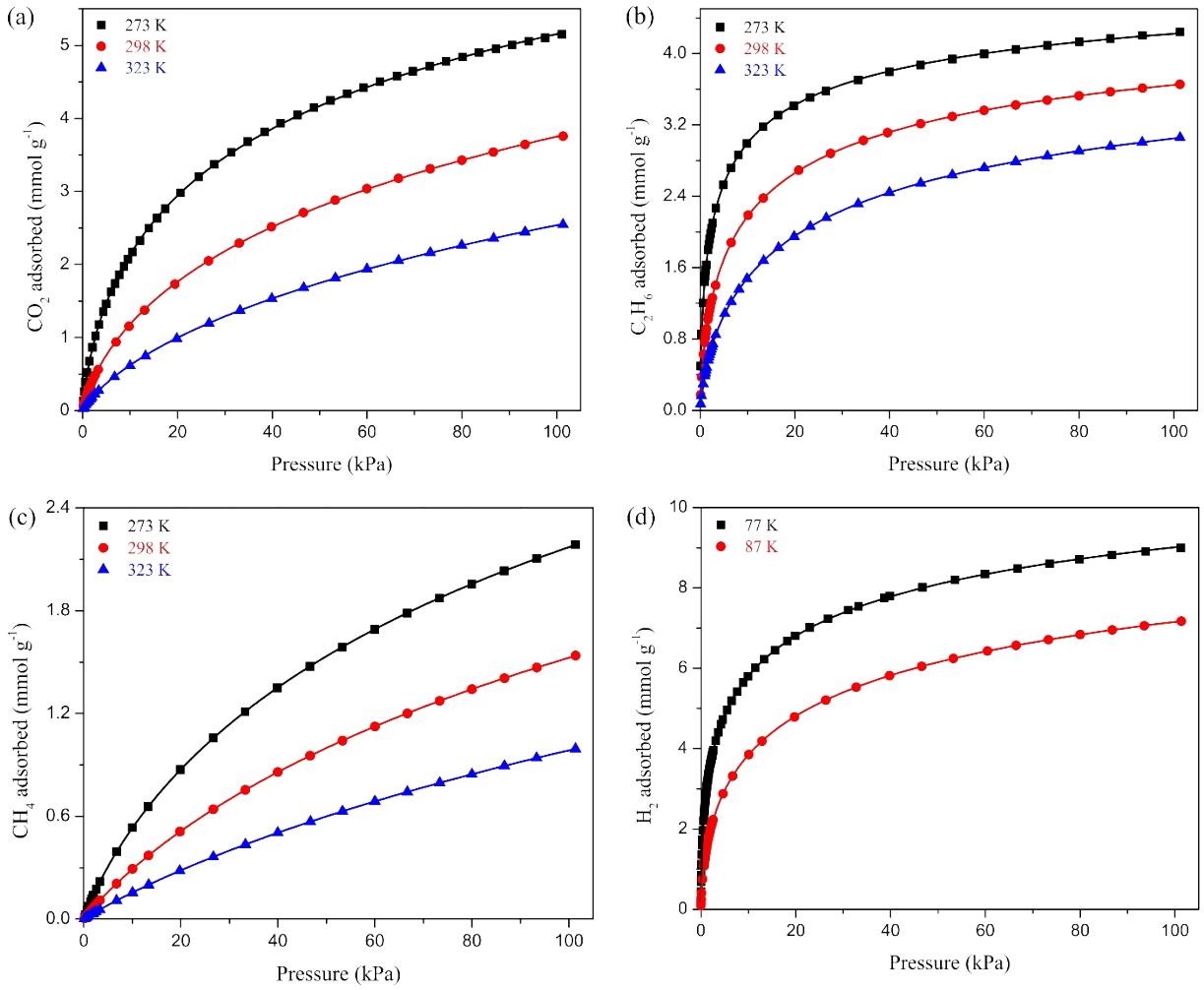

Fig. S6 CO_2 (a), C_2H_6 (b), and CH_4 (c) isotherms of NAHA-1 at 273, 298, and 323 K. H2 (d) isotherms of NAHA-1 at 77 and 87 K. The lines represent Toth isotherm fitting.

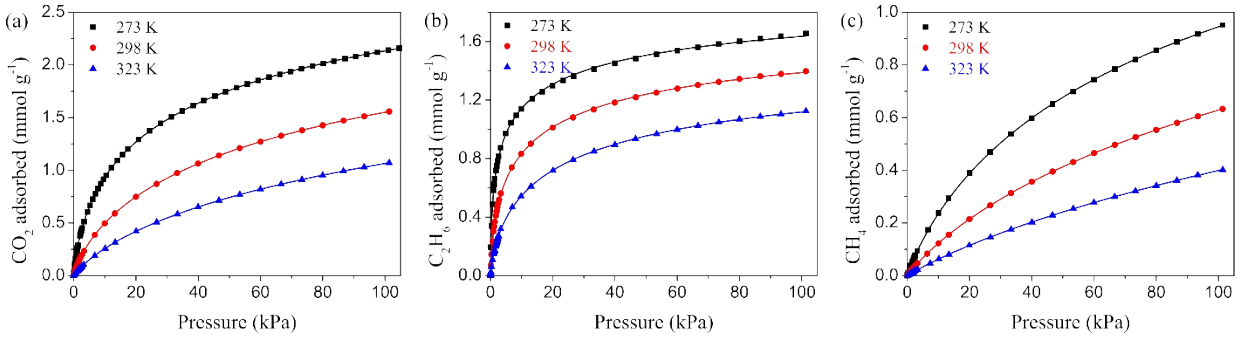

Fig. S7 CO_2 (a), C_2H_6 (b), and CH_4 (c) isotherms of PHA at 273, 298, and 323 K. The lines represent Toth isotherm fitting.

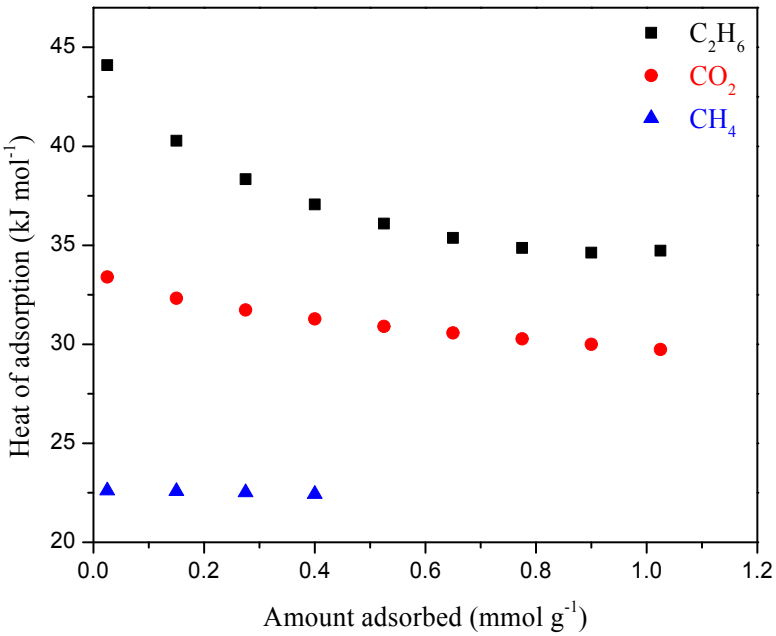

Fig. S8 Isosteric heat of adsorption for PHA at different gas loadings.

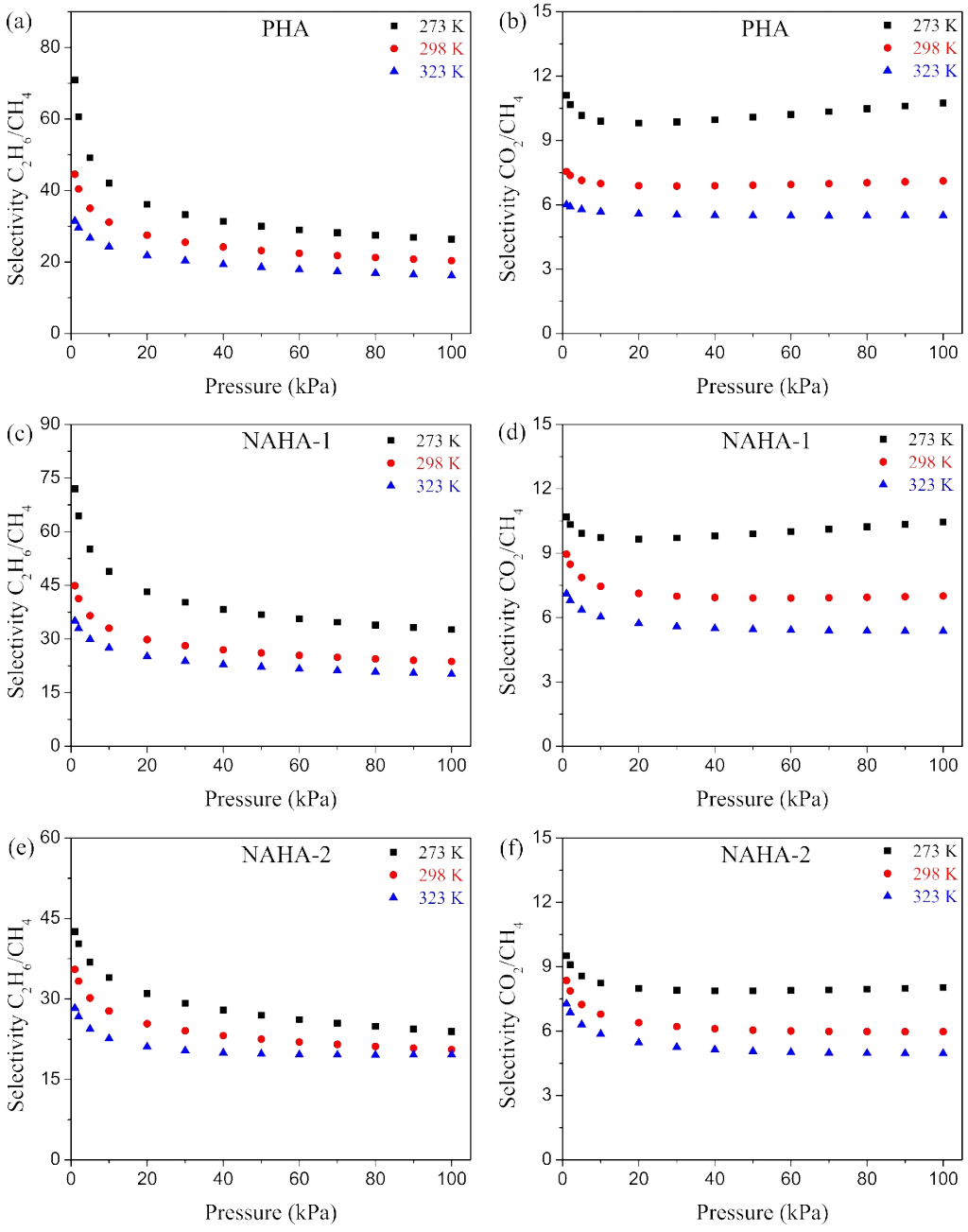

Fig. S9 IAST predicted selectivities of C_2H_6 over CH_4 (a,c,e) and CO_2 over CH_4 (b,d,f) for equimolar binary mixtures at 273, 298, and 323 K in PAH (a,b), NAHA-1 (c,d), and NAHA-2 (e,f).

Table S1 Comparison of CO_2 uptakes of various carbons at 100 kPa

Sample	CO_2 uptake (mmol g^{-1})		Reference
	273 K	**298 K**	
NAHA-2	6.0	4.0	This study
commercial activated carbon (e.g. BPL, Maxsorb, Norit R1 Extra)	< 5	< 2.5	(1)
RFL-500	–	3.1	(2)
CEM750	6.9	4.4	(3)
CN500	4.4	3.1	(4)
AS-2-700	6.6	4.3	(5)
CP-2–600	6.2	3.9	(6)
SK-0.5-700	–	4.2	(7)
$C_{RHC111\text{-}DES}$ after thermally treated at 800 C	–	3.1	(8)
VR-5-M	8.6	4.2	(9)
CS*-P-A	8.9	4.6 (296 K)	(10)
micro-TiC chlorinated at 700 C and then annealed in H2 at 600 C	7.1	4.1	(11)
ACM-5	11.5	5.1	(12)
HCM-ZC-1	5.4	3.8	(13)
HCM-DAH-1-900-1	4.8	3.2	(14)
CPC-550	8.3	5.8	(15)
SC800	–	3.4	(16)
AC-2–635	5.9	3.9	(17)
NC800	5.7	3.8	(18)
Bamboo-3-873	7.0	4.5	(19)
HPC74-1000	–	3.4 (300 K)	(20)
NC900	5.1	3.9	(21)
AG-2-700	7.4	4.5	(22)
PCN-71	4.5	2.9	(23)
EBI-B	4.1	2.7	(24)
activated carbon monoliths	–	< 3	(25)
K4-700	–	3.5	(26)
CSA-800	6.6	3.2	(27)
N-HCSs	–	2.7	(28)
KNC-A-HCl	6.0	4.0	(29)

Table S2 Comparison of C_2H_6 uptakes of various sorbents at 100 kPa

Sample		C_2H_6 uptake (mmol g^{-1})		Reference
		273 K	**298 K**	
Carbons	NAHA-2	5.5	4.6	This study
	activated carbon	–	3.75 (293 K)	(30)
	BPL	–	2.8 (301 K)	(31)
	BPL	4.7	3.6	(32)
	activated carbon	–	3.5	(33)
	kureha activated carbon	5.5	4.3	(34)
	date-pit activated carbon	–	2.6 (303 K)	(35)
	zeolite-templated carbon	4	–	(36)
	zeolite-templated carbon	10	6.5	(37)
	MSC-30 (Maxsorb)	10	6.5	(37)
	AC-40	–	2.2 (293 K)	(38)
	CMK-3	–	3.7	(39)
	Nuxit-AL	–	3.3 (293 K)	(40)
	coconut activated carbon	–	4.5	(41)
	Norit-activated carbon	–	3.3 (303 K)	(42)
	Ajax-activated carbon	4.9 (283 K)	4 (303 K)	(42)
Other adsorbents (MOFs, Polymeric Organic Frameworks, zeolites, ordered mesoporous silica, and clays)	UTSA-33a	3.5	2.7 (296 K)	(43)
	ZJU-60a	7.8	5.9 (296 K)	(44)
	Mg-MOF-74	7.8	–	(45)
	ZIF-7	–	1.9	(46)
	NOTT-300	–	0.9 (293 K)	(47)
	FJI-C1	5.5	3.9	(48)
	Fe_2(dobdc)	–	0.77 (318 K)	(49)
	La(BTB)H_2O	4.6	–	(50)
	mesoPOF-1	2.5	–	(51)
	PAF-40-Mn	2.8	2	(52)
	silicalite	2.2 (277 K)	–	(53)
	ETS-10	–	1.5 (300 K)	(54)
	zeolite 13X	–	3.4 (305 K)	(55)
	MCM-41	1.5	–	(56)
	SBA-15	–	0.6 (303K)	(57)
	clays	–	< 0.8	(58)

Table S3 Fitting parameters of Toth model for the pure-component isotherms on the as-prepared carbons

Sample	Gas	Temp. (K)	q_m	b	t	Adjusted R^2	ARD, %
NAHA-0.5	C_2H_6	273	4.427	3.692	0.4057	0.99987	1.55
	CO_2	273	9.875	0.1898	0.3750	0.99982	4.75
	CH_4	273	5.153	0.0201	0.5694	1	1.81
	H_2	273	62.51	2.65E-05	0.2532	0.99913	7.38
	H_2	87	11.75	0.9989	0.3371	0.99977	1.99
NAHA-1	C_2H_6	273	5.386	2.2836	0.4135	0.99998	0.19
	C_2H_6	298	5.078	0.4837	0.4635	0.99998	0.59
	C_2H_6	323	4.829	0.1632	0.4913	1	0.35
	CO_2	273	11.19	0.1020	0.4161	0.99991	1.64
	CO_2	298	14.17	0.03127	0.3772	0.99994	2.85
	CO_2	323	16.84	0.00932	0.3733	0.99995	3.82
	CH_4	273	6.130	0.01404	0.5780	1	0.96
	CH_4	298	5.281	0.00707	0.6549	1	0.96
	CH_4	323	5.051	0.00354	0.6756	1	1.33
	H_2	273	1.408	5.21E-04	0.8330	0.99994	6.24
	H_2	87	13.85	0.6292	0.3362	0.99998	2.20
	H_2	77	15.20	4.509	0.2938	0.99997	0.41
NAHA-2	C_2H_6	273	7.329	0.4591	0.4892	0.9999	1.03
	C_2H_6	298	7.618	0.1628	0.4706	0.99997	0.52
	C_2H_6	323	7.470	0.05654	0.4941	1	0.28
	CO_2	273	25.80	0.03169	0.3497	0.99994	1.49
	CO_2	298	38.88	0.00813	0.3188	0.99998	2.55
	CO_2	323	49.58	0.00236	0.3187	0.99998	2.79
	CH_4	273	10.02	0.00642	0.5461	1	1.47
	CH_4	298	7.610	0.00356	0.6580	1	1.54
	CH_4	323	3.870	0.00319	0.9412	0.99998	4.28
	H_2	273	2.111	4.22E-04	0.6958	0.99989	9.92
	H_2	87	19.04	0.2422	0.3292	0.99998	4.33
	H_2	77	20.93	1.672	0.2818	0.99988	3.31
NAHA-4	C_2H_6	273	23.11	0.2376	0.2610	0.99996	0.96
	CO_2	273	4109	0.01571	0.1005	0.99985	1.98
	CH_4	273	17.30	0.00352	0.4091	0.99997	8.22
	H_2	273	132.2	2.47E-05	0.2128	0.99934	22.78
	H_2	87	44.52	0.2117	0.2302	0.99999	1.81
PHA	C_2H_6	273	2.239	3.689	0.3594	0.99946	1.17
	C_2H_6	298	1.971	0.5833	0.4401	0.99987	1.16
	C_2H_6	323	1.759	0.1638	0.4945	0.99995	8.48
	CO_2	273	4.090	0.1216	0.4410	0.99999	1.84
	CO_2	298	4.061	0.03372	0.4667	0.99999	1.86
	CO_2	323	3.928	0.01188	0.4985	1	3.92
	CH_4	273	2.246	0.0159	0.6415	0.99998	5.94
	CH_4	298	2.292	0.00711	0.6220	0.99999	2.40
	CH_4	323	2.431	0.00303	0.6306	0.99994	4.37
	H_2	273	0.6428	6.55E-04	0.8238	0.99979	23.97

Table S4 Comparison of C_2H_6/CH_4, CO_2/CH_4, CO_2/H_2 separation performance (uptake capacity and selectivity) of various carbons for corresponding equimolar binary mixtures between 0–100 kPa or under similar conditions[a]

Sample	C_2H_6 uptake[b]	CO_2 uptake[b]	C_2H_6/CH_4 selectivity	CO_2/CH_4 selectivity	CO_2/H_2 selectivity	Ref.

	273 K	298 K	273 K	298 K	273 K	298 K	273 K	298 K	273 K	298 K	
NAHA-1	4.2	3.7	5.2	3.8	33–72	24–45	9.7–10.7	6.9–9.0	2.0×10^4		This study
NAHA-2	5.5	4.6	6.0	4.0	24–43	21–36	7.9–9.5	6.0–8.4	3.5×10^3		This study
SC700P				3.0				4.3–7			(16)
PAF-1-450[c]			4.5				8.5		400		(59)
C125-220[d]				2.1				14.8			(60)
Zeolite templated carbon				< 2.5				< 2.7		17–18	(61)
AC35				< 2.5				2.4			(61)
BG-ENO				< 2.5				3.4			(61)
activated carbon[e]										< 90	(62)
BPL[f]		2.8				17					(31)
N-doped carbon			1.4				8–13				(63)
ACB-5				2.2				< 2			(64)
A35/4[g]				2.2				3.5			(65)
CMK-3		3.7		2.3		12–16		< 2.1			(39)
JX101[h]				1.5						< 100	(66)
Norit				2.0				2			(67)
Maxorb				2.2				2			(67)
N-doped carbon			5.1				11				(21)
activated carbon[i]		3.8				*11*					(30)
BPL[j]				< 2				*2.5*		*91*	(68)
BPL				1.0				*4.5*			(69)
N-Doped Carbon			8.3	5.8			*13*	*12*			(15)
FCDTPA-K-500			4.4				*8*				(70)
Norit R1 Extra, Maxsorb			< 5	< 2.5			*<3.2*	*<2.2*			(1)

[a] A cell is left blank if the data is not available for that cell, selectivity values in italics are Henry's law selectivities. [b] Gas uptake at 100 kPa in mmol g^{-1}. [c] At a CO_2:CH_4 ratio of 15:85, CO_2:H_2 ratio of 20:80. [d] At 120 kPa, a CO_2:CH_4 ratio of 30:70 [e] At a CO_2:H_2 ratio of 1:8, pressure of 1.11 MPa. [f] At 301 K. [g] At 293 K. [h] At 313 K, a CO_2:H_2 ratio of 20:80. [i] At 293 K. [j] At 303 K.

Table S5 Comparison of C_2H_6/CH_4, CO_2/CH_4, CO_2/H_2 separation performance (uptake capacity and selectivity) of the carbons prepared in this study with those of various adsorbents (carbons are not included here) for corresponding equimolar binary mixtures between 0–100 kPa or under similar conditions[a]

Sample	C_2H_6 uptake[b]		CO_2 uptake[b]		C_2H_6/CH_4 selectivity		CO_2/CH_4 selectivity		CO_2/H_2 selectivity		Ref.
	273 K	298 K	273 K	298 K	273 K	298 K	273 K	298 K	273 K	298 K	
NAHA-1	4.2	3.7	5.2	3.8	33–72	24–45	9.7–10.7	6.9–9.0	2.0×10^4		This study
NAHA-2	5.5	4.6	6.0	4.0	24–43	21–36	7.9–9.5	6.0–8.4	3.5×10^3		This study
bio-MOF-11[c]				4.1						< 300	(71)
SUMOF-4[d]				3.2						< 180	(72)
$Zn_5(BTA)_6(TDA)_2$[e]				2				10			(73)
UTSA-25a[e]				3.2				8			(73)
Cu(BDC-OH)[e]				1.9				6.5			(73)
UTSA-33a[e]				2.5				6.5			(73)
UTSA-34b[e]				2.6				4.5			(73)
Yb(BPT)[e]				0.7				3			(73)
UTSA-33a[e]		2.7				16–20					(43)
UTSA-34b[e]		4.4				17–18					(74)
UTSA-34a[e]		2.8				19–25					(74)
IFP-5			< 2				7.5				(75)
NOTT-300[f]		0.9				5–6					(47)
MCOF-1		2				50–88					(76)
MOF	4.6		2.3		12–22		4.7–8				(50)
FJI-C1		3.9				13–24					(48)
FIR-7a-ht		4				14–15					(77)
FIR-51	5.4	4.7			14–19	10–14.5					(78)
Cu–TDPAT		6.7				15–46					(79)
2a	5.2				18–20						(80)
Mg2(dobdc)[g]				8						< 900	(66)
Zeolite 13X[g]				4.3						< 400	(66)
Na-ETS-10[h]		1.4				46–52					(81)
MCM-41		0.5		0.8		5–5.7		5.8–6.8			(82)
MCM-41				0.7						< 35	(83)
SBA-15				0.5				4.9–5.5			(39)
mesoPOF-2	1.6		1.7		25–40		10–15				(51)
ZnP-CTF-500		4				21–40					(84)
PAF-40-Mn		2				30–35					(52)
$CoMo_3S_{13}$ aerogel			0.9						85–120		(85)
Ge-rich chalcogenide			< 1						< 90		(86)
PCH		0.4		0.7		4.5–5	5.8–7				(82)
Zr_W		0.3		0.4		18–25		14–35			(87)
MOF-177				1.6				*4.4*			(88)
Compound 1A			1.7						*266*		(89)
UTSA-36 a	2.8	2.1			*24.7*	*16.6*					(90)
CG-9			8.3				*7.3*				(91)
ZIF-100				1				*5.9*			(92)
ZIF-78				2.7				*10.5*			(69)
NOTT-202a			2.3				*2.9*		*10^5*		(93)
ZJU-30	2.8	2.1			*29.8*	*19.5*					(94)
ZJU-61	6	4.7			*12.3*	*11*					(95)

[a] A cell is left blank if the data is not available for that cell, selectivity values in italics are Henry's law selectivities. [b] Gas uptake at 100 kPa in mmol g^{-1}. [c] At a CO_2:H_2 ratio of 10:90. [d] At a CO_2:H_2 ratio of 15:85. [e] At 296 K. [f] At 293 K. [g] At 313 K, CO_2:H_2 ratio of 80:20. [h] At a C_2H_6:CH_4 ratio of 95:5.

References

1 S. Himeno, T. Komatsu and S. Fujita, *Journal of Chemical & Engineering Data*, 2005, **50**, 369-376.

2 G. P. Hao, W. C. Li, D. Qian and A. H. Lu, *Adv Mater*, 2010, **22**, 853-857.

3 Y. Xia, R. Mokaya, G. S. Walker and Y. Zhu, *Advanced Energy Materials*, 2011, **1**, 678-683.
4 X. Zhu, P. C. Hillesheim, S. M. Mahurin, C. Wang, C. Tian, S. Brown, H. Luo, G. M. Veith, K. S. Han and E. W. Hagaman, *ChemSusChem*, 2012, **5**, 1912-1917.
5 M. Sevilla and A. B. Fuertes, *Energy & Environmental Science*, 2011, **4**, 1765-1771.
6 M. Sevilla, P. Valle-Vigón and A. B. Fuertes, *Advanced Functional Materials*, 2011, **21**, 2781-2787.
7 W. Xing, C. Liu, Z. Zhou, L. Zhang, J. Zhou, S. Zhuo, Z. Yan, H. Gao, G. Wang and S. Z. Qiao, *Energy & Environmental Science*, 2012, **5**, 7323-7327.
8 M. C. Gutiérrez, D. Carriazo, C. O. Ania, J. B. Parra, M. L. Ferrer and F. del Monte, *Energy & Environmental Science*, 2011, **4**, 3535-3544.
9 A. Wahby, J. M. Ramos-Fernández, M. Martínez-Escandell, A. Sepúlveda-Escribano, J. Silvestre-Albero and F. Rodríguez-Reinoso, *ChemSusChem*, 2010, **3**, 974-981.
10 N. P. Wickramaratne and M. Jaroniec, *Journal of Materials Chemistry A*, 2013, **1**, 112-116.
11 V. Presser, J. McDonough, S.-H. Yeon and Y. Gogotsi, *Energy & Environmental Science*, 2011, **4**, 3059-3066.
12 M. Nandi, K. Okada, A. Dutta, A. Bhaumik, J. Maruyama, D. Derks and H. Uyama, *Chem. Commun.*, 2012, **48**, 10283-10285.
13 D. Qian, C. Lei, E. M. Wang, W. C. Li and A. H. Lu, *ChemSusChem*, 2014, **7**, 291-298.
14 G.-P. Hao, W.-C. Li, D. Qian, G.-H. Wang, W.-P. Zhang, T. Zhang, A.-Q. Wang, F. Schüth, H.-J. Bongard and A.-H. Lu, *Journal of the American Chemical Society*, 2011, **133**, 11378-11388.
15 B. Ashourirad, A. K. Sekizkardes, S. Altarawneh and H. M. El-Kaderi, *Chemistry of Materials*, 2015, **27**, 1349-1358.
16 A. S. Mestre, C. Freire, J. Pires, A. P. Carvalho and M. L. Pinto, *Journal of Materials Chemistry A*, 2014, **2**, 15337-15344.
17 X. Fan, L. Zhang, G. Zhang, Z. Shu and J. Shi, *Carbon*, 2013, **61**, 423-430.
18 A. Aijaz, T. Akita, H. Yang and Q. Xu, *Chemical Communications*, 2014, **50**, 6498-6501.
19 H. Wei, S. Deng, B. Hu, Z. Chen, B. Wang, J. Huang and G. Yu, *ChemSusChem*, 2012, **5**, 2354-2360.
20 G. Srinivas, V. Krungleviciute, Z.-X. Guo and T. Yildirim, *Energy & Environmental Science*, 2014, **7**, 335-342.
21 A. Aijaz, N. Fujiwara and Q. Xu, *Journal of the American Chemical Society*, 2014, **136**, 6790-6793.
22 M. Sevilla, C. Falco, M.-M. Titirici and A. B. Fuertes, *RSC Advances*, 2012, **2**, 12792-12797.
23 G.-P. Hao, Z.-Y. Jin, Q. Sun, X.-Q. Zhang, J.-T. Zhang and A.-H. Lu, *Energy & Environmental Science*, 2013, **6**, 3740-3747.
24 S. M. Mahurin, P. F. Fulvio, P. C. Hillesheim, K. M. Nelson, G. M. Veith and S. Dai, *ChemSusChem*, 2014, **7**, 3284-3289.
25 J. Marco-Lozar, M. Kunowsky, F. Suárez-García, J. Carruthers and A. Linares-Solano, *Energy & Environmental Science*, 2012, **5**, 9833-9842.
26 X. Hu, M. Radosz, K. A. Cychosz and M. Thommes, *Environmental science & technology*, 2011, **45**, 7068-7074.
27 B. Zhu, K. Li, J. Liu, H. Liu, C. Sun, C. E. Snape and Z. Guo, *Journal of Materials Chemistry A*, 2014, **2**, 5481-5489.
28 S. Feng, W. Li, Q. Shi, Y. Li, J. Chen, Y. Ling, A. M. Asiri and D. Zhao, *Chemical Communications*, 2014, **50**, 329-331.
29 Y. Zhao, X. Liu, K. X. Yao, L. Zhao and Y. Han, *Chemistry of Materials*, 2012, **24**, 4725-4734.
30 B.-U. Choi, D.-K. Choi, Y.-W. Lee, B.-K. Lee and S.-H. Kim, *Journal of Chemical & Engineering Data*, 2003, **48**, 603-607.
31 Y. He, J.-H. Yun and N. A. Seaton, *Langmuir*, 2004, **20**, 6668-6678.
32 B. P. Russell and M. D. LeVan, *Industrial & engineering chemistry research*, 1997, **36**, 2380-2389.
33 I. A. Esteves, M. S. Lopes, P. M. Nunes and J. P. Mota, *Separation and Purification Technology*, 2008, **62**, 281-296.
34 W. Zhu, J. Groen, A. Van Miltenburg, F. Kapteijn and J. Moulijn, *Carbon*, 2005, **43**, 1416-1423.
35 S. A. Al-Muhtaseb, *Journal of Chemical & Engineering Data*, 2009, **55**, 313-319.
36 J. Chen, L. S. Loo and K. Wang, *Journal of Chemical & Engineering Data*, 2011, **56**, 1209-1212.
37 M. Murialdo, N. P. Stadie, C. C. Ahn and B. Fultz, *The Journal of Physical Chemistry C*, 2015, **119**, 944-950.
38 E. Costa, G. Calleja, C. Marron, A. Jimenez and J. Pau, *Journal of Chemical and Engineering Data*, 1989, **34**, 156-160.
39 V. K. Saini, M. Andrade, M. L. Pinto, A. P. Carvalho and J. Pires, *Separation and Purification Technology*, 2010, **75**, 366-376.
40 S. Suwanayuen and R. P. Danner, *AIChE Journal*, 1980, **26**, 68-76.
41 K. S. Walton, C. L. Cavalcante Jr and M. D. Levan, *Adsorption*, 2005, **11**, 107-111.
42 S. Qiao, K. Wang and X. Hu, *Langmuir*, 2000, **16**, 1292-1298.
43 Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chemistry-A European Journal*, 2012, **18**, 613-619.
44 X. Duan, Q. Zhang, J. Cai, Y. Yang, Y. Cui, Y. He, C. Wu, R. Krishna, B. Chen and G. Qian, *Journal of Materials Chemistry A*, 2014, **2**, 2628-2633.
45 Z. Bao, S. Alnemrat, L. Yu, I. Vasiliev, Q. Ren, X. Lu and S. Deng, *Langmuir*, 2011, **27**, 13554-13562.
46 C. Gücüyener, J. van den Bergh, J. Gascon and F. Kapteijn, *Journal of the American Chemical Society*, 2010, **132**, 17704-17706.
47 S. Yang, A. J. Ramirez-Cuesta, R. Newby, V. Garcia-Sakai, P. Manuel, S. K. Callear, S. I. Campbell, C. C. Tang and M. Schröder, *Nature Chemistry*, 2015, **7**, 121-129.
48 Y. Huang, Z. Lin, H. Fu, F. Wang, M. Shen, X. Wang and R. Cao, *ChemSusChem*, 2014, **7**, 2647-2653.

49 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606-1610.
50 J. Duan, M. Higuchi, S. Horike, M. L. Foo, K. P. Rao, Y. Inubushi, T. Fukushima and S. Kitagawa, *Advanced Functional Materials*, 2013, **23**, 3525-3530.
51 A. P. Katsoulidis and M. G. Kanatzidis, *Chemistry of Materials*, 2012, **24**, 471-479.
52 S. Meng, H. Ma, L. Jiang, H. Ren and G. Zhu, *Journal of Materials Chemistry A*, 2014, **2**, 14536-14541.
53 M. S. Sun, D. Shah, H. H. Xu and O. Talu, *The Journal of Physical Chemistry B*, 1998, **102**, 1466-1473.
54 N. A. Al-Baghli and K. F. Loughlin, *Journal of Chemical & Engineering Data*, 2005, **50**, 843-848.
55 A. Anson, C. C. Lin, S. M. Kuznicki and J. A. Sawada, *Chemical Engineering Science*, 2009, **64**, 3683-3687.
56 J.-H. Yun, T. Düren, F. J. Keil and N. A. Seaton, *Langmuir*, 2002, **18**, 2693-2701.
57 B. L. Newalkar, N. V. Choudary, P. Kumar, S. Komarneni and T. S. Bhat, *Chemistry of Materials*, 2002, **14**, 304-309.
58 M. L. Pinto, J. o. Pires and J. Rocha, *The Journal of Physical Chemistry C*, 2008, **112**, 14394-14402.
59 T. Ben, Y. Li, L. Zhu, D. Zhang, D. Cao, Z. Xiang, X. Yao and S. Qiu, *Energy & Environmental Science*, 2012, **5**, 8370-8376.
60 J. Patiño, M. C. Gutiérrez, D. Carriazo, C. O. Ania, J. B. Parra, M. L. Ferrer and F. del Monte, *Energy & Environmental Science*, 2012, **5**, 8699-8707.
61 C. Ducrot-Boisgontier, J. Parmentier, A. Faour, J. l. Patarin and G. D. Pirngruber, *Energy & fuels*, 2010, **24**, 3595-3602.
62 D. Cao and J. Wu, *Carbon*, 2005, **43**, 1364-1370.
63 Y. Shen and J. Bai, *Chemical Communications*, 2010, **46**, 1308-1310.
64 X. Shao, Z. Feng, R. Xue, C. Ma, W. Wang, X. Peng and D. Cao, *AIChE Journal*, 2011, **57**, 3042-3051.
65 M. Heuchel, G. Davies, E. Buss and N. Seaton, *Langmuir*, 1999, **15**, 8695-8705.
66 Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *Journal of the American Chemical Society*, 2011, **133**, 5664-5667.
67 S. Cavenati, C. A. Grande, A. E. Rodrigues, C. Kiener and U. Müller, *Industrial & engineering chemistry research*, 2008, **47**, 6333-6335.
68 S. Sircar, T. Golden and M. Rao, *Carbon*, 1996, **34**, 1-12.
69 R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *Journal of the American Chemical Society*, 2009, **131**, 3875-3877.
70 X. Yang, M. Yu, Y. Zhao, C. Zhang, X. Wang and J.-X. Jiang, *Journal of Materials Chemistry A*, 2014, **2**, 15139-15145.
71 E. Atci, I. Erucar and S. Keskin, *The Journal of Physical Chemistry C*, 2011, **115**, 6833-6840.
72 S. S. Han, D.-H. Jung and J. Heo, *The Journal of Physical Chemistry C*, 2012, **117**, 71-77.
73 S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nature communications*, 2012, **3**, 954.
74 Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O'Keeffe and B. Chen, *Chemistry-A European Journal*, 2012, **18**, 1901-1904.
75 F. Debatin, J. Möllmer, S. S. Mondal, K. Behrens, A. Möller, R. Staudt, A. Thomas and H.-J. Holdt, *Journal of Materials Chemistry*, 2012, **22**, 10221-10227.
76 H. Ma, H. Ren, S. Meng, Z. Yan, H. Zhao, F. Sun and G. Zhu, *Chemical Communications*, 2013, **49**, 9773-9775.
77 Y.-P. He, Y.-X. Tan and J. Zhang, *Chemical Communications*, 2013, **49**, 11323-11325.
78 H.-R. Fu, F. Wang and J. Zhang, *Dalton Transactions*, 2015, **44**, 2893-2896.
79 K. Liu, D. Ma, B. Li, Y. Li, K. Yao, Z. Zhang, Y. Han and Z. Shi, *Journal of Materials Chemistry A*, 2014, **2**, 15823-15828.
80 Y.-X. Tan, Y. Zhang, Y.-P. He, Y.-J. Zheng and J. Zhang, *Inorganic chemistry*, 2014, **53**, 12973-12976.
81 N. Magnowski, A. Avila, C. Lin, M. Shi and S. Kuznicki, *Chemical Engineering Science*, 2011, **66**, 1697-1701.
82 V. K. Saini, M. Pinto and J. Pires, *Green Chemistry*, 2011, **13**, 1251-1259.
83 Y. Belmabkhout and A. Sayari, *Chemical Engineering Science*, 2009, **64**, 3729-3735.
84 H. Ma, H. Ren, S. Meng, F. Sun and G. Zhu, *Scientific reports*, 2013, **3**.
85 M. Shafaei-Fallah, A. Rothenberger, A. P. Katsoulidis, J. He, C. D. Malliakas and M. G. Kanatzidis, *Adv Mater*, 2011, **23**, 4857-4860.
86 G. S. Armatas and M. G. Kanatzidis, *Nature materials*, 2009, **8**, 217-222.
87 J. Pires, V. K. Saini and M. L. Pinto, *Environmental science & technology*, 2008, **42**, 8727-8732.
88 D. Saha, Z. Bao, F. Jia and S. Deng, *Environmental science & technology*, 2010, **44**, 1820-1826.
89 S. S. Nagarkar, A. K. Chaudhari and S. K. Ghosh, *Inorganic chemistry*, 2011, **51**, 572-576.
90 M. C. Das, H. Xu, S. Xiang, Z. Zhang, H. D. Arman, G. Qian and B. Chen, *Chemistry-A European Journal*, 2011, **17**, 7817-7822.
91 S. Liu, L. Sun, F. Xu, J. Zhang, C. Jiao, F. Li, Z. Li, S. Wang, Z. Wang and X. Jiang, *Energy & Environmental Science*, 2013, **6**, 818-823.
92 B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207-211.
93 S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah and P. Hubberstey, *Nature materials*, 2012, **11**, 710-716.
94 J. Cai, J. Yu, H. Xu, Y. He, X. Duan, Y. Cui, C. Wu, B. Chen and G. Qian, *Crystal Growth & Design*, 2013, **13**, 2094-2097.

95 X. Duan, Q. Zhang, J. Cai, Y. Cui, C. Wu, Y. Yang and G. Qian, *Microporous and Mesoporous Materials*, 2014, **190**, 32-37.