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Dual Optimization of Microporosity in Carbon Spheres for CO_2 Adsorption by using Pyrrole as Carbon Precursor and Potassium Salt as Activator

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EXPERIMENAL

Materials

Resorcinol (98%), Pyrrole (99%) and Ethylenediamine (99%) were obtained from Acros Organics, NJ, USA. 3-aminophenol was purchased from Alfa Aesar, Ward Hill, MA,USA. Formaldehyde (37wt%) and Potassium citrate monohydrate were purchased from Fisher scientific, USA. Ammonium Persulfate was obtained from Sigma Aldrich. Deionized water (DW) was obtained from in-house Ion pure Plus 150 Service Deionization ion-exchange purification system and Aqua One (Amarillo, TX). All reagents were of analytical grade and were used without further purification.

Characterization

Nitrogen adsorption by each sample was measured at -196 ^{o}C using ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA) and respective isotherms were obtained. All samples were out gassed under vacuum at 200 ^{o}C for 2 h prior to adsorption measurements.

Thermogravimetric (TG) profiles were recorded using High resolution thermogravimetric measurements were recorded on TGA Q-500 analyzer (TA Instruments, Inc., New Castle, DE), from 25 to 900 ^{o}C in flowing oxygen with a heating rate of 10 ^{o}C / min using a high resolution mode. The initial weight of each sample analyzed ranged 5-15 mg. TG profiles were used to obtain information about the stability of carbon samples studied.

Scanning electron microscopy (SEM) images were obtained using Hitachi S-2600N scanning electron microscope. Prior to SEM analysis samples were dispersed in ethanol followed by sonication at concentrations of ~5-10 wt. %. Sonicated samples were deposited on SEM Hitachi specimen holder and were dried under vacuum at 100 ˚C for 1h.

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 microscope. Prior to TEM analysis, the samples were dispersed in ethanol by moderate sonication at concentrations of ~5-10 wt. %, followed by deposition of samples on a Lacy carbon coated, 200-mesh, copper TEM grid by dipping into the sample suspension and was then dried under vacuum at 100 ^{o}C for 1 h.

Particle size data was obtained using Horiba scientific SZ-100 nanoparticle analyzer. Prior to measurements samples were dispersed in 95% (v/v) ethanol/water solution and was sonicated for 10 minutes to obtain homogeneously dispersed solution. Each measurement was performed in triplicate.

Low temperature (0 ˚C) and ambient temperature (25 ˚C) CO_2 adsorption measurements

CO_2 adsorption measurements were carried out at 0 ˚C and 25 ˚C on samples up-to 1.2 atm on ASAP 2020 volumetric adsorption analyzer (Micromeritics, Inc., GA) at 25 ºC using ultrahigh purity (99.99 %) gaseous CO_2. Prior to adsorption analysis each sample was outgassed at 200 ºC for 2 h under vacuum.

Calculations

Brunauer-Emmet-Teller (BET) method[1] was used to evaluate specific surface area of samples within the relative pressure range of 0.05-0.20. Adsorption branch of nitrogen adsorption-desorption isotherms were used to evaluate pore size distributions (PSD) using the 2DNLDFT heterogeneous surface model for carbon materials implemented in SAIEUS program provided by Micromeritics.[2] PSD curves were calculated by Density Functional Theory (DFT) method.

Quantitative analysis of CO_2/N_2 selectivity (S)

CO_2/N_2 selectivity was evaluated according to the ideal adsorbed solution theory (IAST) model[3] using the following formulae:
$S = n(CO_2)\ p(N_2)/[n(N_2)\ p(CO_2)]$, where S denotes the CO_2/N_2 is selectivity, $n(CO_2)$ and $n(N_2)$ denote the CO_2 and N_2 uptake in mmol/g at CO_2 pressure of 0.15 bar and N_2 pressure of 0.85 bar, respectively.

References

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2. Jagiello, J.; Olivier, J. P. Carbon slit pore model incorporating surface energetical heterogeneity and geometrical corrugation. *Adsorption* **2013**, *19*, 777-783.

3. Myers, A.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE J.* **1965**, *11*, 121-127.

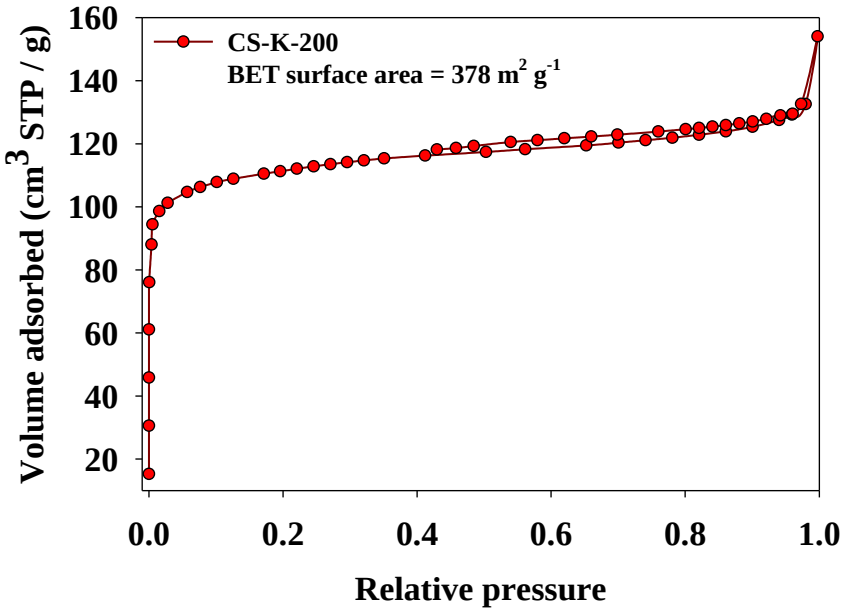

Figure S1. N_2 adsorption isotherm recorded for CS-K-200 sample.

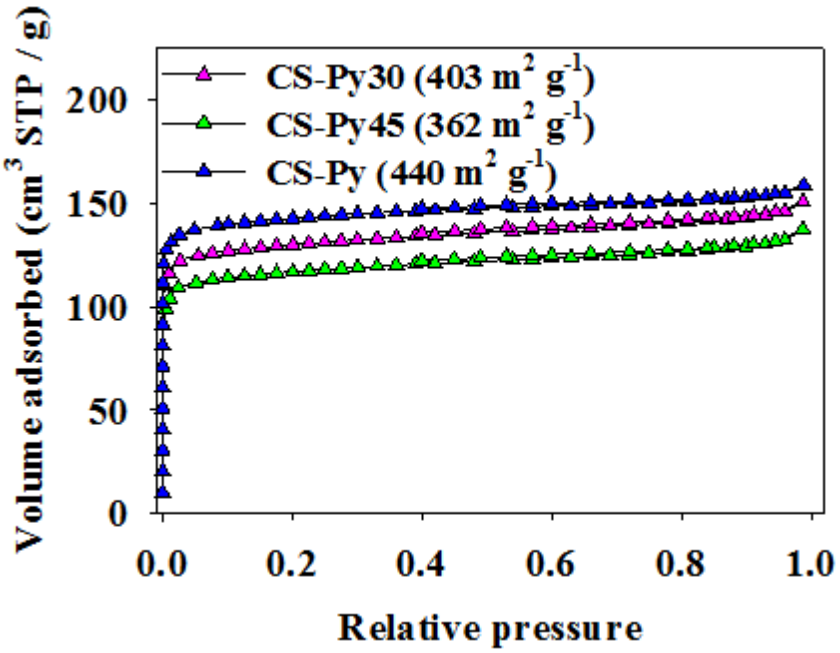

Figure S2. N_2 adsorption isotherms recorded for CS-Py samples.

Table S1. CO_2 uptakes recorded for CS-Kx series of carbons.

Sample	Pressure (bar)	CO_2 uptake at 0 ˚C (mmol g^{-1})	Pressure (bar)	CO_2 uptake at 25 ˚C (mmol g^{-1})
CS-K50	0.0089	0.5481	0.0065	0.1640
	0.0139	0.7036	0.0174	0.3354
	0.0175	0.7989	0.0354	0.5453
	0.0270	0.9811	0.0475	0.6583
	0.0327	1.0757	0.0643	0.7949
	0.0349	1.1095	0.0966	1.0106
	0.0969	1.6937	0.1781	1.4034
	0.2070	2.1968	0.2562	1.6779
	0.3577	2.5682	0.3846	2.0150
	0.4824	2.7726	0.5141	2.2709
	0.6261	2.9458	0.6424	2.4798
	0.6960	3.0232	0.7721	2.6567
	0.8376	3.1438	0.9008	2.8092
	0.9054	3.2059	1.0295	2.9434
	1.0472	3.3008		
CS-K75	0.0092	0.3584	0.0069	0.1054
	0.0137	0.4826	0.0175	0.2330
	0.0168	0.5564	0.0320	0.3761
	0.0262	0.7515	0.0483	0.5119
	0.0304	0.8284	0.0645	0.6310
	0.0350	0.9072	0.0969	0.8342
	0.0948	1.6258	0.1771	1.2232
	0.2104	2.4118	0.2570	1.5187
	0.3621	3.0338	0.3849	1.8852
	0.5041	3.4362	0.5139	2.1766
	0.6241	3.6997	0.6426	2.4166
	0.6956	3.8368	0.7718	2.6217
	0.8371	4.0644	0.9006	2.8003
	0.9054	4.1647	1.0295	2.9578
	1.0466	4.3383		
CS-K100	0.0084	0.6908	0.0061	0.4286
	0.0135	0.9113	0.0174	0.6760
	0.0172	1.0429	0.0355	0.9532
	0.0264	1.3228	0.0482	1.1110
	0.0301	1.4234	0.0646	1.3014
	0.0350	1.5441	0.0971	1.5768
	0.0953	2.5822	0.1798	2.1136
	0.2088	3.7354	0.2575	2.5034
	0.3623	4.7242	0.3862	3.0175
	0.5048	5.3782	0.5147	3.4443
	0.6245	5.8123	0.6436	3.8137
	0.6956	6.0404	0.7724	4.1500
	0.8373	6.4187	0.9010	4.4511
	0.9052	6.5888	1.0295	4.7354
	1.0469	6.8892		

Table S2. CO_2 uptakes recorded for CS-E-Kx series of carbons.

Sample	Pressure (bar)	CO_2 uptake at 0 ˚C (mmol g^{-1})	Pressure (bar)	CO_2 uptake at 25 ˚C (mmol g^{-1})
CS-E-K50	0.0085	0.4650	0.0065	0.2367
	0.0135	0.6193	0.0172	0.4306
	0.0183	0.7423	0.0345	0.6509
	0.0263	0.9110	0.0473	0.7767
	0.0303	0.9845	0.0643	0.9187
	0.0350	1.0639	0.0971	1.1297
	0.0961	1.7378	0.1790	1.5006
	0.2071	2.3735	0.2565	1.7448
	0.3643	2.8852	0.3846	2.0345
	0.5055	3.1908	0.5140	2.2463
	0.6247	3.3902	0.6425	2.4166
	0.6962	3.4952	0.7722	2.5584
	0.8371	3.6640	0.9008	2.6796
	0.9055	3.7418	1.0296	2.7855
	1.0467	3.8738		
CS-E-K75	0.0089	0.5781	0.0065	0.1841
	0.0131	0.7197	0.0162	0.3581
	0.0178	0.8536	0.0347	0.5907
	0.0267	1.0429	0.0468	0.7110
	0.0295	1.0998	0.0640	0.8554
	0.0354	1.2035	0.0969	1.0737
	0.0962	1.8599	0.1785	1.4539
	0.2057	2.4341	0.2559	1.7068
	0.3530	2.8481	0.3841	2.0098
	0.5060	3.1173	0.5136	2.2354
	0.6239	3.2711	0.6423	2.4130
	0.6961	3.3528	0.7718	2.5599
	0.8372	3.4799	0.9007	2.6832
	0.9056	3.5390	1.0294	2.7903
	1.0468	3.6368		
CS-E-K100	0.0086	0.8866	0.0076	0.0562
	0.0135	1.0663	0.0182	0.1451
	0.0186	1.2322	0.0329	0.2568
	0.0265	1.4426	0.0486	0.3612
	0.0307	1.5391	0.0648	0.4603
	0.0351	1.6301	0.0966	0.6583
	0.0977	2.4959	0.1793	1.1144
	0.2087	3.3471	0.2579	1.4758
	0.3443	4.0200	0.3864	1.9803
	0.4865	4.5374	0.5148	2.4181
	0.6271	4.9475	0.6436	2.8117
	0.6966	5.1424	0.7723	3.1749
	0.8375	5.4634	0.9010	3.5129
	0.9058	5.6208	1.0296	3.8337
	1.0466	5.8959		

Table S3. CO_2 uptakes recorded for CS-Py-Kx series of carbons.

Sample	Pressure (bar)	CO_2 uptake at 0 ˚C (mmol g^{-1})	Pressure (bar)	CO_2 uptake at 25 ˚C (mmol g^{-1})
CS-Py	0.0089	0.7658	0.0067	0.3018
	0.0132	0.9275	0.0163	0.5120
	0.0169	1.0410	0.0353	0.7829
	0.0265	1.2634	0.0463	0.8977
	0.0297	1.3267	0.0637	1.0532
	0.0350	1.4200	0.0971	1.2870
	0.0953	2.0669	0.1791	1.6789
	0.2056	2.6449	0.2558	1.9370
	0.3552	3.0737	0.3845	2.2502
	0.4815	3.3130	0.5137	2.4844
	0.6257	3.5129	0.6426	2.6691
	0.6956	3.5993	0.7719	2.8239
	0.8375	3.7372	0.9008	2.9558
	0.9056	3.8030	1.0295	3.0708
	1.0469	3.9089		
CS-Py-K50	0.0094	0.4493	0.0067	0.1558
	0.0133	0.5623	0.0164	0.3163
	0.0169	0.6539	0.0319	0.5187
	0.0261	0.8493	0.0485	0.6933
	0.0306	0.9310	0.0644	0.8462
	0.0351	1.0098	0.0972	1.0949
	0.0974	1.7419	0.1790	1.5666
	0.2085	2.4987	0.2571	1.9109
	0.3429	3.0986	0.3857	2.3551
	0.4856	3.5670	0.5144	2.7205
	0.6267	3.9346	0.6434	3.0276
	0.6960	4.1009	0.7721	3.2958
	0.8374	4.3825	0.9008	3.5350
	0.9057	4.5157	1.0295	3.7514
	1.0467	4.7447		
CS-Py-K100	0.0094	0.2800	0.0064	0.2562
	0.0142	0.3849	0.0173	0.5050
	0.0175	0.4503	0.0351	0.7985
	0.0266	0.6109	0.0472	0.9602
	0.0308	0.6801	0.0643	1.1592
	0.0352	0.7478	0.0965	1.4762
	0.0982	1.5278	0.1772	2.0866
	0.2097	2.5430	0.2567	2.5485
	0.3467	3.5411	0.3849	3.1340
	0.4870	4.4263	0.5140	3.6082
	0.6273	5.2262	0.6428	4.0049
	0.6967	5.6161	0.7718	4.3455
	0.8376	6.3355	0.9006	4.6481
	0.9058	6.6870	1.0295	4.9197
	1.0469	7.3509		

Table S4. N_2 uptakes recorded up to 1 bar for CS-K100, CS-E-K100 and CS-Py-K100 samples.

Sample	Pressure (bar)	N_2 uptake at 0 ˚C (mmol g^{-1})	Pressure (bar)	N_2 uptake at 25 ˚C (mmol g^{-1})
CS-K100	0.0125	0.0193	0.0124	0.0096
	0.0300	0.0442	0.0301	0.0228
	0.0388	0.0566	0.0395	0.0295
	0.0524	0.0758	0.0525	0.0387
	0.0643	0.0919	0.0650	0.0472
	0.0711	0.1010	0.0711	0.0514
	0.0773	0.1092	0.0776	0.0561
	0.0900	0.1266	0.0904	0.0654
	0.1030	0.1435	0.1029	0.0736
	0.1532	0.2079	0.1538	0.1093
	0.2049	0.2713	0.2050	0.1437
	0.2558	0.3298	0.2561	0.1775
	0.3070	0.3870	0.3070	0.2099
	0.4083	0.4929	0.4087	0.2721
	0.5104	0.5916	0.5110	0.3317
	0.6122	0.6843	0.6125	0.3885
	0.7143	0.7717	0.7145	0.4434
	0.8165	0.8540	0.8165	0.4966
	0.9184	0.9315	0.9184	0.5472
	0.9694	0.9714	0.9694	0.5734
	1.0153	1.0068	1.0154	0.5974
CS-E-K100	0.0131	0.0244	0.0127	0.0168
	0.0302	0.0454	0.0303	0.0315
	0.0449	0.0735	0.0450	0.0501
	0.0525	0.0912	0.0516	0.0573
	0.0650	0.1126	0.0652	0.0705
	0.0709	0.1199	0.0712	0.0741
	0.0774	0.1268	0.0777	0.0839
	0.0903	0.1471	0.0901	0.0985
	0.1029	0.1657	0.1033	0.1112
	0.1534	0.2375	0.1543	0.1606
	0.2047	0.3054	0.2046	0.2042
	0.2559	0.3658	0.2555	0.2466
	0.3066	0.4216	0.3070	0.2931
	0.4087	0.5295	0.4088	0.3668
	0.5104	0.6284	0.5109	0.4429
	0.6125	0.7047	0.6126	0.5091
	0.7144	0.7818	0.7142	0.5782
	0.8164	0.8679	0.8163	0.6434

	0.9184	0.9496	0.9184	0.7018
	0.9694	1.0034	0.9694	0.7399
	1.0156	1.0382	1.0153	0.7827
CS-Py-K100	0.0128	0.0170	0.0128	0.0046
	0.0304	0.0338	0.0305	0.0045
	0.0387	0.0501	0.0397	0.0102
	0.0520	0.0701	0.0520	0.0194
	0.0644	0.0818	0.0648	0.0276
	0.0711	0.0900	0.0713	0.0319
	0.0775	0.0955	0.0776	0.0344
	0.0904	0.1085	0.0901	0.0416
	0.1033	0.1192	0.1029	0.0496
	0.1538	0.1648	0.1541	0.0744
	0.2044	0.2095	0.2047	0.0975
	0.2555	0.2517	0.2559	0.1196
	0.3068	0.2924	0.3069	0.1409
	0.4088	0.3687	0.4088	0.1790
	0.5107	0.4394	0.5109	0.2146
	0.6125	0.5059	0.6126	0.2467
	0.7143	0.5677	0.7149	0.2777
	0.8163	0.6332	0.8165	0.3071
	0.9186	0.6882	0.9186	0.3360
	0.9693	0.7150	0.9695	0.3550
	1.0153	0.7497	1.0154	0.3710

Table S5. CO_2 uptake for CS-Py-K100 sample over five cycles

Pressure (bar)	CO_2 uptake at 0 ˚C (mmol g^{-1})				
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
0.0094	0.2800	0.2795	0.2700	0.2697	0.2690
0.0142	0.3849	0.3840	0.3835	0.3830	0.3826
0.0175	0.4503	0.4499	0.4490	0.4488	0.4480
0.0266	0.6109	0.6107	0.6100	0.6095	0.6092
0.0308	0.6801	0.6798	0.6795	0.6780	0.6777
0.0352	0.7478	0.7470	0.7465	0.7460	0.7453
0.0982	1.5278	1.5274	1.5260	1.5258	1.5255
0.2097	2.5430	2.5425	2.5418	2.5413	2.5410
0.3467	3.5411	3.5400	3.5401	3.5400	3.5395
0.487	4.4263	4.4258	4.4256	4.4255	4.4250
0.6273	5.2262	5.2258	5.2250	5.2243	5.2240
0.6967	5.6161	5.6159	5.6150	5.6140	5.6132
0.8376	6.3355	6.3352	6.3348	6.3340	6.3335
0.9058	6.6870	6.6865	6.6850	6.6845	6.6840
1.0469	7.3509	7.3500	7.3497	7.3490	7.3486