

HYDROGEN ADSORPTION ON ACTIVATED CARBON

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Introduction

The adsorption of hydrogen on carbon nanotubes and activated carbons has generated considerable interest in relation to hydrogen storage for fuel cells applications[1-3]. However, the widespread use of hydrogen as a fuel is limited by the lack of a convenient and cost-effective method of hydrogen storage. Adsorption of supercritical hydrogen is limited by the low interaction energy between hydrogen and the carbon surface, which is only enhanced in nanoporosity. Activated carbons have hydrophobic sites consisting of the graphene basal plane layers and hydrophilic sites comprising the functional groups. The hydrophobic graphene layer surfaces act as primary adsorption sites for neutral species, such as hydrogen, whereas the hydrophilic oxygen functional groups are primary sites for adsorption of polar species. It is envisaged that an adsorbent material consisting exclusively of ultramicropores with molecular dimensions could adsorb sufficient hydrogen to meet the requirements for transportation use. However, to date, there have only been limited detailed published studies of the results for hydrogen adsorption on carbon materials. In this study, we systematically investigate the influence of porous structure and functional groups characteristics on the adsorption/desorption of hydrogen on activated carbons. The effect of temperature on the amounts adsorbed and the adsorption dynamics of hydrogen on activated carbon were also studied.

Experimental

Carbon Samples used The PANC and G series of carbons used in this study were derived by heat treatment of oxidized carbon using nitric acid to provide a suite of carbons where the oxygen functional groups of various thermal stabilities were varied progressively by heat treatment. Carbon G is a commercially available coconut shell carbon supplied by Pica, Vierzon, France. The PANC carbon was made from polyacrylonitrile (PAN) powder. Carbon oxidation using nitric acid introduces various oxygen functional groups on the carbon surface. Carbons G209 and PANC were refluxed in HNO₃ solution (7.5 M) for 48 hours to give oxidized carbons GOX and PANCOX. The product was filtered and washed before Soxhlet extraction with distilled water until the solution pH was constant. The carbon was dried at 383K. The samples were then heat treated at 3°Cmin⁻¹ to the heat treatment temperature in helium and held at this temperature for 1h. The samples were designated with the code of the carbon and the heat treatment code e.g. PANCOX3 is sample PANCOX heat treated to 300°C.

Adsorption measurements

An Intelligent Gravimetric Analyzer (I.G.A.) was used for adsorption kinetic studies. It was supplied by Hiden Analytical Ltd, UK. This apparatus is an ultra high vacuum system, which allows isotherms and the corresponding kinetics of adsorption and

desorption to be determined, for set pressure steps. The samples were degassed at 473K and 10^{-10} bar, prior to the adsorption measurements. Care was taken to ensure that all the impurities in the system were removed. Ultra pure hydrogen supplied by BOC was used for the experiments.

Results and Discussion

The analytical data for the carbons used in this study are given in Table 1. The oxygen contents of the low nitrogen content G suite of nanoporous carbons varied from ~ 3 wt% daf ~ 22 wt% daf while the high (7 – 8 wt% daf) nitrogen content

Table 1. Analytical data for the carbons used in this study

Carbon Samples	Proximate analyses		Elemental analyses, % daf				Porous structure characterization		
	V ^a , %daf	A ^b , %db	C	H	N	O	V _{CO₂} , cm ³ g ⁻¹	V _{N₂} , cm ³ g ⁻¹	V _{CO₂} / V _{N₂}
G series									
GOX	33.77	0.49	76.34	0.89	1.05	22.36	0.262	0.366	0.716
GOX3	29.66	0.23	79.45	0.74	1.07	17.21	0.258	0.413	0.625
GOX4	19.68	0.92	83.94	0.63	1.05	13.65	0.235	0.443	0.530
GOX5	17.92	0.76	85.64	0.71	1.10	12.87	0.234	0.448	0.522
GOX6	13.18	0.66	89.28	0.52	1.17	9.00	0.225	0.455	0.495
GOX8	5.20	0.84	94.03	0.49	1.24	3.56	0.230	0.503	0.385
G209	4.46	2.73	96.22	0.42	0.28	2.95	0.334	0.484	0.756
G210	3.39	1.78	97.59	0.27	0.0	2.13	0.331	0.442	0.784
G212	3.21	3.21	99.14	0.24	0.0	1.95	0.298	0.426	0.700
PAN series									
PANCOX	24.44	1.18	73.20	1.00	7.61	19.88	0.112	0.181	0.619
PANCOX3	18.72	0.35	75.55	0.85	7.94	14.22	0.141	0.213	0.662
PANCOX4	16.28	0.42	77.07	0.95	8.16	13.40	0.127	0.216	0.588
PANCOX6	10.27	0.32	82.33	0.93	8.70	7.99	0.148	0.236	0.627
PAN	1.03	0.70	89.28	0.37	8.19	2.18	0.153	0.204	0.750

a volatile content, %daf;

b ash content, %db.

The PAN series varied in the range $\sim 2 - 20$ wt% daf oxygen. It is apparent that the two series have low ash contents and are very similar except for the consistent high nitrogen content in the PAN series of carbons. The porous structures of the carbon materials were characterized using both nitrogen adsorption at 77K and carbon dioxide adsorption at 273K and the results are given in Table 1. The micropore volumes of the microporous carbons were obtained using the Dubinin-Radushkevich equation. The total pore volume was obtained from the amount of nitrogen adsorbed at $p/p^0 = 1$. The data show that the total and micropore volumes do not change greatly with heat treatment within both the G and PAN series of activated carbons. Therefore, the effect of surface functional groups, on the adsorption characteristics of a given series, can be studied without having marked effects due to changes in porous structure. The other carbons are included to give a range of porous structure characteristics and cover carbons with varying degrees of activation and pore size distributions.

Figure 1 shows a typical adsorption and desorption isotherms for hydrogen adsorption on activated carbon at 77K. The adsorption isotherm is Type 1 in the IUPAC classification scheme and is reversible with little or no hysteresis. The other carbons used in this study have similar shaped isotherms.

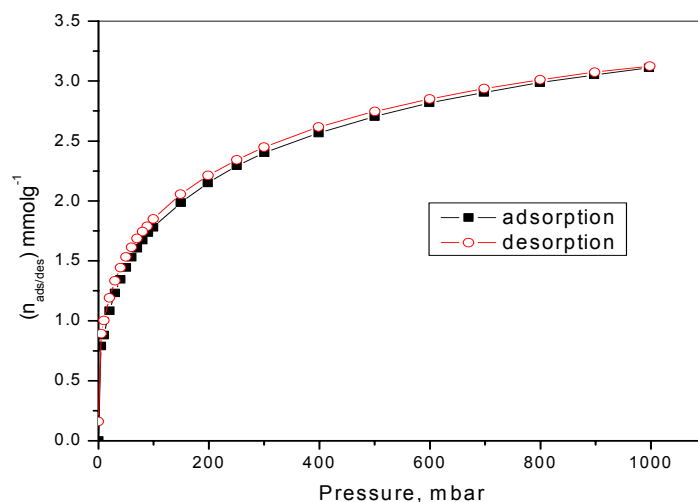


Figure 1. Adsorption/desorption isotherms for hydrogen adsorption on carbon PANCOX6 at 77K.

The Langmuir isotherm can be expressed in the following form:

$$p/n = 1/n_m b + p/n_m \quad (1)$$

where p is the pressure, n the amount adsorbed, n_m is the monolayer capacity and b is the coefficient of adsorption specific to the adsorbate/adsorbent system. For hydrogen adsorption in this study, the graph is linear in the high-pressure region thereby allowing an accurate assessment of the amount adsorbed corresponding to the isotherm plateau (n_m). The data for n_m are given in Table 2.

Table 2. Langmuir parameters for hydrogen adsorption at 77K on the carbons used in this study.

PAN series		G series	
Carbons	$n_m, \text{mmol g}^{-1}$	Carbons	$n_m, \text{mmol g}^{-1}$
PANCOX	2.894 ± 0.279	GOX	5.853 ± 0.106
PANCOX3	2.919 ± 0.310	GOX3	6.209 ± 0.125
PANCOX4	3.072 ± 0.252	GOX4	6.551 ± 0.134
PANCOX6	3.427 ± 0.194	GOX5	6.667 ± 0.139
		GOX6	7.781 ± 0.139
PAN	4.585 ± 0.064	GOX8	9.334 ± 0.152
		G209	10.108 ± 0.157
		G210	9.463 ± 0.106
		G212	10.661 ± 0.185

The maximum amount adsorbed, n_m , increases with decreasing oxygen surface functional groups concentration systematically. It is interesting that the hydrogen uptake varies clearly with concentration of surface groups while the micropore volumes determined from CO_2 adsorption do not change greatly. H_2 has smaller dimensions than CO_2 [4] and may have greater accessibility to the nanoporosity than CO_2 . Exclusion of

various adsorptives from parts of the porous structure has been clearly demonstrated for adsorption on carbon molecular sieves[5-7]. Another possible explanation is an interaction between the adsorbed hydrogen and the hydrophilic functional groups. The adsorption kinetics for hydrogen adsorption on all the carbons studied was very fast.

Conclusions

The study has shown hydrogen adsorption/desorption on microporous carbons under supercritical conditions at low temperature is reversible with little or no hysteresis. The porous structure is the biggest factor in determining the amount adsorbed but functional groups also have a significant effect. The sensitivity of hydrogen adsorption to temperature is quite marked. This is entirely consistent with the thermodynamic considerations.

References

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