PREPARATION OF CARBON MOLECULAR SIEVE FROM A NEW NATURAL SOURCE

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Introduction

Due to the high pore volume and adsorption capacities as well as its relative chemical inertness, activated carbons have been known as the most widely used adsorbents for liquid and gas phase treatments[1]. Extensive research activities are in progress worldwide to increase the adsorption capacity and selectivity of various activated carbons.
There are two very well known techniques to produce activated carbons namely gaseous or physical and chemical activation methods. In the chemical activation technique, due to the contribution of water to decompose the chemical structure of the raw material, the activation may be achieved in a lower temperature. Furthermore, by preventing tar formation the chemical activating agent improves the micropores formation and increases the surface area to a large extent[2].
In this work an Iranian natural plant shell was used to prepare a particular carbon molecular sieve to separate methane from nitrogen and also nitrogen from oxygen. The procedure to prepare the initial activated carbon from the shell is presented. The prepared samples were analyzed by various techniques such as molecular probe and BET methods. The results show that a CMS with high adsorption selectivity and a pore size distribution with an average pore size diameter of smaller than 4Å could be prepared The effect of zinc chloride concentration on the surface area and adsorption characteristics was investigated. The significance of the size of raw material particles on the above mentioned properties of the final carbon has also been examined.

Experimental

A local Persian nutshell was used as the raw material for the experiments. The advantageous properties of similar nutshells have been reported[3]. The shells were first crushed and sieved to the desired size. The particles were then added to a concentrated aqueous solution of zinc chloride and stirred while smoothly heated until a rather complete water evaporation was achieved. The level of impregnation was calculated by dividing the initial zinc chloride content by the mass of shell particles added to the initial solution and reported as percentages. The impregnated particles were dried in an oven for six hours and then packed in a 10 mm ID quartz tube and heated in an electrical tubular furnace to a maximum temperature of 500 ^{o}C. The temperature ramp was adjusted at 2 ^{o}C/min. and the particles were kept at the maximum temperature for about one hour. Throughout the experiments a continuous flow of pure nitrogen (200 ml/min.) carried the vapors out of the quartz tube. The samples were characterized by measuring the surface area using BET (ASAP 2010, Micromeritics) and iodine number (ASTM D4607) techniques. The initial samples of activated carbon with the highest surface area were treated to reduce the pore diameters and prepare the desired molecular sieve carbons. Several methods were examined among which impregnation by coal tar pitch produced the best results. The carbon samples were added to known amount of coal tar pitch dissolved in boiling benzene and refluxed for one hour, then dried in an oven at a temperature of 105 ^{o}C for three hours, packed in the quartz tube, heated in the tubular furnace to a maximum temperature of 700 ^{o}C. The temperature ramp adjusted at 5 ^{o}C/min and the samples were kept at the maximum temperature for about 30 minutes. The samples were qualitatively tested to determine the pore size distribution using molecular probe technique[4]. CCl_4, $CHCl_3$, CH_2Cl_2 and CS_2 were used as the compounds with known molecular diameters.

Results and Discussions

Figure 1 shows the effect of level of impregnation on the BET surface area for two particle sizes. The surface area increases with the level of impregnation; however there is very little effect on the surface area for the two particle sizes (e.g., 45 and 24 mesh). Figure 2 shows the same results for the iodine numbers. The iodine number increases with the percentage of impregnation up to 50 percent level and then rather flattens. A surface area of about 2351 m^2/g could be produced when a 100 percent impregnation was performed on the particles. However a 50 percent level seems to be the optimum impregnation because the surface area curves somewhat level off around the 50 percent impregnation. Figure 3 shows a typical isotherm diagram for one of the initial activated carbons. The molecular probe test results for one of the samples are shown in Table 1. The results show that the average pore diameter could be reduced to 4 Å.

Table 1: Molecular probe results for a typical carbon molecular sieve

Compound Name	Molecule Diameter (Å)	Equilibrium Adsorption (cm^3/g)
CCl_4	6.0	0.00
$CHCl_3$	4.6	0.00
CH_2Cl_2	4.0	0.12
CS_2	3.7	0.15

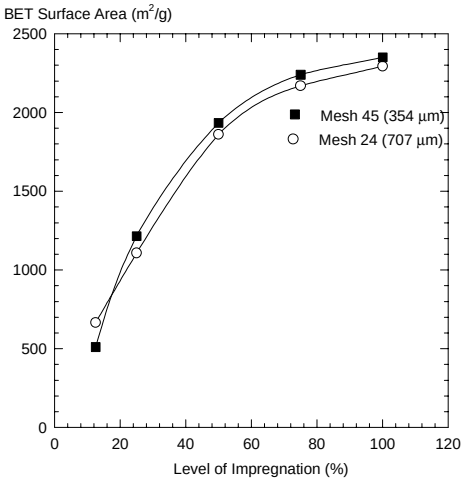

Figure 1: Effect of impregnation on the BET surface Area

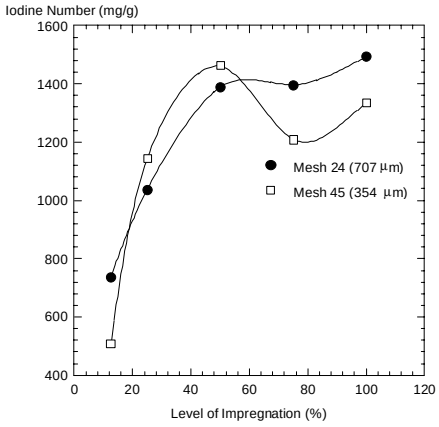

Figure 2: Effect of impregnation on iodine number

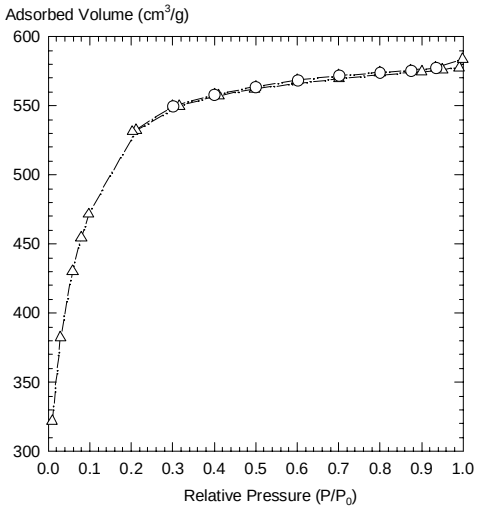

Figure 3: BET isotherm for a typical initial activated carbon; level of impregnation:50%; particle size: mesh 24; sample weight: 22 g; adsorption gas: N_2; adsorption temperature: 77.78 K; average pore radius by BET: 9.58 Å

References

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