# Carbon Molecular Sieves Produced by the Fixation of Sulphur Surface Complexes

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## Introduction

It is known that carbon may form a variety of surface compounds (1,2). These surface compounds or surface complexes may often determine, in more or less extent, the properties of surfaces which are important in heterogeneous catalysis, waste cleanup and other technological applications. In a previous paper (3), by ussing a gas-chromatographic technique, we showed that the introduction of oxygen surface complexes in a Saran carbon did not change significantly the benzene/cyclohexane separation ratio, that is to say the oxidized carbon did not present molecular sieve properties for cyclohexane. Following in this line, we have undertaken the study of the effect of carbon-sulphur surface complexes on the molecular sieve properties of a Saran carbon and another comercial one. In the case of this kind of surface complexes, Puri pointed out (4) the possibility to produce carbon molecular sieves by the fixation of the appropiate amounts of sulphur.

## Experimental

A Saran carbon was obtained by carbonizing the co-polymer Saran 872 at 1173K in a $N_2$ atmosphere as stated before (3). This sample will be referred to as S. Portions of this carbon were treated at 873K with a $N_2$ flow saturated at room temperature with $CS_2$ for 30 min. and 60 min. The procedure followed was similar to that described elsewhere (5). The two samples thus obtained will be named as S1 (30 min. treatment) and S2 (60 min. treatment). Furthermore, another sample referrred in the text as S3, was prepared by heating at 773K a mixture of sample S and sulphur. All samples prepared were washed with carbon disulphide, in order to remove the sulphur physically deposited. After that, they were dried in a vacuum-oven at 383K and kept in a dessicator until their use. Also, a comercial activated carbon was used, this carbon was treated with $CS_2$ as mentioned before. Samples will be referred to as A (as-received) and A1 (sulphurized). Particle size of carbons was between 0.08 and 0.2 mm.

All samples were characterized by $N_2$ and $CO_2$ adsorption at 77K and 298K respectively. BET method was applied to the $N_2$ isotherm, taking as 0.162 $nm^2$ the area occupied by a $N_2$ molecule at 77K. Dubinin-Radushkevich method was used for the $CO_2$ isotherm and 0.253 $nm^2$ was taken as the molecular area of this adsorbate.

In order to know the total open pore volume ($V_T$), helium and mercury densities were measured. Also, benzene and cyclohexane densities were obtained by picnometry at 298K. Mercury porosimetries up to 2000 $Kg.cm^{-2}$ were carried out in a Carlo Erba equipment, model 200.

Adsorption of benzene and cyclohexane on the samples was performed within the temperature range of 473 to 548K by using a Carlo Erba gas-chromatograph (model Fractovap 2350) using FID. This technique was described elsewhere (3). Ultrapure $N_2$ was used as the carrier at a flow of 60 $cm^3$ (STP).$min^{-1}$. Before adsorption the adsorbents were preconditioned at 573K for 1h. Quantities of the hydrocarbons were injected by a Hamilton syringe. Net retention volumes were obtained from the maxima of the chromatographic peaks (3).

## Results and Discussion

As it is seen in Table 1, nitrogen surface areas ($S_{N_2}$) decrease after sulphur fixation by the carbon. Carbon dioxide surface areas ($S_{CO_2}$) also decrease except in the case of S1 and S2 samples with regard to the original one (S). Because these two samples were obtained reacting $CS_2$ with carbon S it is probable that sulphur is fixed together with carbon. Thus the aperture size of the microporosity in the original Saran sample would be reduced to the range of the ultra-microporosity. This fact would likely decrease the molar volume of the adsorbed $CO_2$, decreasing in this way its molecular area (6) and therefore affecting the $S_{CO_2}$ value obtained.

From the density values of Table 1, we have calculated the total open pore volume ($V_T$) and the percentage of porosity accesible to benzene ($P_B$) and cyclohexane ($P_C$). These values are summarized in Table 2. It is seen that the sulphur fixation in sample S from carbon disulphide (S1 and S2 carbons), progressively diminishes the $P_C$ value and the porosity with diameter higher than 7.6 nm, which produces an increase in the separation ratio of the pair benzene/cyclohexane, as it is shown in column 6 of Table 2 at a temperature of 498K as an example, becoming the

Table 1. Surface areas and densities of carbon samples

| Sample | % S | $S_{N_2}$ $m^2.g^{-1}$ | $S_{CO_2}$ $m^2.g^{-1}$ | Density ($g.cm^{-3}$) Hg | He | Benzene | Cyclohexane |
|---|---|---|---|---|---|---|---|
| S | 0 | 936 | 1357 | 1.223 | 2.148 | 2.244 | 1.809 |
| S1 | 3.14 | 900 | 1700 | 1.260 | 2.329 | 2.183 | 1.503 |
| S2 | 4.20 | 890 | 1790 | 1.368 | 2.594 | 2.105 | 1.249 |
| S3 | 8.12 | 765 | 928 | 1.303 | 2.206 | 2.180 | 1.504 |
| A | 2.23 | 861 | 953 | 0.906 | 2.044 | 1.922 | 1.889 |
| A1 | 7.21 | 719 | 923 | 1.220 | 2.029 | 2.025 | 1.562 |

Table 2. Porosity of the carbons and benzene/cyclohexane separation ratios

| Sample | $V_T$ | % $P_B$ | % $P_C$ | % P Ø > 7.6 nm | $\frac{V_{C_6H_6}}{V_{C_6H_{12}}}$ (498K) |
|---|---|---|---|---|---|
| S | 0.35 | 100 | 74.3 | 8.6 | 1.13 |
| S1 | 0.36 | 100 | 36.1 | 0.03 | 20.7 |
| S2 | 0.35 | 74.3 | 0 | 0 | 660 |
| S3 | 0.31 | 100 | 32.3 | - | 4.2 |
| A | 0.55 | 94.5 | 92.7 | 36.4 | 1.76 |
| A1 | 0.33 | 100 | 54.5 | 54.5 | 1.77 |

S2 carbon a molecular sieve for cyclohexane.

Introduction of sulphur surface complexes from sulphur (S3 sample) fixed the highest sulphur amount, but did not produce a molecular sieve for cyclohexane although it reduced the $P_C$ value. On the other hand, when carbon A is used the sulphur surface complexes introduced from $CS_2$ did not produce a molecular sieve carbon for cyclohexane (A1 carbon).

Therefore, it seems that the fixation of small amounts of sulphur from $CS_2$ may produce a molecular sieve for cyclohexane only when a highly microporous carbon as the Saran sample S is used.

## References


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