

CHROMATOGRAPHIC CHARACTERIZATION OF ADSORPTION PROPERTIES OF CARBON AND SILICA ADSORBENTS

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Introduction

Adsorption isotherms and specific retention volumes of benzene on MCM-41C16 mesoporous silica and F4O porous carbon were determined at different temperatures by employing inverse gas chromatography. The differential isosteric enthalpies, $-\Delta H_{ads}$, and entropies, $-\Delta S_{ads}$, of adsorption were calculated from the retention time data and compared with the results obtained from the adsorption second virial coefficients.

The relation between the $-\Delta H_{ads}$ and $-\Delta S_{ads}$ quantities and experimental data was derived through the Antoine-type equation, which enables the evaluation of both $-\Delta H_{ads}$ and $-\Delta S_{ads}$ from adsorption second virial coefficient, B_{2S} , calculated on the basis of chromatographically determined adsorption isotherms [1]. The values of this virial coefficient were calculated by employing the parameters of the Tóth and Unilan equations. The adsorption second virial coefficient is a linear function of the reciprocal column temperature, T , akin to the specific retention volume. The three parameter equations employed, i.e., the Tóth and Unilan, appeared to be the best equations for the description of chromatographic data on the adsorbents studied. Their surface and structural properties were characterized by gravimetric and volumetric methods [2,3].

Experimental

Adsorbents

A mesoporous siliceous adsorbent of hexagonally ordered porosity, MCM-41C16, has been synthesized using cetyltrimethylammonium bromide surfactant as template. Its synthesis has been carried out by applying a relatively long hydrothermal treatment at 373 K as reported elsewhere [4].

The F4O active carbon was obtained by double deashing of commercial Filtrasorb 400 material and fractionated [5].

Nitrogen adsorption measurements

Adsorption/desorption isotherms of nitrogen at 77 K were measured on the MCM-41C16 and F4O samples by using an ASAP 2010 (Micromeritics, Inc.) automatic adsorption apparatus [3,5]. These isotherms, shown in Figure 1, were used to characterize the surface and structural parameters of both materials. As can be

seen from Figure 1, there is no adsorption hysteresis in the case of the MCM-41C16 material studied.

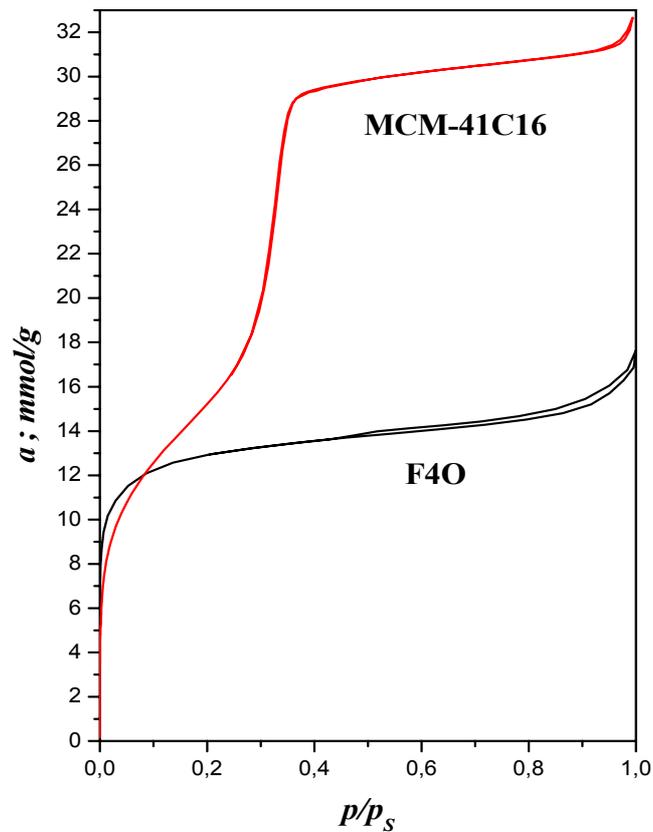


Figure 1. Nitrogen adsorption isotherms for the adsorbents studied.

Chromatographic measurements

Chromatographic measurements were carried out by using a Unicam type gas chromatograph equipped with on-line Unicam 4880 Chromatography Data Handling System, which was switched on when the adsorbate sample was injected [5]. The propane peaks, as signals creating the frequency functions, $f(t)$, were acquired over 240 minutes at the digital acquisition rate of 10 Hz and stored. For the acquisition time employed the benzene elution peaks reached the base line. The adsorbents were placed in 65 cm x 0.2 cm i.d. glass column. The length of the adsorbent bed in the column was 7 cm. The part of the column unoccupied by the adsorbent was filled with glass beads of 80 mesh size. The measurements were performed using helium at a flow rate of 15 ± 0.05 cm³/min.

The gas hold-up time, t_M , was calculated from the linear dependence:

$$\ln[(t_{Ri} - t_M)\sqrt{M_i}] = a + bU(r)$$

where: t_{Ri} and M_i are the retention time and molar mass of the i -th inert gas (Ar, Kr, Ne and Xe);

a and b - are constants;

$U(r)$ - is the value of the Kirkwood-Müller potential function.

The basic idea of calculating the t_M values was to assume that molecules (Ar, Kr, Ne and Xe) and the active carbon surface consist of spherical sites, which interact according to the simple potential functions such as the Kirkwood-Müller or Lennard-

Jones 12-6 or 9-3 that are widely used in the modeling of bulk phases. The Kirkwood-Müller and Lennard-Jones potentials give a satisfactory representation of the interaction between simple molecular species [5].

X-ray diffraction measurements

X-ray diffraction spectra were recorded by means of HZG-4 apparatus (VEB Freiburg Präzisionmechanik, Germany) using $\text{CuK}\alpha$ radiation with Ni filter. Figure 2 shows the XRD spectra with Miller's indices [6].

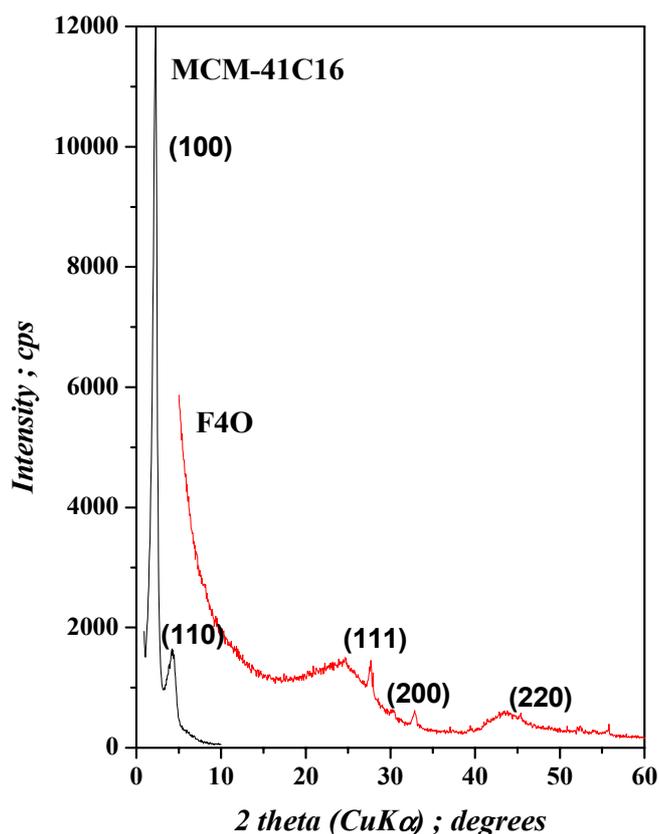


Figure 2. The XRD spectra for the adsorbents studied.

The space group $Pm3m$ (with the lattice constant $a=0.545$ nm – crystallographic phase 18-311 ASTM) was observed for the F4O. The XRD pattern for the MCM-41C16 material exhibits two distinct peaks, which resemble the pattern reported by Kresge *et al.* [7] for hexagonal arrangement of uniform channels.

Results and discussion

The chromatographic peaks obtained were slightly asymmetrical in shape. The retention times collected showed a small dependence on the size of the sample injected. Hence, the peak maxima method was employed for calculation of the adsorption isotherms. This method is often used for the determination of adsorption isotherms because the peak maximum is not influenced by diffusion [1]. Some characteristic features of the adsorbents studied are presented in Table 1.

Table 1. Some parameters characterizing the adsorbents studied.

Adsorbent	S_{BET} ; m ² /g	V_{meso} ; cm ³ /g	V_{total} ; cm ³ /g
MCM-41C16	1235	0.99	1.10
F4O	1020	0.18	0.61

The Unilan equation [1] was employed to analyze the chromatographically obtained adsorption isotherms for benzene on both materials. This equation was chosen because it is usually used to characterize the energetically heterogeneous adsorbents, predicts the Henry law behavior, contains only three constants and gives analytical expressions for the amount adsorbed. The values of the differential isosteric enthalpies and entropies of adsorption are presented in Table 2.

Table 2. The values of the differential isosteric enthalpies and entropies of adsorption for the adsorbents studied.

Adsorbent	Temp. range ; K	$-\Delta H_{ads}$; kJ/mol	$-\Delta S_{ads}$; J/mol·K
MCM-41C16	343-393	38	154
F4O	523-593	76	191

The higher values of the adsorption enthalpy and entropy for F4O are probably connected with the higher interaction energy between the π -electrons of benzene molecule and graphene plane in tree-like pore network of the active carbon. The delocalized π -electrons in the benzene ring are polarizable and control interactions between aromatic rings and surface hydroxyls of the MCM-41 adsorbent. Choudhary and Mantri determined the isosteric enthalpy of adsorption as a function of surface coverage for benzene, mesitylene, *p*-xylene and toluene on Si-MCM-41 [8]. For every adsorption system studied the isosteric enthalpy of adsorption decreased with increasing of the surface coverage. The isosteric enthalpy of adsorption on Si-MCM-41 decreased when the molecular weight of adsorbate decreased: mesitylene>*p*-xylene>toluene>benzene [8]. In conclusion, an increase in the molecular weight cause some increase in the isosteric enthalpy of adsorption due to the stronger adsorbate-adsorbent interactions.

Conclusions

Analysis of the results for the chromatographic systems studied revealed the following:

- i) the adsorption data for benzene on MCM-41C16 and F4O can be successfully described by Unilan equation;
- ii) the isosteric enthalpy and entropy of adsorption significantly depend on the presence of double bonds or lone-pair electrons.

Acknowledgments

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