ADSORPTION OF FORMALDEHYDE ON CARBON MATERIALS

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Introduction

Formaldehyde is a very important industrial intermediate product which is normally obtained on industrial scale. However in many cases it is a by-product produced in small amounts and therefore it should be desirable to concentrate it in order to use for industrial purposes. Moreover formaldehyde is released to the atmosphere as a result of the combustion, degradation and photochemical decomposition of organic materials [1].For these reasons the adsorption of formaldehyde has potential interest. Nevertheless in the cases above mentioned the adsorption should be under dynamic conditions and at relatively high temperatures in order to reproduce the real conditions. For this Inverse Gas - Solicd Chromatography (IGSC) is a very useful technique, which, in addition, allows to measure the adsorption at very low vapor concentration.

Experimental

The adsorption of formaldehyde has been carried out at zero surface coverage in a gas chromatograph Carlo Erba, model Fractovap 2350. Nitrogen was used as carrier gas, the detector was a flame ionization detector (FID) and the adsorption temperatures were between 393 and 553 K. The adsorbents used were two chars (C0, and S700), a sample obtained by oxidation of S700 (S700-ox) and a commercial activated carbon (Gae). Sample C0 was obtained by carbonization of almond shells on nitrogen flow (300cm^3/min)at 1273 K for 30 minutes. Sample S700 was prepared by carbonization of Saran copolymer on nitrogen flow (100 cm^3/min) at 973 K for 4 hours. The preparation of sample S700-ox was carried out by treating S700 in aqueous solution of H_2O_2. The textural characteristics of the adsorbents were obtained by N_2 and CO_2 adsorption at 77 and 273 K respectively and by mercury porosimetry up to 4000 Kg/m^2. Formaldehyde was prepared by heating paraformaldehyde at 358 K in a sampling bulb from which different amounts were withdrawn with a syringe and injected into the column. The experimental retention volumes obtained from the chromatograms were constant at each temperature and independent of the vapor concentration in the gas phase. Therefore the equilibrium constant is the net retention volume per unit of surface area of the adsorbent inside the column Vs, and the standard enthalpy change of adsorption ΔH^o_A can be obtained from the slope of ln Vs against 1/T plots [2]

Results and Discussion

Values of Vs at 413 and 493 K collected in the Table 1 show low adsorption capacities with no direct relation with the micropore volume (W_0) of the samples, obtained from the CO_2 adsorption at 273 K. This is not

Table1

		V_S (cm^3/m^2)	
	W_0 (cm^3/g)	413 K	493 K
C0	0.22	0.115	0.034
S700	0.36	0.054	0.023
S700-ox	0.32	0.088	0.027
GAe	0.27	0.097	0.025

surprising because it has been reported [3] that the adsorption at low vapor concentration is controlled by the micropore distribution instead of by the total micropore volume.

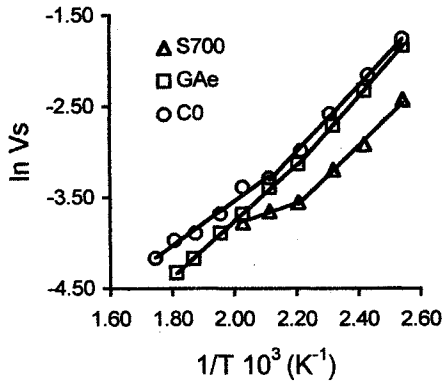

Figure 1.- Adsorption of formaldehyde on porous carbons

The plots of ln Vs vs 1/T are shown in Figure 1 for C0, GAe and S700 samples. What it is noteworthy is that the plot shows two straights lines for the adsorption of formaldehyde on each adsorbent. This can be attributed to a catalytic activity of the carbon materials, as it is known [1,4] that formaldehyde is easily transformed into: trioxane, methyl formate and methanol. Therefore is has beeen checked these three possibilities on C0. For this purpose it has been injected benzene and cyclohexane which are molecules similar in shape and size to trioxane. For the other posibilities of transformation formic acid, methyl formate and methanol were injected. The values of Vs obtained for

Table 2

	V_S (cm^3/m^2)	
	413 K	493 K
Benzene	-	1.561
Ciclohexane	5.228	0.305
Methyl Formate	3.347	0.236
Methanol	0.462	0.059

these adsorbates (Table 2) are in all cases higher than those obtained when formaldehyde is injected. Moreover in Table 3 and for C0 the standard enthalpies of adsorption of these adsorbates and the two standard

Table 3

	ΔH^0_A (kJ/mol)
Formaldehyde (Low T)	30.0
Formaldehyde (High T)	20.3
Benzene	91.0
Ciclohexane	66.7
Methyl Formate	56.6
Methanol	44.5

enthalpies of adsorption of formaldehyde, obtained from the slopes of the two straights lines, are collected. In all cases the values of ΔH^0_A of these adsorbentes are higher than of formaldehyde. All these data suggest that the two straights lines are not produced by a catalytic effect of the adsorbent and therefore it could be possible that the two straights lines (see Figure) mean a two different adsorption modes [5]. Moreover the fact that the crossing point of the two straights lines is not the same for all the samples suggests that the change in the adsorption mode could be a consequence of the porosity of the samples. To check this last possibility is has been studied the adsorption of formaldehyde on Graphon which is a non-porous carbon black. The plot obtained is shown in the Figure 2. It is interesting to note that only a stright line appears in the whole range of temperatures, which suggests that the adsorption of formaldehyde in the porous carbon materials is produce

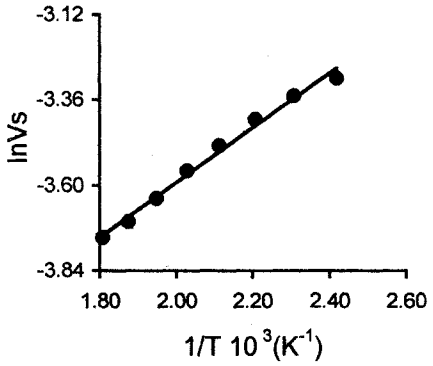

Figure 2.- Adsorption of formaldehyde on non porous carbon

in two different modes depending on the temperature an on the porosity of the samples.

Acknowledgment

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References

1. Ullman's. Encyclopedia of Industrial Chemistry, VCH Verlagsgesellshaft mbH, Weinheim (Germany), 1988, Vol A11, p. 620.
2. Domingo-Garcia, M., Fernández-Morales, I., López-Garzón, F. J., Moreno-Castilla, C. and Pyda, M., J. of Colloid and Interface Sci., 1995, **176**, 128.
3. Salas-Peregrín, M. A., Carrasco-Marín, F., López-Garzón, F. J. and Moreno-Castilla, C., Energy & Fuels, 1994, **8**, 239.
4. Millar, G. J., Rochester, C. H. and Waugh, K. C., J. Chem. Soc., Faraday Trans., 1991, **87**, 2785.
5. Delbecq, F. and Sautet, P., Surface Sci., 1993, **295**, 353.