

## Use of N<sub>2</sub>, Ar and CO<sub>2</sub> adsorption for the determination of microporosity and surface fractal dimension of carbon blacks and silicas

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**Abstract** - The microporosity of silicas and carbon blacks is characterized by using the Dubinin-Radushkevitch (D-R) equation. It is shown that the shape of the D-R lines corresponding to the adsorption of N<sub>2</sub> and Ar on silicas are very different from that obtained on carbon blacks. It is explained by differences in the accessibility of the micropores for small molecules at low temperature. The Ar and N<sub>2</sub> BET surface areas are determined and the value of the molecular area of N<sub>2</sub> on silicas is discussed. The surface fractal dimensions of the two types of adsorbents are determined by means of the FHH fractal equation from the N<sub>2</sub> adsorption isotherm above the monolayer coverage.

### INTRODUCTION

The interest of the comparison between the adsorption of nitrogen at low temperature (77 K) in the very low pressure range and the adsorption of carbon dioxide at a higher temperature (273 K) was shown by Rodriguez-Reinoso et al. (ref. 1) for the characterization of activated carbons. As the size of the two molecules is very similar (0.28 nm for CO<sub>2</sub> and 0.30 nm for N<sub>2</sub> (ref. 2)), both adsorbates are expected to lead to the same value of the microporous volume. However, if the entry of the micropores is too narrow, the diffusion time of N<sub>2</sub> at 77 K may be too large to allow equilibrium within a reasonable experimental time period or even to forbid any diffusion within the micropores. On the other hand, due to their larger thermal energy, CO<sub>2</sub> molecules at 273 K are able to diffuse (by activated diffusion) (ref. 2) through such constrictions but, for the same reason, the adsorption is limited to the narrow micropores. N<sub>2</sub> is also adsorbed in the larger micropores and on the non microporous surface. It follows that the adsorption of N<sub>2</sub> at 77 K and that of CO<sub>2</sub> at 273 K complement each other and allow a more precise characterization of the porous texture as we have already shown in the case of oxidized resin based carbons (ref. 3).

The characterization of the micropore texture of an adsorbent by CO<sub>2</sub> adsorption is widely used for carbon materials but seems not to have been applied to silica. One of our goals, therefore, was to evidence the presence of micropores in different silicas from the analysis of CO<sub>2</sub> adsorption at 273 K and to compare these results with that obtained on different carbon blacks. In each cases, both CO<sub>2</sub> and low pressure N<sub>2</sub> and Ar isotherms have been plotted following the Dubinin-Radushkevich equation:

$$\ln W = \ln W_0 - (1/E_0)^2 (A/\beta)^2 \quad (1)$$

$$\text{with } A = RT \ln (p_0/p) \quad (2)$$

In this equation,  $W$  is the volume of the adsorbate, assumed to be in the liquid state,  $W_0$  is the micropore volume and  $\beta$  is the affinity coefficient, related to the molar specific volume.  $E_0$  is the characteristic energy related to the mean radius  $x_\mu$  of the micropores by means of the equation:

$$x_\mu = k/E_0 \quad (3)$$

Dubinin and Stoeckli (ref. 4) have shown that, over the whole range of characteristic dimensions (0.25-1.6 nm), the relationship between  $k$  and  $E_0$  can be expressed with a good approximation by the following equation:

$$k = (13.028 - 1.53 \cdot 10^{-5} E_0^{3.5}) \text{ kJ nm /mole} \quad (4)$$

It is well known (ref. 5) that, due to its quadrupole moment, the nitrogen molecule interacts more strongly with the hydroxylated silica surface than with the carbon black surface. In order to investigate a possible influence of such an interaction on the shape of the D-R plots, we have also compared the results obtained from the adsorption of argon, at the same temperature (77 K).

Pfeifer and Cole (ref. 6) have shown that the adsorption isotherm on a fractal surface, in the multilayer range, depends on the surface fractal dimension. When the number of adsorbed molecules  $n$  depends only on the surface potential (i.e. there is no capillary condensation), the adsorption isotherm, above the monolayer, follows the fractal FHH (Frenkel, Halsey, Hill) equation:

$$n \propto [\ln(p_0/p)]^{-1/m} \quad (5)$$

$$\text{with } m = 3/(3-D) \quad (6)$$

As  $2 < D < 3$ ,  $m$  is larger than 3. For smooth, non fractal surfaces,  $D$  equals 2 and the classical FHH with  $m = 3$  is recovered.

However, most experimental results obtained from the nitrogen adsorption on different surfaces indicate that generally  $m$  is smaller than 3 (ref. 7). Pfeifer and Cole (ref. 6) explain these results by the effect of cross over between the BET regime, governed by the surface potential and the capillary condensation (CC), governed by the surface tension. In this regime (CC), the exponent in equation (5) becomes:

$$m = 1/(3-D) \quad (7)$$

with  $m > 1$ .

In the case  $m = 3$ , equation (7) leads to  $D = 8/3 = 2.67$  whereas equation (6) leads to  $D = 2$ . Physically, this situation corresponds to surfaces where the increase of the number of adsorbed molecules  $n$ , due to the capillary condensation is exactly compensated by the decrease of  $n$  expected from the decrease of the available space due to the fractal character of the surface. It follows that, for  $m \geq 3$ , the value of  $D$  cannot be unambiguously determined from the adsorption isotherm alone. The desorption isotherm has also to be measured in order to assess the presence or absence of capillary condensation within mesopores and/or the  $D$  values have to be compared with that obtained by Small Angle Neutron or X-ray Scattering (SANS or SAXS).

## EXPERIMENTAL

### Samples

Two different types of carbon blacks were investigated. The first one is an acetylene black (DENKA, Japan). The second ones, TB#4500 and TB#5500 (TOKAI CARBON, Japan) are furnace blacks. TB#4500 HT has been heat treated at 1500 °C. These carbon blacks are electrical grades and present a high DBP volume (above 1.5 cm<sup>3</sup>/g).

The silica samples originate from three different methods of synthesis:

- precipitated silicas are obtained from the precipitation of a solution of an alkaline silicate by an acid followed by drying of the precipitate. We have studied two commercial silicas, SIPERNAT 22 LS and FK 320 DS (DEGUSSA) and a laboratory sample, TIXOSIL 382 (RHONE POULENC).

- pyrogenic silica, AEROSIL 200 (DEGUSSA) results from the pyrohydrolysis of SiCl<sub>4</sub>

- two aerogel silicas, called Aerogel A and B, were provided by G. M. Pajonk (University of Lyon, France). Both samples were obtained from the base catalyzed hydrolysis of tetramethoxysilane (TMOS) dissolved into methanol and dried under hypercritical conditions. More details concerning the preparation are given elsewhere (ref. 3).

All samples are fluffy, non pelletized powders.

### Adsorption measurements

A classical volumetric device is used for the determination of the adsorption isotherms. The room temperature is regulated to 293 K. The temperature for nitrogen and argon adsorption is 77 K and 273 K for carbon dioxide adsorption. The pressure is measured by three different pressure sensors (BAROCEL 1, 100 and 1000 torrs) in order to cover the whole range of pressures. The samples are outgassed during 12 hours at 200 °C in vacuum (10<sup>-6</sup> torrs) before adsorption measurements. The time allowed for equilibrium is generally 45 minutes. High purity gases (purity better than 99.9995 provided by L'Air Liquide) are used as adsorbates.

**Physical constants used for the calculations**

For the calculation of the micropore volume, by means of the Dubinin-Radushkevitch equation and the BET surface area, the following constants were used:

- CO<sub>2</sub> adsorption at 273 K (ref. 8):

$$p_0 = 26142 \text{ torrs} \quad d = 1.023 \text{ g/cm}^3 \quad \beta = 0.35 \quad \sigma = 18.7 \text{ nm}^2$$

- N<sub>2</sub> adsorption at 77 K (ref. 1)

$$p_0 = 760 \text{ torrs} \quad d = 0.808 \text{ g/cm}^3 \quad \beta = 0.33 \quad \sigma = 16.2 \text{ nm}^2$$

- Ar adsorption at 77 K (ref. 9)

$$p_0 = 217 \text{ torrs} \quad d = 1.456 \text{ g/cm}^3 \quad \beta = 0.31 \quad \sigma = 13.8 \text{ nm}^2$$

**EXPERIMENTAL RESULTS AND DISCUSSION****Dubinin-Radushkevitch plots**

Figures 1a and b show the D-R plots obtained for CO<sub>2</sub> and N<sub>2</sub> adsorption on silicas and carbon blacks respectively. For all samples, the adsorption of CO<sub>2</sub> fits very well the D-R equation within the range of investigated relative pressures. The values obtained for Aerosil 200, acetylene black and TB#4500HT are more scattered as a result of the very low CO<sub>2</sub> uptake. The micropore volume,  $W_0$ , the characteristic energy,  $E_0$  and the micropore size  $x_\mu$  obtained by a least square method, are indicated in Table 1.

The most important point is the difference in the shapes of the nitrogen D-R plots obtained for silica samples and carbon blacks.

**Carbon blacks.** For all carbon blacks investigated here, the D-R plot consists of two linear regions crossing each other at  $(A/\beta)^2$  values close to 220 (kJ/mole)<sup>2</sup>, i. e.  $A \approx 4.9$  kJ/mole. Similar results were obtained for the adsorption of nitrogen and other adsorbates on activated carbons as shown for example by Bradley and Rand (ref. 10) and also for oxidized resin-based carbons, as shown earlier by us (ref. 11).

**Silicas.** Figure 1a shows that, for all our silica samples, the N<sub>2</sub> adsorption in the low pressure range (corresponding to  $100 < (A/\beta)^2 < 420$ ) can be described by a unique D-R linear region. The results obtained for the two other precipitated silicas are very similar to that obtained for Sipernat plotted in Fig. 1a.

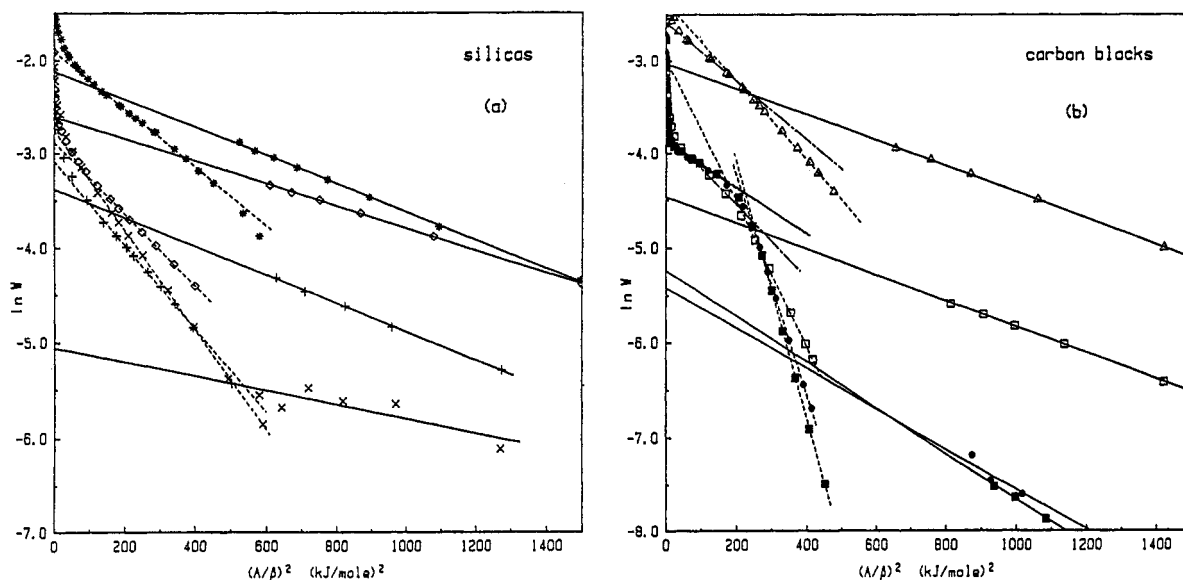


Fig. 1. Comparison of the D-R plots corresponding to adsorption of CO<sub>2</sub> (273 K) and N<sub>2</sub> (77 K) on:

(a) silicas: x Aerosil 200,  $\diamond$  Sipernat, \* Aerogel A and + Aerogel B

(b) carbon blacks:  $\Delta$  TB#5500,  $\square$  TB#4500,  $\blacksquare$  TB#4500 HT and  $\bullet$  acetylene black.

Particularly, for these silicas which are actually microporous, as evidenced by the adsorption of CO<sub>2</sub> (273 K), the value of W<sub>1</sub> obtained from the nitrogen D-R equation is smaller than W<sub>0</sub>. If it is assumed, as seen later, that the adsorbed nitrogen is rather solid-like than liquid-like, the value of the density is higher, leading to a smaller value of the volume and a larger difference between W<sub>0</sub> and W<sub>1</sub>.

One may, thus, conclude that N<sub>2</sub> at 77 K does not penetrate into the micropores. Such an effect is generally attributed to constrictions at the entrance of the micropores. However, due to the stronger interaction between the N<sub>2</sub> molecules and the surface hydroxyl groups on a silica surface, one may also imagine that the resulting adsorption potential could be larger than the one arising from narrow micropores. This hypothesis will be examined in the next paragraph by means of Ar adsorption measurements.

As the shapes of the D-R plots obtained for the other silica samples is very similar to these ones, the same conclusion could be drawn, although W<sub>1</sub> is larger than W<sub>0</sub> as a possible result of a larger amount of supermicropores in the aerogel samples.

TABLE 1. Results of the analysis of the data obtained by CO<sub>2</sub>, N<sub>2</sub> and Ar (indicated by \*) adsorption, by means of the D-R equation. The uncertainty of these results are estimated to about 5%.

Samples	CO <sub>2</sub> (273 K)			N <sub>2</sub> and Ar* (77 K)						
	D-R			D-R 1st region			D-R 2nd region			
	W <sub>0</sub>	E <sub>0</sub>	x <sub>μ</sub>	W <sub>1</sub>	E <sub>1</sub>	x <sub>1</sub>	W <sub>2</sub>	E <sub>2</sub>	x <sub>2</sub>	
	cm <sup>3</sup> /g	kJ/mol	nm	cm <sup>3</sup> /g	kJ/mol	nm	cm <sup>3</sup> /g	kJ/mol	nm	
<u>silicas</u>										
Aerosil 200	(0.006)	(3.67)	(0.23)	0.06	13.8	0.93				
				0.03*	11.8*	1.10*				
Sipernat	0.073	29.1	0.38	0.056	16.2	0.79				
FK 320 DS	0.068	28.6	0.39	0.051	16.2	0.79				
				0.024*	14.1*	0.91*				
Tixosil 382	0.077	29.1	0.38	0.055	16.2	0.79				
Aerogel A	0.12	25.9	0.45	0.14	18.5	0.68				
				0.062*	14.4*	0.89*				
Aerogel B	0.034	25.7	0.46	0.044	15.3	0.84				
<u>carbon blacks</u>										
TB#5500	0.048	26.9	0.43	0.094	15.3	0.84	0.075	17.8	0.71	
				0.083*	13.9*	0.93*	0.071*	15.5*	0.83*	
TB#4500	0.011	27.0	0.42	0.051	11.4	1.14	0.023	16.1	0.79	
TB#4500HT	0.005	20.3	0.61	0.25	8.6	1.51	0.021	20.1	0.62	
acet. black	0.004	21.7	0.57	0.14	9.3	1.41	0.02	20.5	0.60	
				0.16*	7.8*	1.67*	0.02*	17.6*	0.83*	

#### Argon adsorption isotherms

**Carbon blacks.** The argon D-R plots obtained for TB#5500 (Fig. 2b) and acetylene black are very similar to that of nitrogen. The higher adsorption of N<sub>2</sub> at low relative pressure may result from a stronger interaction for N<sub>2</sub> than for Ar with the different chemical groups present on the carbon black surface. It is noteworthy that, for both carbon blacks, the volumes W<sub>2</sub> obtained from the second linear domain, are very similar (Table 1) and that the two curves become identical, within the experimental errors, if one takes β=0.28 for Ar (instead of 0.31) in equation (1). It follows that the adsorption process within this pressure range is governed by the same micropore volume filling and no longer by surface coverage as suggested to explain the origin of the first domain. As shown earlier by Rouquerol and coworkers (Ref. 5), the crossing of the argon and the nitrogen isotherms, measured at the same temperature (Fig. 3b), characterizes the adsorption on a microporous solid. One may conclude that the micropores are completely accessible to small molecules at low temperature and therefrom that they are located near the surface of the carbon black

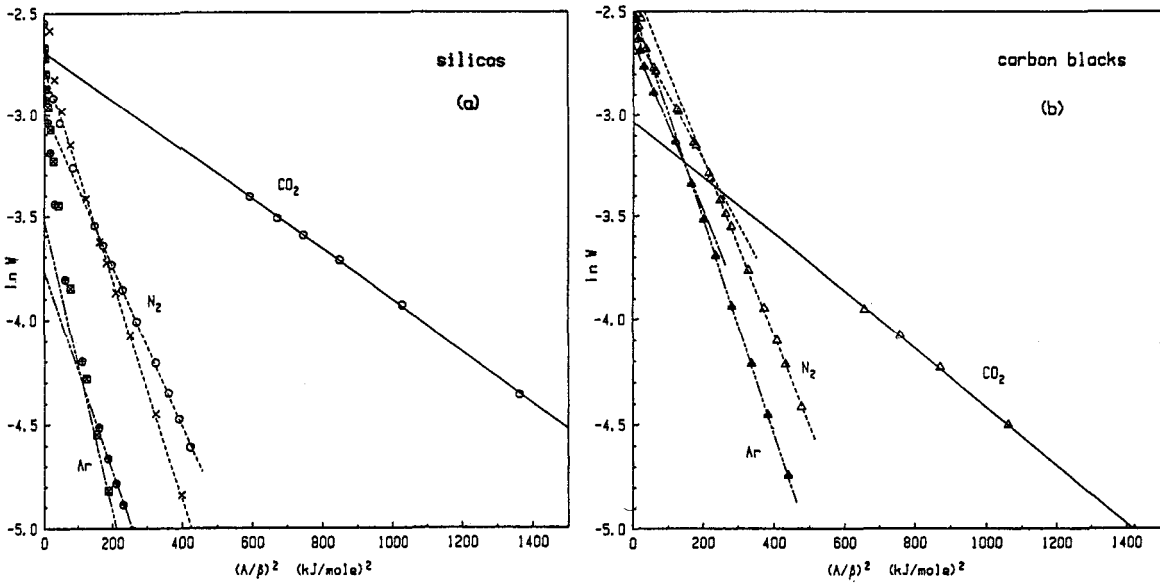


Fig. 2. Comparison between the D-R plots obtained for CO<sub>2</sub> (273 K) (—●—), N<sub>2</sub> (---▲---) and Ar (77 K) (—■—) on: (a) silicas: x, ■ Aerosil 200 and o, ● FK 320 DS (b) carbon black: Δ, ▲ TB#5500.

particles and directly accessible from the outside. This surface microporosity could originate from the slight oxidation of the carbon black particles during the processing. The effect of the high temperature treatment is the collapse of the narrower micropores as evidenced from the shift of the mean size  $x_{\mu}$  (Table 1) toward larger values for TB#4500 HT.

**Silicas.** The D-R plots (Fig. 2a) obtained for Ar are located much below the N<sub>2</sub> ones for the precipitated silicas, the highly microporous aerogel A sample (not shown in this figure) and also the nonmicroporous Aerosil 200. Clearly, argon molecules do not penetrate the micropore network evidenced by CO<sub>2</sub> adsorption at higher temperature. Moreover, for all silicas investigated here, the Ar and N<sub>2</sub> isotherm do not cross (Fig. 3a). This result also strengthens the assumption that these silica surfaces act as nonmicroporous solids for small molecules adsorbed at low temperature. It follows that their microporous texture is very different

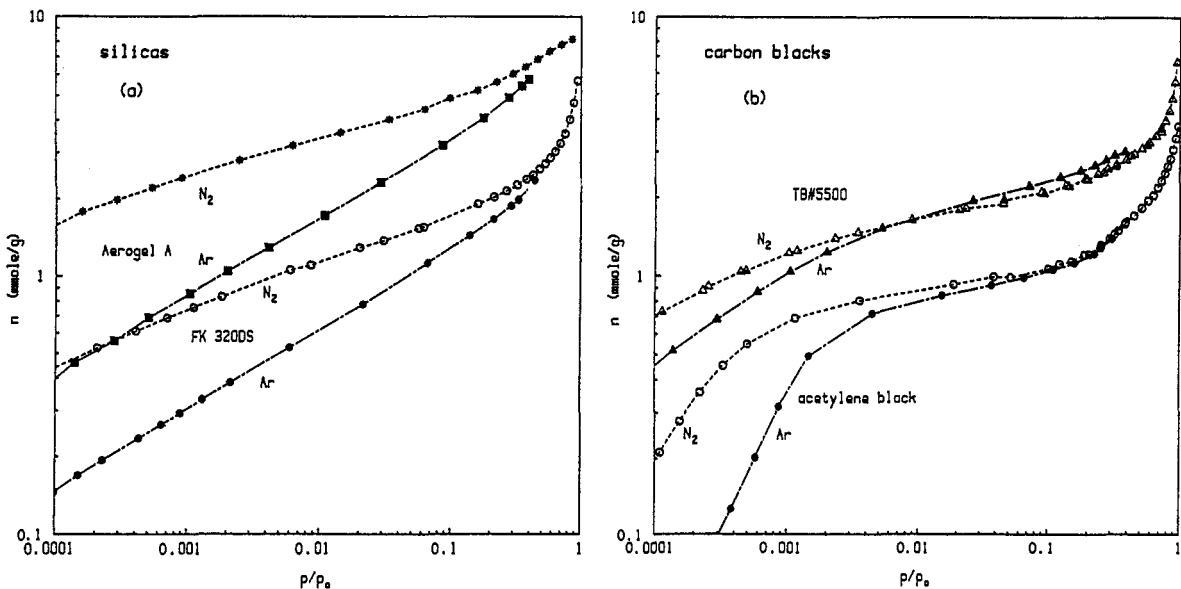


Fig. 3. Comparison between the isotherms of adsorption of N<sub>2</sub> (---▲---) and Ar (—■—) at 77 K on: (a) silicas: \*, ■ Aerogel A and o, ● FK 320 DS (b) carbon blacks: Δ, ▲ TB#5500 and o, ● acetylene black.

from that of the Gasil II investigated by Rouquerol (ref. 5) and also from that of carbon blacks. Our results are in agreement with the idea (ref. 12) that the micropores are the cavities in a packing (forming the secondary particles) of spheres (the primary particles) for which the radius of the throat is smaller than that of the cavity (ref. 13).

#### BET surface areas

Table 2 shows that, for carbon blacks, the BET surface areas determined from the adsorption isotherms of  $N_2$  and Ar are very similar. On the contrary, for silicas, the  $N_2$  BET surface areas are about 40% larger than the Ar ones. Such a result is well known (ref. 5) and is attributed to the effect of the interaction between the quadrupole moment of the  $N_2$  molecule and the surface hydroxyl groups. Although the question of the value of the molecular area of adsorptives is still under discussion (ref. 14), we think that it is more than likely that the value ( $0.138 \text{ nm}^2$ ) of  $(\sigma_0)_{Ar}$  is correct whereas the  $N_2$  one ( $0.162 \text{ nm}^2$ ) is too high.

Considering that the  $N_2$  molecule is "standing" on the surface (ref. 5), the most probable value of  $(\sigma_0)_{N_2}$  is  $0.112 \text{ nm}^2$ . It appears that the  $N_2$  BET surface areas calculated therefrom (in brackets in Table 2) agree fairly well with the ones obtained by Ar and correspond very likely to the real non microporous surface of the silica particles. As an immediate consequence of the above assumption, the density of  $N_2$  ( $d_{liq} = 0.808$ ) used in the D-R equation is probably too small. It follows that the values of  $(W_1)_{N_2}$  (in Table 1) which are much larger than  $W_1^*$  are probably too large and that they may become closer by using a higher density (probably larger than the solid density  $d = 1.026$ ) for the calculation of  $(W_1)_{N_2}$ .

TABLE 2. Results of the analysis, by means of the BET and fractal FHH equations, of the data obtained by  $N_2$  and Ar (indicated by \*) adsorption. The BET surface areas calculated by using  $\sigma_0 = 0.112 \text{ nm}^2$  for  $N_2$  are indicated in brackets. The uncertainty on the surface areas is about 5% and the values of the fractal dimension  $D$  are estimated to lie within a range of  $\pm 0.05$ .

Samples	BET		FHH			
	$n_m$ mmole/g	S $m^2/g$	m	D	range of $p/p_0$	range of $n/n_m$
<u>silicas</u>						
Aerosil 200	2.17 1.72*	211 (146) 143*	3.11	2.03	0.22 - 0.91	1.2 - 3.0
Sipernat	1.71	167	3.10	2.03	0.10 - 0.90	1.1 - 3.1
FK 320DS	1.68 1.48*	163 (113) 123*	3.03	2.01	0.10 - 0.94	1.1 - 3.1
Tixosil	1.71	167	3.03	2.01	0.28 - 0.90	1.2 - 3.1
Aerogel A	4.50 3.82*	440 (304) 317*	3.15 18	2.05 2.83	0.11 - 0.43 0.69 - 0.89	1.1 - 1.5 1.7 - 1.8
Aerogel B	1.42	138	4.30	2.30	0.25 - 0.96	1.3 - 2.9
<u>carbon blacks</u>						
TB#5500	1.88 2.15*	183 179*	3.33	2.11	0.05 - 0.94	1.0 - 3.6
TB#4500	0.61	60	3.03	2.01	0.39 - 0.91	1.6 - 3.6
TB#4500HT	0.52	51	3.03	2.01	0.40 - 0.90	1.8 - 3.6
acetyl. black	0.52 0.59*	51 49*	3.00	2.00	0.37 - 0.94	1.6 - 4.1

### Surface fractal dimension

The plots corresponding to the variation of the surface coverage  $n/n_m$ , where  $n_m$  is the number of moles forming the monolayer (Table 2), versus  $\ln(p_0/p)$ , in logarithmic coordinates, are shown in Fig. 4a and 4b for silicas and carbon blacks respectively. The domains of linearity are indicated in Table 2. Quite surprisingly, the fit of our experimental data by the FHH equation (5) leads to  $m \geq 3$ , whereas  $m$  close to 2.7 were generally reported (ref. 15). It follows that, in this case, the fractal dimension  $D$  cannot be determined unambiguously. Thermoporometry measurements have shown that, neither these silicas (ref. 3), nor these carbon blacks (ref. 16) do exhibit a significant pore volume between 2 and 15 to 20 nm. Therefore no capillary condensation is expected and  $D$  has to be evaluated from equations (5) and (6). It follows that, for most samples (Table 2),  $D \approx 2$ , i.e. the surface of the particles is not fractal but smooth.

The surface fractal dimension obtained by SANS (ref. 17), in the case of a pyrogenic silica (Cab-O-Sil M5), similar to Aerosil 200, agrees with the above result.

One may notice that, in the case of the two furnace blacks (TB#5500 and TB#4500), the one characterized by a high specific surface area (TB#5500) is a surface fractal whereas the second one, characterized by a much smaller surface area is not fractal.

Both Aerogels appear to be surface fractals. The  $D$  values obtained are in agreement with the ones deduced from Small Angle Neutron Scattering (SANS) (ref. 18). In the case of Aerogel B, however, two domains are evident, in a range of coverage below 2 layers. Although the concept of fractal dimension may become questionable in this case, the high  $D$  value ( $D = 2.83$ ) obtained in the upper range clearly indicates that the surface is almost space filling. It follows that at the scale of the molecular sizes, this adsorbent has to be characterized rather by the value of the external pore volume than the surface area.

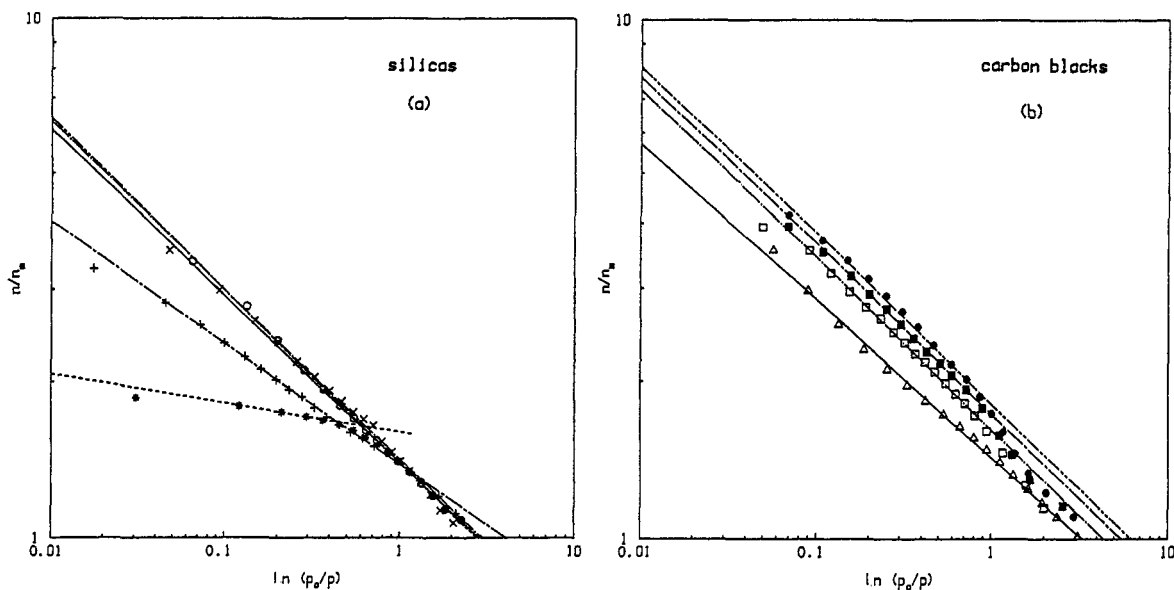


Fig. 4. FHH plots corresponding to the adsorption of N<sub>2</sub> (77K) on:

(a) silicas: x Aerosil 200, o FK 320 DS, \* Aerogel A and + Aerogel B

(b) carbon blacks: Δ TB#5500, □ TB#4500, ■ TB#4500 HT and ● acetylene black.

### CONCLUSION

In the present work we have compared the results obtained from the adsorption of three different gases. We chose low temperature (77 K) adsorption of nitrogen and argon and adsorption of carbon dioxide at 273 K as these methods are almost standard for the characterization of powder surfaces. From this study it is obvious that, for carbon materials, the combination of N<sub>2</sub> adsorption in the range of  $p/p_0$  leading to the BET surface area (and/or at higher relative pressure for the determination of the surface fractal dimension) and CO<sub>2</sub> adsorption is enough to completely characterize the morphology of the surface and to apply the Carbon Dioxide Subtraction (CDS) method developed by Rodriguez-Reinoso (ref. 1).

It is not the same for silica materials, at least for hydroxylated surfaces. From the present results it appears likely that the nitrogen and argon molecules, because of the low temperature of adsorption, do not enter within the micropores evidenced by carbon dioxide adsorption at 273 K. It follows that, for the microporous silicas we have investigated here, the N<sub>2</sub> BET surface area, generally used to characterize a given particulate solid, does not take into account the surface of the narrow micropores. The real surface accessible to molecules of the same size, at higher temperature, is therefore larger than the BET one as already evidenced by SANS (ref. 19) experiments. However, the adsorption of argon evidences that the BET surface area, calculated by using the value of the molecular area obtained from the liquid density ( $\sigma_0=0.162 \text{ nm}^2$ ), is overestimated. Therefore, the conclusion of the present work is that great care has to be taken in the choice of the adsorbates used for the characterization of the surface morphology of hydroxylated silica materials and that the combination of adsorbates we have used here could be a solution.

**Acknowledgements** We thank Pr. G. M. Pajonk (Université de Lyon, France) for providing the Aerogel samples and for interesting discussions.

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