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QUASI-EQUILIBRIUM ADSORPTION MICROCALORIMETRY (OF Kr, Ar AND N_2) TO CHARACTERIZE REAL MICROCRYSTALLINE SURFACES : APPLICATION TO ZnO.

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ABSTRACT

This work shows how selecting two sensitive adsorption techniques (namely : quasi-equilibrium adsorption volumetry and adsorption microcalorimetry at 77 K) and appropriate probe molecules (krypton, for accurate measurements, and N_2 and Ar, for their different response to local electrical fields) one may observe a complex adsorption behaviour of polycrystalline ZnO samples. The proportions of homogeneous polar faces, heterogeneous polar faces (edges and defects) and lateral faces are established from the above adsorption experiments for five different samples.

INTRODUCTION

The fact that the different crystalline faces could play a different part in adsorption has been suspected for a long time but is receiving experimental support only in the last a few years. The main difficulty lies of course in the limited surface area (sometimes less than 1 $m^2 g^{-1}$) of crystallized samples. This is why we found it worthwhile to apply, in this type of study, two techniques of high sensitivity formerly developed in the laboratory, namely *quasi-equilibrium adsorption volumetry* and *gas adsorption microcalorimetry at 77 K*. The adsorbent selected here is ZnO, for which interesting studies were recently carried out, in particular concerning the part of the polar hexagonal faces (0001) in the adsorption of CO and H_2 during methanol synthesis (1) and concerning the various proportions of polar faces, depending on the origin of the oxide : using CO

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adsorption (which occurs on the Zn^{2+} cations of the polar faces) and dissociative H_2 adsorption, Fubini *et al.* (2) show that the proportion of polar faces increases from the ZnO sample obtained by oxalate thermolysis, to that obtained by carbonate thermolysis and finally to that obtained by Zn combustion. Comparable conclusions were arrived at by Lavalley et al. (3)(4) from IR spectroscopy data obtained on similar samples. We therefore decided to have a further look at the possibility of determining the percentage of such polar faces.

EXPERIMENTAL

Five ZnO samples were selected. Three of them were obtained industrially by combustion of Zn. We call them here S-ZnO (kindly supplied by Mr. Fujiwara, from Sakai Chemical Industry Co., Fukushima, Japan. This is the special sample n°5905), A-ZnO ("Analar", from B.D.H. Chemicals Ltd., Poole, U.K.) and k-ZnO ("Kadok", from New Jersey Zinc Co., USA), respectively. The two others (which, like the k-ZnO, were kindly supplied by Mrs. B. Fubini and V. Boris, from the Faculty of Pharmacy of Turin University) were obtained by the thermolysis of a carbonate (C-ZnO) or of an oxalate (O-ZnO).

The association of quasi-equilibrium adsorption volumetry with adsorption microcalorimetry at 77 K is described elsewhere (5 and 6), together with the experimental set ups.

Prior to any adsorption experiment, outgassing is carried out by Controlled Transformation Rate EGD, whose application to the production of adsorbents in a standard state was already described (7).

RESULTS AND DISCUSSION

Fig. 1 gives the adsorption isotherm of Kr on sample S-ZnO, at 77 K, after outgassing up to 450°C by Controlled Transformation Rate EGD. One knows that such stepwise isotherms are typical of homogeneous surfaces and were observed for other metal oxides such as MgO (8), ZnO, SnO_2 and CdO (9). The extent of surface homogeneity may even be figured out by the value of the ratio Y_2/Y_1 of the height of the second step compared to the first (10). In the case of Fig. 1, the extent of surface homogeneity happens to amount to 0.59 (which may be compared with values of *ca.* 0.6 for a boron nitride and *ca.* 0.9 for exfoliated graphite which is among the most homogeneous samples known to-day (10)). Another interesting feature of the adsorption isotherm of Fig. 1 is the existence of

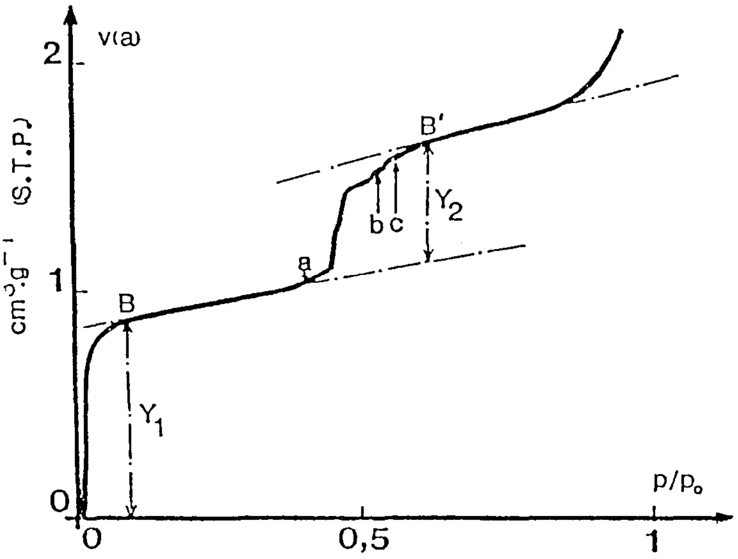

Figure 1 - Adsorption isotherm of krypton at 77K on S-ZnO outgassed up to 450°C

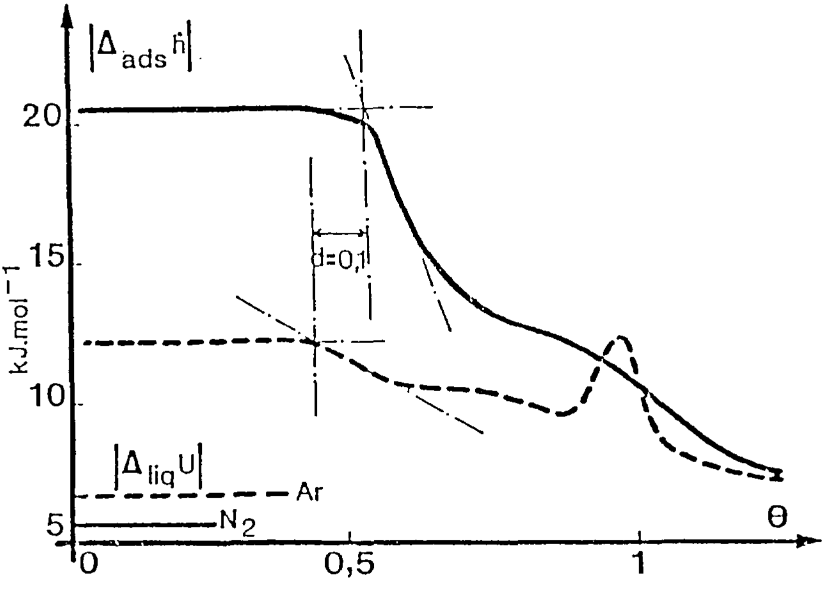

Figure 2 - Differential enthalpies of adsorption of nitrogen (full line) and argon (dashed line) at 77K

three small, but reproducible sub-steps (denoted a, b and c) which of course are only detected because of the continuous and direct recording of the adsorption isotherm, which is made possible by using the quasi-equilibrium procedure. It is quite likely that each of them corresponds to adsorption on different faces of the prismatic crystals of ZnO (hexagonal prisms with the wurtzite structure). As may be seen from the top of Table I, our S-ZnO sample is the most homogeneous.

Let us now come to the derivative enthalpies of adsorption of N_2 (continuous line) and Ar (dashed line) represented in Figure 2.

These curves suggest the following observations :

(a) Both adsorptives give rise to a constant derivative enthalpy of adsorption up to *ca.* half-coverage, showing a good energetical homogeneity of the types of sites involved in that first step.

(b) That enthalpy of adsorption is *ca.* twice higher than the enthalpy of liquefaction, in the case of argon, whereas it is *ca.* four times higher in the case of nitrogen. This is typical of a "specific" interaction between the permanent quadrupole moment of the nitrogen molecule and a local gradient of electrical field such as the one created by metallic ions (11 and 12). So, it is most reasonable to explain the plateau, in the case of N_2, by an adsorption involving the polar faces of the ZnO crystals, *i.e.* those presenting Zn^{2+} cations. The absence of any permanent dipole or quadrupole moment in the argon molecule explains the much lower energy of interaction.

Table 1

Analysis of the *adsorption isotherms* (the surface areas are calculated with $\sigma = 0.143$, 0.138 and 0.162 nm^2 for Kr, Ar and N_2, respectively)

Samples		S-ZnO	A-ZnO	K-ZnO	C-ZnO	O-ZnO
Outgassing temperature/°C		450	450	430	380	325
Homogeneity (from Kr steps)		0.59	0.52	0.40	-	-
Specific surface area /$m^2 g^{-1}$	Kr	3.53	3.67	8.22	19.8	14.4
	Ar	3.56	3.67	8.27	19.9	14.6
	N_2	3.76	3.87	8.88	21.3	15.7

(c) The length of the plateau is somewhat shorter in the case of Ar (and this was also observed by us for the other samples). This may indicate that less polar parts of the surface, such as the edges of the basal planes and possibly also defects of the crystal are able to be in high interaction with N_2, just as Lavalley et al. (3) had suggested in the case of CO adsorption, whereas they are too weak to induce an appreciable dipole moment in the Ar molecule. In these conditions, the difference in length of the plateaus may be used to figure out the proportion of defects and edges, whereas the length of the plateau for Ar must be proportional to the extent of homogeneous polar faces. We previously used a similar reasoning to determine the proportion of basal planes and lateral surface in the case of kaolinite and a good agreement was found with other methods, including electron microscopy and image analysis (13). The major interest of the microcalorimetric approach is therefore to provide a means of *measuring* this proportion of surface defects (cf. Table II).

(d) The peak observed around $\theta = 1$ on the curve for Ar also occurs for samples A-ZnO and K-ZnO, *i.e.* it occurs for the three most homogeneous samples. It is therefore most likely that it indicates a sudden phase change, possibly a two-dimensional freezing of the monolayer, similar to the one observed on graphite with the same techniques (14).

Table 2

Analysis of the *curves of derivative enthalpy* of N_2 or Ar adsorption

Samples	S-ZnO	A-ZnO	K-ZnO	C-ZnO	O-ZnO
% of polar faces (Ar plateau)	43	43	27	22	19
% of edges and defects (N_2-Ar)	10	7	16	6	4
% of lateral faces (the rest)	47	50	57	72	77

The above observations show the interest of physisorption microcalorimetry as a non-destructive, sensitive and quantitative technique to learn more about the proportions of various adsorbing faces, specially on microcrystalline samples whose perfection is limited but whose practical interest is high.

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