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Comparison of two techniques for the surface analysis of alumina (Al_2O_3): Inverse Gas Chromatography at Finite Concentration (IGC-FC) and Dynamic Vapor Sorption (DVS)

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ABSTRACT

Inverse Gas Chromatography and Dynamic Vapor Sorption are two methods of solid surface characterization isotherms. The exploitation of the adsorption and desorption isotherms leads to the calculation of specific surface area and surface energy of the divided solids under test. The powders used are γ and α alumina. The aim of this study is to compare the results obtained by these both techniques.

1. Introduction

This paper deals with two methods of characterization of finely divided solids: Inverse Gas Chromatography at Finite Concentration (IGC-FC) and Dynamic Vapor Sorption (DVS). They give access to physico-chemical properties such as specific surface area, surface energy, BET constant, of the powder surface under test. Both techniques consist in sending a gas stream of water or organic molecules on the surface of the solid. IGC is a method based on chromatographic peak analysis to determine the desorption isotherm of the probe molecule while DVS is a method based on the increase of the solid mass to determine the adsorption and desorption isotherms. The object of the present study is to determine the isotherms of water and different organic molecules and to compare the results obtained by IGC-FC and DVS.

2. Theory

2.1. Inverse Gas Chromatography

In contrast to conventional gas chromatography, Inverse Gas Chromatography involves the adsorption of a known adsorptive on an unknown adsorbent (solid sample). IGC uses clearly identified molecules, called probes, to determine surface properties of the material packed into the column. The adsorbent is placed in the GC column while the adsorptive is a gas carrying the probe molecules. Two types of IGC may be distinguished: Infinite Dilution (IGC-ID) or Finite solute Concentration (IGC-FC) [1]. This paper deals with IGC-FC where all the surface of the solid is covered with the probe molecule, so all the solid surface interacts with the probes, contrary to IGC-ID where only a few molecules are injected and interact mainly with high energy sites. IGC-FC gives access to isotherms of water or different organic molecules and allows calculating specific surface areas, BET constants, and distribution functions of adsorption sites. Two different experimental methods to obtain sorption isotherms may be distinguished: the Elution Characteristic Point method (ECP) and Frontal Analysis.

2.1.1. Inverse Gas Chromatography with the Elution Characteristic Point method (ECP)

This method allows the determination of desorption isotherms of organic vapors. It is a simple technique, requiring no special equipment other than a commercial analytical chromatograph, and only one experiment is required to determine each isotherm. In ECP, a large quantity of probe is passed through the column leading to a very deformed chromatographic peak. This deformation is due to the fact that the last molecules leaving the injector arrive at a saturated surface, which decreases their retention time. In the experiment, increasing quantities of probes are injected, and the diffuse fronts of the chromatographic peaks are as shown on Fig. 1. The peak summits appear at lower retention times (chromatograms c1, c2 and c3) until the chromatogram c4 is obtained when there is a monolayer of probe at the surface of the solid. If the amount injected is further increased, we obtain the chromatogram c5, where the plateau shows a multilayer adsorption of the probe.

Fig. 2 presents the evolution of chromatographic peaks obtained with the injection of increasing volumes of probe molecules according to the type of isotherms II or III [1]. The shape of the chromatographic

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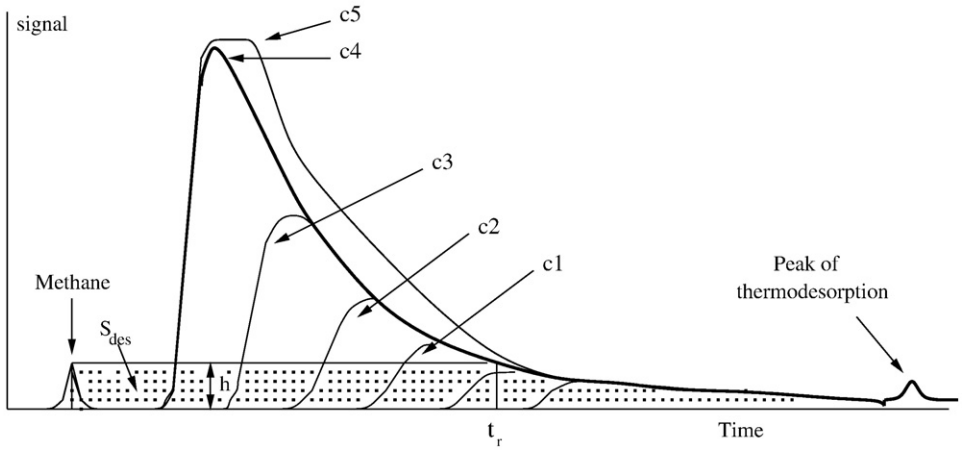

Fig. 1. Shapes of the chromatographic peaks for increasing quantities of probe injected.

peak is in relation with the type of isotherm of desorption and here corresponds to an isotherm of type II.

There are always high energy sites at the surface of the solid. When the signal seems to return to the baseline, a small amount of probe molecules can remain fixed irreversibly on the surface of the solid. Thus at the end of the analysis, the temperature of the oven is increased to be higher than the temperature of analysis but lower than the temperature of conditioning. A second peak can then appear corresponding to the thermodesorption of the molecules fixed irreversibly on the surface of the solid at the analysis temperature. In the ECP method the desorption isotherm corresponds to the variation of the desorbed quantity Q at the point of the retention time t_r which is directly related to the net retention volume V_r'.

$$\left(\frac{\partial Q}{\partial c}\right)_{t_r} = \frac{V_r'}{m} \tag{1}$$

Thus the variation of the quantity desorbed is in relation with the retention volume corresponding to the apparition of a concentration c of the liquid at the exit of the column divided by the mass m of the powder. This equation is only valid if the gas could be considered to be incompressible. However, different parameters such as the shape of the isotherm, the effect of sorption, the compressibility of the gas, the real nature of the gas, the non-ideality of the chromatographic procedure, the thermic effects with the adsorption of the liquid, the variation of the viscosity of the gas with the concentration of the liquid, must also be taken into account as in the following equation due to Conder and Purnell [2].

$$\left(\frac{\partial Q}{\partial c}\right)_{t_r} = \frac{V_r'}{m(1-\alpha\cdot J\cdot y_0)} \tag{2}$$

Here y_0 is the mole fraction at the exit of the column, J the James–Martin correction factor involving the compressibility of the gas [3], α a factor for the non-ideality of the vapor of the liquid. We obtain the equation:

$$\left(\frac{\partial Q}{\partial c}\right)_{t_r} = \frac{J\cdot D_s\cdot t_r'}{m(1-\alpha\cdot J\cdot y_0)} \tag{3}$$

with t_r' the net retention time and D_s the flow rate of the gas phase at the exit of the column.

The vapor of the liquid is considered to be a perfect gas, so $\alpha = 1, J\cdot y_0$ becomes negligible in front of 1 if the contribution of the probe to the gas flow rate is less than 5% of the flow rate in the absence of probe molecules, and the pressure is proportional to the concentration of the liquid. The characteristic equation of IGC-FC is therefore:

$$\left(\frac{\partial Q}{\partial P}\right)_{t_r} = \frac{J\cdot D_s\cdot t_r'}{m\cdot R\cdot T_{col}} \tag{4}$$

By integration, the desorbed quantity is obtained with the relation:

$$Q = \frac{J\cdot D_s}{m\cdot R\cdot T_{col}}\int_0^{P'} t_r'\,dP \tag{5}$$

The integral $\int_0^{P'} t_r'\,dP$ of Eq. (5) can be determined from the area S_{des} under the chromatogram (Fig. 1), the desorbed quantity at t_r' is proportional to S_{des}. The surface S_{des} can be calculated from the detector coefficient k_v which is the proportionality between the mass m_{probe} of injected probe and the area under the chromatographic peak S_{peak}. The following equation gives this as:

$$k_v = \frac{m_{probe}}{S_{peak}}\left(\frac{g}{\mu V\cdot s}\right) \tag{6}$$

The following relation gives also an expression of k_v:

$$k_v = 60.10^6\,\frac{V_{inj}\cdot\rho}{M\cdot D_s\cdot S_{peak}}\left(\frac{\mu mol}{cm^3\cdot\mu V}\right) \tag{7}$$

with V_{inj} the volume of probe injected (cm^3), ρ the density of the probe ($g{\cdot}cm^{-3}$), M the molecular mass of the probe ($g{\cdot}mol^{-1}$), D_s the

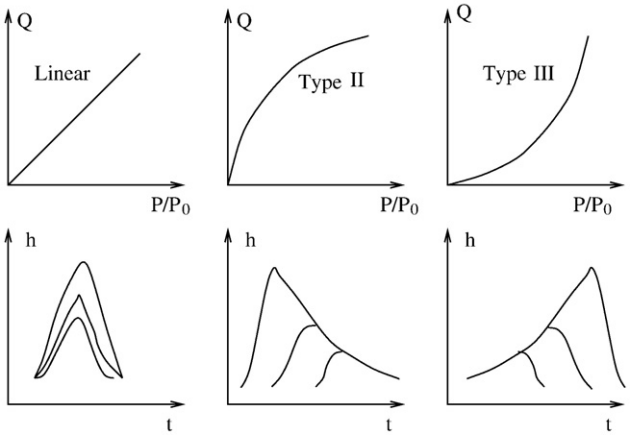

Fig. 2. Sorption isotherms and shapes of the chromatographic peaks.