



An Overview of characterization of Alumina and Related Surfaces by Inverse Gas Chromatography

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The flexibility of the IGC SEA method makes it a valid tool in the characterization of various materials. This is the reason for its frequent use in the characterization of metal oxides, especially for catalyst supports. This paper will give an overview of IGC SEA application in the field of alumina and related oxides.

Introduction

Aluminas as well as other metal oxides are of great importance in many applications in modern industry. These applications involve their use as catalyst supports, ceramics, and building materials, for example.

Therefore physico-chemical properties of these materials are the subject of innumerable studies by various techniques. Among all the different techniques measurements relying on the sorption of gaseous probe molecules belong to the most applied analytical methods.

In general sorption methods can be either dynamic or static. Standard procedures such as the determination of the surface area by nitrogen adsorption at 77 K are based on the latter. In recent years dynamic methods have become more and more important since they provide several advantages over common static techniques. For a dynamic measurement a carrier gas is used (instead of a vacuum) to transport the probe molecule (adsorptive) to the material under investigation (adsorbent). This allows faster equilibration under the experimental conditions.

The most common dynamic techniques are gravimetric methods and inverse gas chromatography (IGC SEA). IGC SEA exchanges

the roles of the phases in classical gas chromatography. The adsorbent under investigation is placed into a column while a known adsorptive is used in the gas phase. As in analytical gas chromatography one obtains the retention time as a primary information. The retention time can be converted into a retention volume, which is directly related to various physico-chemical properties, which can be calculated from an IGC SEA experiment. Those properties can be the surface energy or heat of sorption as examples for thermodynamic properties. Kinetic parameters such as the diffusion and the activation energy of diffusion are also available. Another possibility is the determination of the uptake both for physisorption and chemisorption. In the first case an isotherm results, which allows the computation of the surface area and porosity. In the latter case titration or thermal desorption techniques provide information about reversible and irreversible uptake.

II. The characterization of metal oxides by IGC SEA

A. Historical development

IGC SEA was developed in the 1950's. Early work was done in the characterization of catalyst support materials such as alumina, silica or





activated carbon. In most cases measurements were done by the pulse technique. In a pulse experiment an injection of the adsorbate is made. This pulse is transported by a carrier gas through the column and adsorbs on the solid sample. The adsorbed vapor is eluted by the carrier gas. The result is a peak in the chromatogram. Another method is the frontal technique. In this case the adsorptive is added continuously to the carrier gas. The chromatogram shows a breakthrough curve.

The benefit of the frontal technique is an easy access to high concentrations and the fact that equilibrium can be always assumed. On the other hand this technique requires more advanced instrumentation. This is the reason why even these days most IGC SEA work is still carried out by pulse measurements.

IGC SEA provides a fast and easy possibility to work with various gases but also with organic vapors under ambient conditions. This made IGC SEA an alternative to static measurements.

Historically the interest was focused on the determination of physisorption isotherms and heat of sorption measurements. The theoretical treatment of such measurements was derived in parallel by Cremer et al [1] and Roginskii et al [2]. Both made a similar approach, which is still in use for the calculation of isotherms from pulse measurements. A more detailed description can be found in a later chapter. Green and Pust were amongst the first to give a detailed explanation of heat of sorption measurements on alumina, silica and charcoal [3].

Another early application of IGC SEA was the determination of diffusion coefficients. Habgood and Hanlan [4] published a remarkable work in 1959 to characterize the micropore diffusion of nitrogen and hydrocarbons in activated charcoals using the van Deemter equation. Several authors later developed this approach further. However, the fundamental theory is still used.

Another milestone in the development of IGC SEA methods was the concept for the calculation of the dispersive surface energy and the free energies of desorption introduced in the 70's. The surface energy is the excess of the total energy a solid has over the value it would have if the surface were in the same state as the interior [5]. Compared to other techniques such as wettability IGC SEA provides the benefit of a variation in

concentration. Usually surface energy measurements are carried out at very small concentration (infinite dilution). This allows access to the higher energy sites on the surface. By increasing the concentration more and more less active sites are involved depending on the heterogeneity. Wettability in contrast to IGC SEA works at high concentration and provides therefore an average value.

The possibility to characterize the heterogeneity profile of a surface was recognized in the 80's. Several similar approaches have been published. A good overview can be found in [6].

B. Heat of sorption

By varying the temperature in an IGC SEA experiment a change in the retention volume can be observed. This relationship can be used for the calculation of the heat of sorption.

At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In this case the experimentally obtained peaks are almost symmetrical (Gaussian) and the retention time from the peak maximum can be used to calculate the retention volume. The net retention volumes V_N are computed using Equation 1.

$$V_N = j \cdot F / m \cdot (t_R - t_0) \frac{T}{273.15} \quad (1)$$

where T is the column temperature, m is the sample mass, F is the exit flow rate at 1 atm and 273.15K, t_R is the retention time for the adsorbing probe and t_0 is the mobile phase hold-up time (dead time). " j " is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

In the Henry's Law region the net retention volume is related to the differential heat of sorption by Equation 2.

$$\ln V_N / T = -\Delta H_A / RT + C \quad (2)$$

where it is assumed that the sorption enthalpy is independent of temperature. Under these conditions the heat of sorption is obtained from a plot of $\ln V_N/T$ versus $1/T$.

This approach was used by various authors to calculate the heat of sorption. An extended study was made by Baumgarten and Weinstrauch [7].

They collected values for many probe molecules on γ -alumina by pulse measurements.

Although pulse measurements have been used quite successfully they are limited to smaller surface area materials or higher measurement temperatures. This is due to the fact that peaks for small injections at infinite dilution are very small and broad and therefore difficult to analyze. This problem cannot always be solved satisfactorily by using higher temperatures since the heat of sorption is different or, in some cases, reaction between the adsorbent and the probe molecule even occurs.

An alternative is the use of frontal measurements. A continuous experiment can provide a well-defined breakthrough curve, even at small concentrations and low temperatures. This is demonstrated below by an octane measurement on an alumina, supplied by Degussa, Germany. Figure. 1 shows the heat of sorption plot.

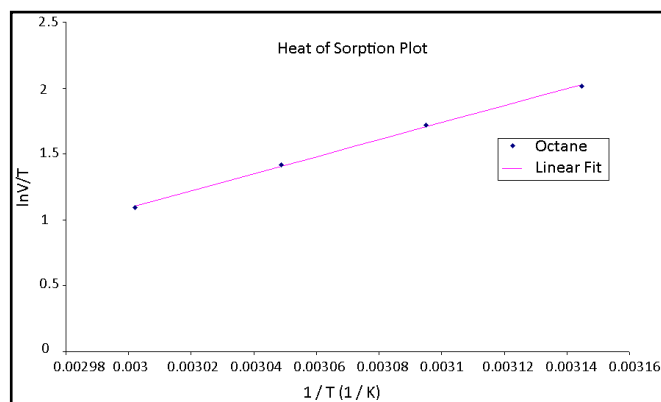


Figure 1. Heat of sorption plot of octane on γ -alumina. Measurements were carried out at infinite dilution in a frontal experiment at 10 ml/min carrier gas flow rate.

The result is 53.72 kJ/Mol. A comparison with literature data is difficult since other data are usually measured at higher temperatures. Further experiments are necessary to prove the reliability of the approach.

C. Isotherm measurements

An IGC SEA isotherm experiment can be carried out in two ways: either a breakthrough curve/pulse is measured for each concentration or a single step/ injection is used. The latter case is called Elution of a Characteristic Point, ECP (for a

pulse) or Frontal Analysis of a Characteristic Point, FACP (for a frontal experiment). This method relies on the correlation between the boundary and the isotherm shape, which is illustrated in Figure. 2 for a pulse chromatogram.

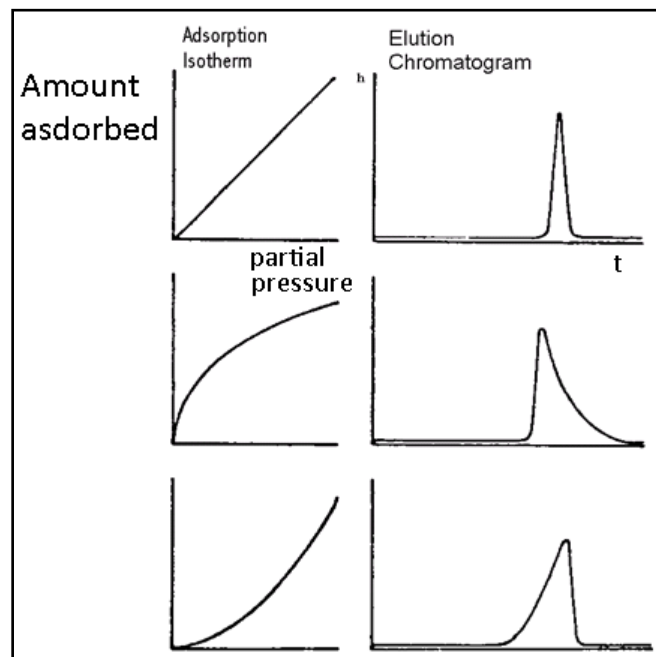


Figure 2. Correlation of peak form and sorption isotherm for finite and infinite dilution.

In the case of physisorption of non-polar adsorptives type II or IV isotherms are often observed. This corresponds to a tailing in the chromatogram. The calculation of such an isotherm is described in [1] and [2]. The peak height is directly related to the partial pressure p and can be converted quite easily. The retention volume is the first derivation of the amount adsorbed/desorbed (Equation 3). Thus, integration provides the amount adsorbed/desorbed n and therefore the isotherm.

$$n = \frac{1}{m} \cdot \int V_N dp \quad (3)$$

The FACP method is applied to calculate the BET surface area for a zirconia VP, manufactured by Degussa. The derived isotherm is shown in Figure. 3.

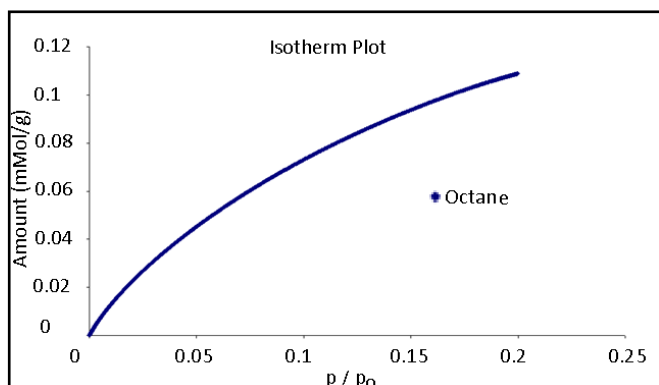


Figure 3. Desorption isotherm of octane on zirconia at 303 K and 10 ml/min carrier gas flow rate from a frontal experiment.

Looking at Figure. 3 it becomes obvious that one of the benefits of IGC SEA is the high number of points available at low concentration. One obtains a value of 46.05 m²/g, which is in good coincidence with the manufacturers value of 47±10 m²/g. Another advantage is the ease of using a large variety of probe molecules, even polar vapors.

D. Energetical Heterogeneity

There exist two types of surface heterogeneity: structural and energetic [6]. A typical example of a structural heterogeneity is a wide pore size distribution. Energetic heterogeneity occurs with a wide distribution of various surface sites of different energetic levels. Such a heterogeneity profile can be represented by an energy distribution function.

The energy distribution function is an important parameter in the characterisation of solids since it can provide important information on surface property variation. A heterogeneity profile constitutes an energy “map” of the material surface. Such information allows a prediction of product properties, especially in the formulation of blends, composites or coatings.

In the following example the distribution of the adsorption potential of two different graphite materials is determined for polar and non-polar probe molecules. Graphite is a particularly interesting example since it is known to have, energetically, a fairly inhomogeneous surface despite the absence of porosity effects.

E. Surface energy and Acid-base chemistry

The surface energy is a very interesting parameter since it can give information about the energetic situation on the surface but, in comparison with the heat of sorption, is independent on the probe molecule. The surface energy can be obtained from a plot of the logarithm of the retention volume of a series of alkane probe molecules versus the product of liquid tension and molecular area [8, 9]. The result is a straight line and the dispersive surface energy γ_s^D is calculated from the slope according to Equation 4.

In this equation N_A is the Avogadro number, γ_L^D the liquid tension of the probe molecule and a its cross sectional area.

$$RT \ln V_N = 2N_A \left(\gamma_s^D \right) a \left(\gamma_L^D \right) + const. \quad (4)$$

Polar probe molecules also have a specific interaction contribution. Therefore, points representing a polar probe are located above the straight line. The difference is equal to the specific component of the free energy of desorption ΔG_{SP} (Equation 5).

$$\Delta G_{SP} = RT \ln V_N - RT \ln V_N^{ref} \quad (5)$$

Other methods use a plot of the logarithm of the retention volume versus the boiling point [10], the vapor pressure [11] or the polarizability [12]. All parameters are sensitive to changes in surface properties such as the surface chemistry or morphology. Therefore, these measurements are often applied to study batch to batch differences and related problems.

The sensitivity of the surface energy and the free energy will be demonstrated on a practical problem in building material characterization. Asphalt is a building material consisting of minerals and bitumen. The latter acts as the binder. Bitumen is produced from heavy fractions during the crude oil refining and contains linear and cyclic alkanes, olefines and aromatic compounds. The quality of the asphalt depends

strongly on the interaction between the minerals and the binder. In practice it was observed that similar minerals gave different affinities with the same bitumen. As demonstrated in the following example surface energy experiments can be a good measure for this affinity.

Four different minerals were investigated: pure quartz with a poor affinity, quartz sand (good affinity), calcite sand (good affinity) and potassium feldspar (medium affinity). Measurements were carried out with a series of alkanes between heptane and decane.

The results are shown in Figure. 4.

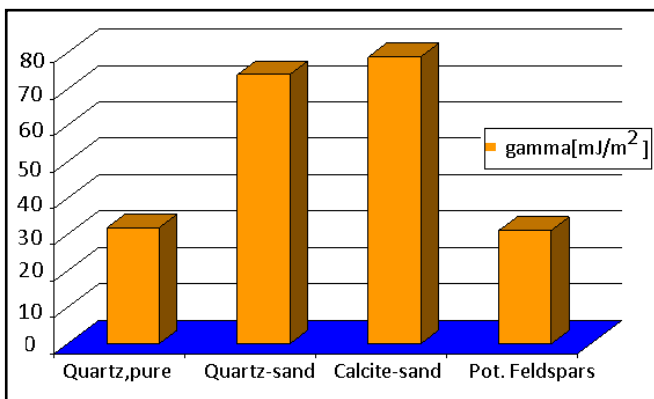


Figure 4. Dispersive surface energies of different minerals measured by a series of alkane injections between heptane and decane at 303 K and 10 ml/min.

The two samples with the best affinity, calcite and quartz sand show a significantly higher surface energy than the other two samples. This suggests that the dispersive surface energy is a good quantitative measure for the affinity.

Polar probes were also studied for potassium feldspar, calcite and quartz sand. Figure. 5 shows the results for toluene, dichloromethane, 1-butanol and ethyl acetate.

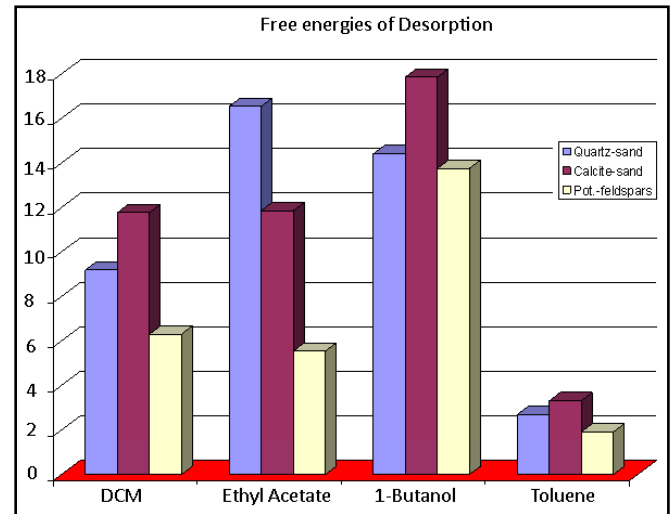


Figure 5. Free energies of desorption for different minerals. Measurements were carried out with toluene, dichloromethane, 1-butanol and ethyl acetate at 303 K and 10 ml/min.

All minerals show their hydrophilic character by a strong interaction with ethyl acetate and butanol. Butanol gives a significantly stronger interaction with calcite and feldspar demonstrating the basic character of these minerals since butanol is a Lewis acid. Quartz shows its slightly acid character by giving the strongest interaction with the Lewis base ethyl acetate.

As mentioned above the surface energy changes with the concentration of the probe molecule on heterogeneous surfaces. This is demonstrated in Figure. 6 for quartz.

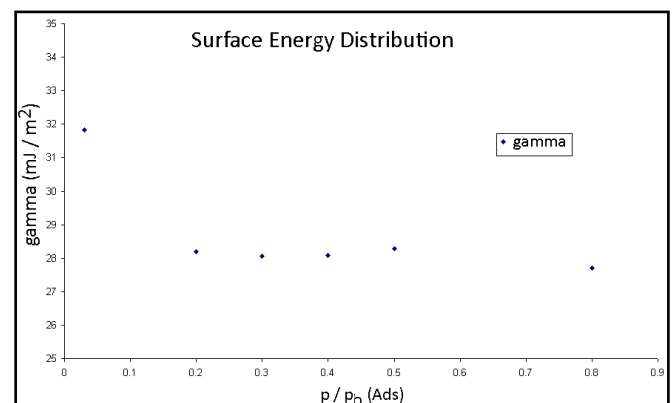


Figure 6. Change of the dispersive surface energy with concentration for pure quartz.

As expected the value for the surface energy decreases with increasing adsorptive concentration.

F. Titration

The titration is an adsorption method where pulses with the same concentration are injected until the eluted peaks have the same height. The difference in the eluted peak area represents the amount chemisorbed.

This method was originally developed for the determination of the metal surface area in metal/support catalysts. Gruber [13] was one of the first to use IGC SEA for this type of experiment. He analysed the degree of dispersion of a platinum/alumina catalyst by using carbon monoxide as a probe molecule. However, measurements are usually carried out with hydrogen due to its simple stoichiometric atom to metal ratio. It adsorbs in a dissoziative chemisorption mechanism. Assuming a Langmuir-type monolayer adsorption it is possible to calculate the metal surface area S_{Me} according to Equation 6 [14]:

$$S_{Me} = N_A \cdot a \cdot D_{Me} / M_{Me} \quad (6).$$

M_{Me} is the molecular weight. The degree of dispersion D_{Me} can be obtained from the following relationship:

$$D_{Me} = f \cdot n^* / n \quad (7).$$

f is the stoichiometric factor ($f=1$ for hydrogen), n^* is the amount of metal atoms on the surface and n is the total amount of metal atoms in the sample.

If the density of the metal atoms ρ_{Me} is available the average particle diameter d_{Me} can be calculated by Equation 8:

$$d_{Me} = 6 / (S_{Me} \cdot \rho_{Me}) \quad (8).$$

Another application of the titration method is for the determination of the uptake of polar organic probe molecules. Cavallaro et al measured the ethanol chemisorption on alumina [15]. An advanced study can be done by variation of temperature since, especially in the case of hydrogen, activated adsorption processes have to be taken into account [16].



Conclusion

IGC SEA has been shown as a versatile tool for the characterization a variety of different properties. These properties include physisorption at finite dilution such as the measurement of isotherms and at infinite dilution the determination of the heat of sorption or the surface energy. Chemisorption effects are measured by titration methods.

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