Quantachrome Autosorb iQ Capabilities

Summary prepared by Steve Creager, Clemson University, Sept 29 2015

The following paragraphs summarize the principal capabilities of the recently acquired Autosorb iQ gas sorption analyzer at Clemson.

1. Physisorption (usually N_2, Ar, Kr, CO_2).

Key measurement is the adsorption isotherm, i.e. the amount of gas adsorbed as a function of gas pressure at a fixed temperature. Method is based upon a series of pressure measurements in response to sequential dosing of sample with known amounts of gas. From analysis of the adsorption isotherm, the following sample attributes may be obtained

- Specific surface area (SSA); from 0.0005 m^2/g, to no known upper limit.
- Specific pore volume; porosity, isosteric heat of adsorption
- Pore size distribution (PSD); from micro and macropores, from 0.35 to 50 nm (depending on the model used for the calculations, analysis up to 400 nm may sometimes be possible)
- A wide range of models may be applied to interpreting adsorption isotherm data. Information on surface areas and pore volumes for select regions of a sample including micropores (smaller than 2 nm), mesopores (2-40 nm) and macropores (larger than 40 nm) in possible.

The following points relate to gas selection and specific capabilities;

- N_2 at 77 K and Ar at 87 K are routinely used for specific surface area (SSA) determinations (e.g. a "BET" analysis) from 0.01 m^2/g to no known upper limit.
- Ar at 87 K is the standard adsorptive for micropore analysis as defined by the IUPAC, and also has noticeable advantages for surface area determinations on highly polar surfaces such as zeolites, silicas and MOFs.
- CO_2 at 273 K is useful for faster micropore measurements in carbons (up to 1.5 nm). Can be combined with N_2 (77 K) or Ar (87 K) to obtain a complete pore size/volume characterization of nanoporous carbon materials
- Kr at 77 K is useful for studying low surface area samples (extends the range down to 0.0005 m^2/g), and for obtaining PSD of thin films when analysis is performed at 87 K.
- Non-corrosive gases that are chemically compatibles with the instrument's elastomers are also possible, e.g. hydrogen, hydrocarbons, etc. (amount adsorbed at a specific relative pressure and temperature).

2. Static chemisorption (usually H_2, CO, sometimes NH_3)

Key measurement is the amount of gas that becomes strongly and irreversibly adsorbed following dosing with a reactive gas. Also based upon pressure measurements following sample dosing. First measurement of a clean sample results in both chemisorption and physisorption, second one results only in physisorption, and amount of chemisorbed gas is then obtained by difference.

- Commonly used to characterize supported catalysts, e.g. Pt, Pd, Ni, etc.

- Provides values for the metal-only area for the supported catalyst, from which values for the number of active sites, metal dispersion, average crystallite size may be obtained (Metal loading must be known).
- Heats of adsorption (isosteric and integral) may be obtained from a series of static chemisorption measurements over a range of temperatures (at least 2).

3. Flow chemisorption. (usually H_2, CO, O2, sometimes NH_3, others are possible)

Measures the amount of strongly adsorbed gas only on a sample. Sample is subjected to a flow stream of mixed gas (reactive + carrier) at ambient pressure, that is then passed through a thermal conductivity detector (TCD). The TCD signal senses the change in TC of the gas due to variation in gas mixture concentration and composition. Variations are related with (1)the removal of reactive species from the flow stream during adsorption, (2) the evolution of previously adsorbed species into the flow stream during desorption, or (3) the decomposition products.

Some representative flow chemisorption experiments are as follows;

Surface (Pulse) titration. Consists of a series of controlled volumes of analysis gas injected into an inert carrier gas stream (usually He), that continuously flows over the sample, with monitoring of the TCD signal as a function of the number of doses. Detector measures the amount of gas that remains unadsorbed by the sample. Subtraction from the total amount injected gives the total amount adsorbed. Provides information on the amount of active sites on a sample surface. Similar to static chemisorption but quantification is faster, and a wider range of gas choices is possible. Can be combined with TPX analyses (see below).

Thermally Programmed Desorption (TPD). Sample is dosed with active gas at low temperature to occupy active sites, then subjected to flow of carrier gas as sample temperature is raised. Gas desorption is detected by change in TCD signal at characteristic temperatures. Provides information on heat of adsorption, binding strength on active sites and desorption kinetics for active gases on surfaces. Can be quantitative if calibration is performed.

Thermally programmed reduction (TPR). A low concentration of pre-mixed gas (usually H_2 (e.g. 5%) in N_2 or Ar) flows over the sample while the temperature is increased. TCD signal variation is due to gas adsorption (depletion of the flow), associated with a reduction reaction on the surface, often involving metal oxides being reduced to metals and evolving water. Provides information on critical temperatures and reaction kinetics for surface reduction reactions. Can be quantitative if calibration is performed.

Thermally programmed oxidation (TPO). Similar to TPR, except the flow gas is oxidizing(i.e., 5%, of O_2 in He) Gas adsorption is associated with an oxidation reaction on the surface that could produce a wide range of products depending upon the surface groups being oxidized (usually CO and CO_2). Provides information on critical temperatures and reaction kinetics for surface oxidation reactions.