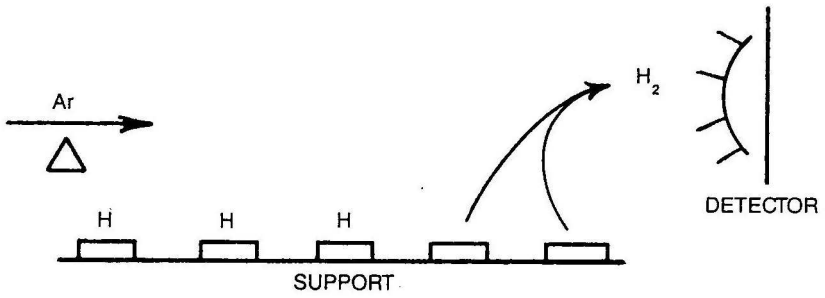
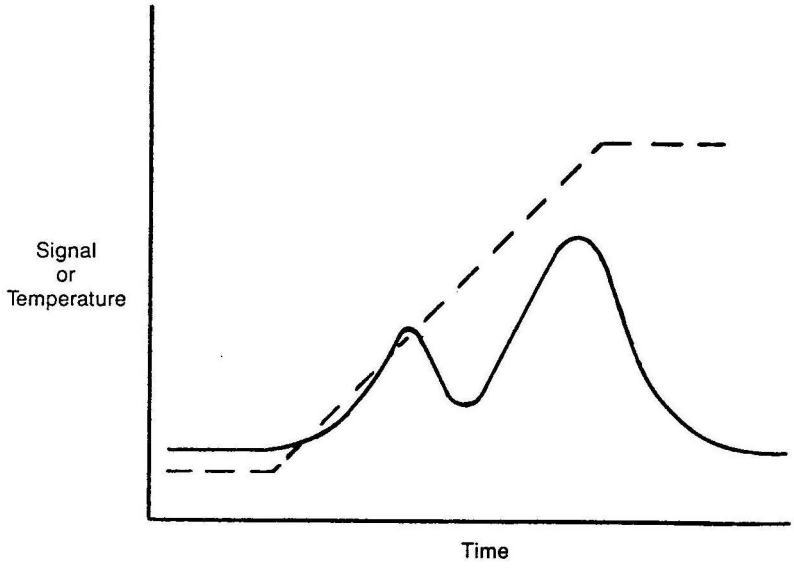
Altamira Instruments

Altamira Notes
Vol. 1.2

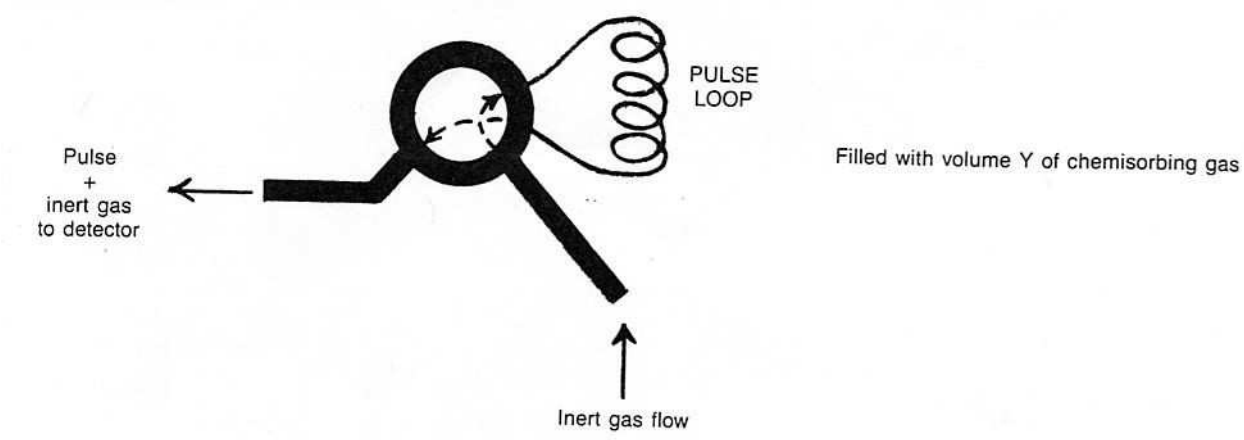
SURFACE AREA MEASUREMENT FROM TEMPERATURE-PROGRAMMED DESORPTION DATA

Temperature-programmed desorption experiments offer a means of obtaining quantitative information about the metallic surface area of supported metal catalysts along with a qualitative measure of the variation in strength of adsorption for different sites on the surface. The method makes use of a detector calibrated to quantify the number of chemisorbed molecules desorbing from the metal catalyst surface into an inert gas stream as the temperature of the catalyst surface is raised in a linear fashion:





The area under this signal vs time curve is related to the number of molecules chemisorbed on the catalyst surface. We derive this signal by calibrating the detector for the chemi sorbing gas. The detector signal is calibrated by sending a controlled volume pulse of the chemisorbing gas into an inert stream which flows into the detector. This is typically accomplished using a GC valve equipped with a calibrated GC loop. From this we can determine that a detector signal of X counts corresponds to a volume Y of chemisorbing gas. This gas volume is in turn converted to micromoles using the ideal gas law.



Using this calibration, detector signal for a TPD experiment can be obtained in terms of "gas uptake" by the catalyst in micromoles/gram catalyst. Several pieces of information must be known before we can make use of this number:

- What is the metal weight loading of the supported metal catalyst? From this we can calculate the actual weight of metal in the catalyst sample used in the experiment.
- What is the molecular weight of the metal? This allows us to convert from grams to micromoles of metal in our sample.
- What is the stoichiometry of the adsorption of the chemisorbing molecule on the metal in question? This enables us to relate the metal and the chemisorbing species to each other on the molar basis.

With this information we determine the value of a parameter known as the dispersion of the supported metal catalyst. The dispersion is defined as the number of surface metal atoms divided by the total number of surface atoms. A catalyst with 100% dispersion has every metal atom available for chemisorptive bonding. A lower value of dispersion means that some of the metal sites are not exposed to the chemisorbing molecules in the gas phase, such as metal atoms below the surface layer in a metal crystallite. Intuitively, a higher value of dispersion means more efficient use of the metal in a catalytic reaction.

This dispersion parameter may be converted to a more accessible and accepted physical parameter, the metal crystallite size, but first an assumption about the crystallite shape must be made. The most common assumed shape is a sphere with volume (pi) dye and surface area (pi)d2. When we divide the volume of the sphere by its surface area we obtain an expression containing the characteristic dimension of the crystallite, the diameter d:

$$V/A = d/6$$

Some physical information about the metal in question is also required:

- What is the surface area of a single metal atom? From this we can calculate the maximum surface area possible on a per gram metal basis. This quantity is called Sg. When we multiply this quantity by the dispersion which we measured, we obtain the specific surface area of our sample:

$$Asp = Sg * D$$

- What is the density of the metal? The inverse of the density gives us the specific volume of the metal, Vsp.

We can divide the specific volume of the metal sample by its specific surface area and set this quantity equal to V/A for the crystallite:

$$Vsp/Asp = V/A$$

Setting these two quantities equal to each other gives:

$$d/6 = l/((rho) * Sg * D)$$

and hence the diameter of the metal crystallite is given by:

$$d = 6/((rho) * Sg * D)$$

The table below lists some physical data for a number of transition metals commonly used in supported metal catalysis:

Metal	Maximum Surface Area (m /g metal)	Density (g metal/cm)
Pt	235	21.4
Pd	432	12.0
Rh	445	12.4
Ir	239	22.5
Ru	453	12.2
OS	242	22.5
Fe	700	7.9
Co	654	8.9
Ni	667	8.9

For a supported Ni catalyst with a dispersion of 33% (D = 0.33), the average crystallite diameter is:

$$rho = (8.9\ g/cm^3) * (cm/10^8\ A)^3 = 8.9 * 10^{-24}\ g/A^3$$

$$Sg = (667\ m^2/g) * (10^{10}\ A/m)^2 = 6.67 * 10^{22}\ A^2/g$$

$$d = 6/((8.9 * 10^{-24}\ g/A) * (6.67 * 10^{22}\ A^2/g) * (0.33))$$

$$d = 31\ A$$