Surface area measurement from temperature programmed desorption data

Introduction

Physisorption experiments for the characterization of solid materials and substances have become a well-established analytical method. They can be considered a first step towards the understanding and development of functional materials and are necessary in both quality control and R&D. Related to physisorption, which is based on the weak interactions (e.g., van-der-Waals and electrostatic relationships) between adsorbate and adsorbent, are chemisorption experiments. The main difference between the two is the nature of the interaction between adsorbate and adsorbent – in chemisorption, a strong chemical bond is formed between the surface and the guest molecule. The scope of chemisorption is also a lot less general than physisorption – where physisorption targets a materials pore system and surface texture in general, chemisorption is tailored towards active centers, catalytical activity and chemical reactions. A common use of chemisorption processes is in the field of so-called temperature-controlled experiments (TPX), which can be roughly categorized as oxidation (TPO), reduction (TPR) and desorption (TPD). This article will give a brief overview on how to obtain and evaluate surface areas from temperature programmed desorption (TPD).

Data-Acquisition in Temperature Programmed Desorption (TPD)

In order to characterize samples by means of TPD, after a suitable activation procedure (which can involve reduction at higher temperature, evacuation or drying, etc.) the sample will be saturated with a chemically active adsorptive which will bond to the target compound or site of the material in question. The procedures may vary, given the highly variable nature of catalysts and other solids in the fields with relevance to sorption studies. 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 (see Fig. 1).

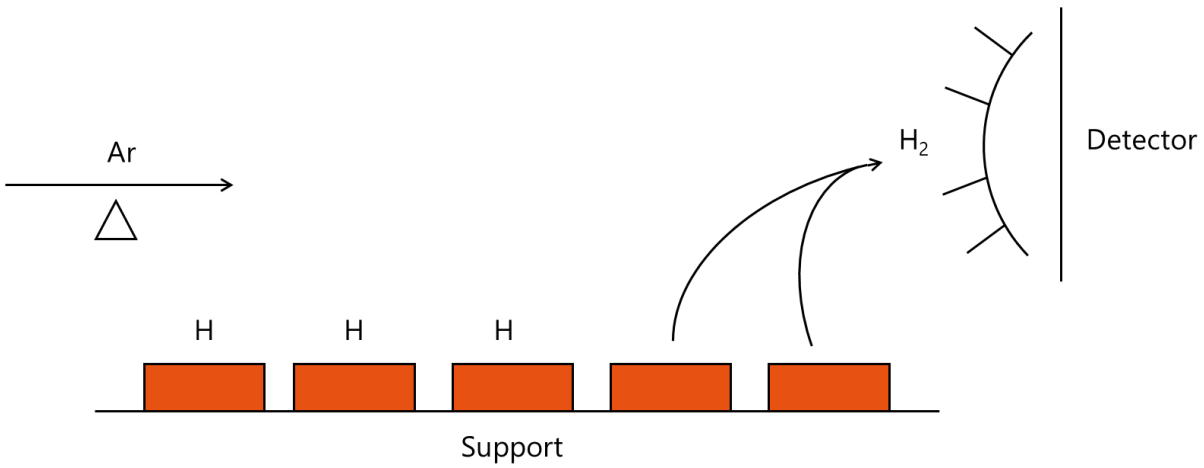


Figure 1 *Schematic depiction of Hydrogen-TPD processes on a catalyst in an Argon stream*

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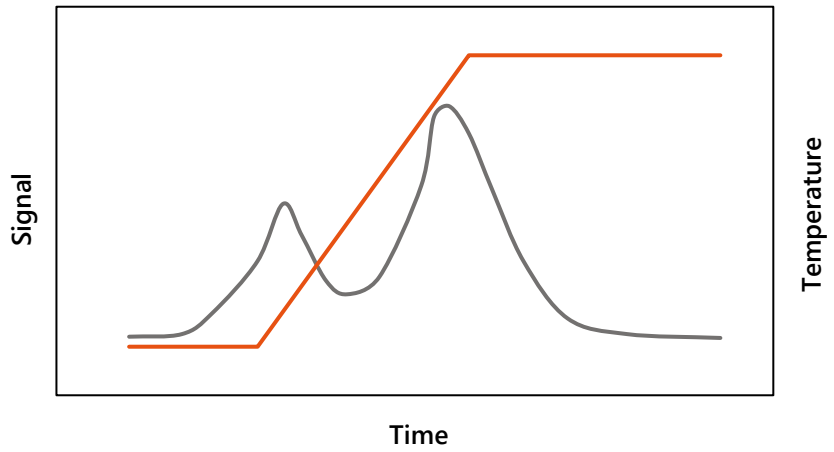


Figure 2 *Schematic detector signals obtained from TPD*

The area under this signal vs. time curve is related to the number of molecules chemisorbed on the catalyst surface (see Fig. 2). The signal is obtained by calibrating the detector for the chemisorbed 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 (see Fig. 3). 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.

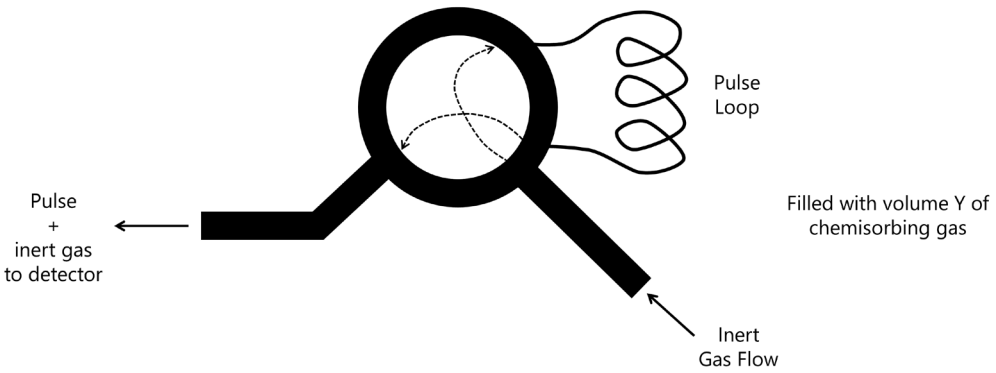


Figure 3 *Scheme of GC valve and loop*

Using this calibration, detector signals for a TPD experiment can be obtained in terms of "gas uptake" by the catalyst in micromoles/gram catalyst. Several 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.

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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 a volume $V = \pi \cdot (d^3/6)$ and a surface area $A = \pi \cdot d^2$. 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:

$$\frac{V}{A} = \frac{d}{6}$$

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 S_g. When we multiply this quantity by the dispersion D which we measured, we obtain the specific surface area of our sample:

$$A_{sp} = S_g \cdot D$$

- What is the density of the metal? The inverse of the density gives us the specific volume of the metal, V_{sp}.

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:

$$\frac{V_{sp}}{A_{sp}} = \frac{V}{A}$$

Setting these two quantities equal to each other gives:

$$\frac{d}{6} = \frac{1}{\rho \cdot S_g \cdot D}$$

Hence, the diameter d of the metal crystallite is given by:

$$d = \frac{6}{\rho \cdot S_g \cdot D}$$

Tab. 1 below lists some physical data for a number of transition metals commonly used in supported metal catalysis:

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Table 1 *Physical data for a number of transition metals*

Metal	Maximum Surface Area / m^2/g metal	Density / g metal/cm^3
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:

$$\rho = (8.9\ g/cm^3) \cdot (cm/10^8\ A)^3 = 8.9 \cdot 10^{-24}\ g/A^3$$
$$S_g = (667\ m^2/g) \cdot (10^{10}\ A/m)^2 = 6.67 \cdot 10^{22}\ A^2/g$$
$$d = 6/((8.9 \cdot 10^{-24}\ g/A) \cdot (6.67 \cdot 10^{22}\ A^2/g) \cdot (0.33))$$
$$d = 31\ A$$

Conducting TPD experiments have established a base for using different metals which are relevant for catalysis and show their relationships between the dispersion and the crystallite sizes of these metals in carrier substrates (see Fig. 4).

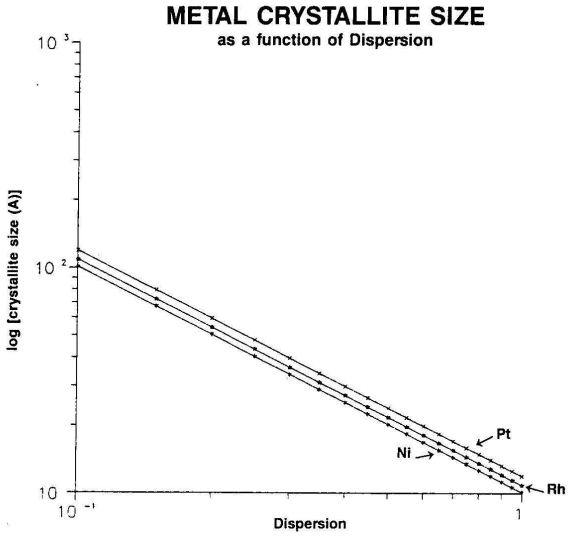


Figure 4 *Logarithmic representation of the relationship between metal dispersion and crystallite sizes for Pt, Rh and Ni metals on solid substrates*

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Conclusion

The approaches shown above illustrate the possibilities of TPD analysis and their relevance for analyzing active surface areas in transition metal-based catalysts with carrier substrates. It gives operators and scientists a possibility to evaluate the dispersion of these metal centers and their respective accessible surface for chemical processes. Quantification of the probe gases (which are usually tailored towards the metal in question, e.g., hydrogen for platinum, etc.) is usually carried out by means of a thermal conductivity sensor, which is put directly into the carrier gas stream. However, different analytical approaches can be used as well or combined with one another, such as mass spectroscopy, infrared spectroscopy and gas chromatography among others.

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