Surface Area Measurement from Temperature-Programmed Desorption Data

1. Background

Temperature-programmed desorption (TPD) 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.(1) 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 overall TPD scheme with H_2 as an example is shown in Figure 1.

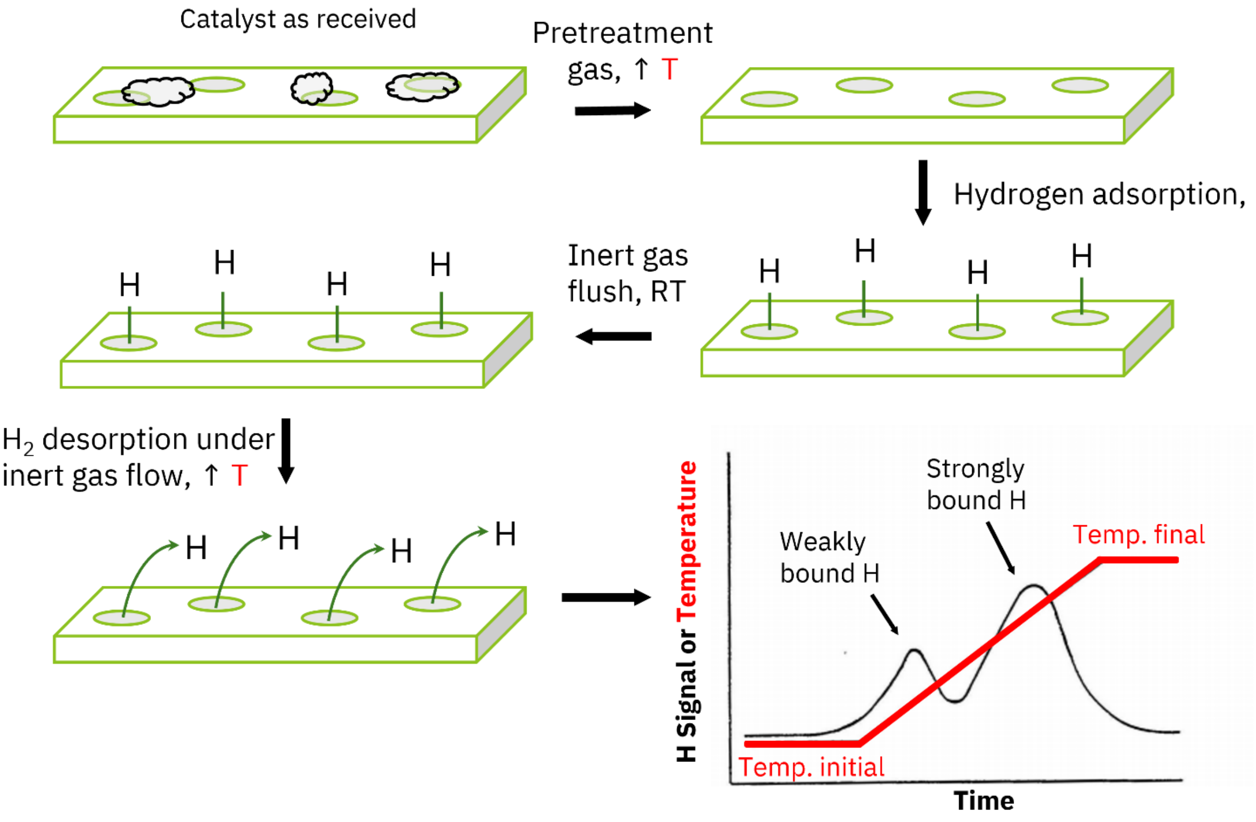

Figure 1: Schematic of H_2 temperature programmed desorption on support metal catalyst, metal catalyst sites shown as green circles

2. TPD Methods

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 chemisorbing 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 accomplished using a GC valve equipped with a calibrated GC loop, shown in Figure 2. From this we can determine that a detector signal of X counts corresponds

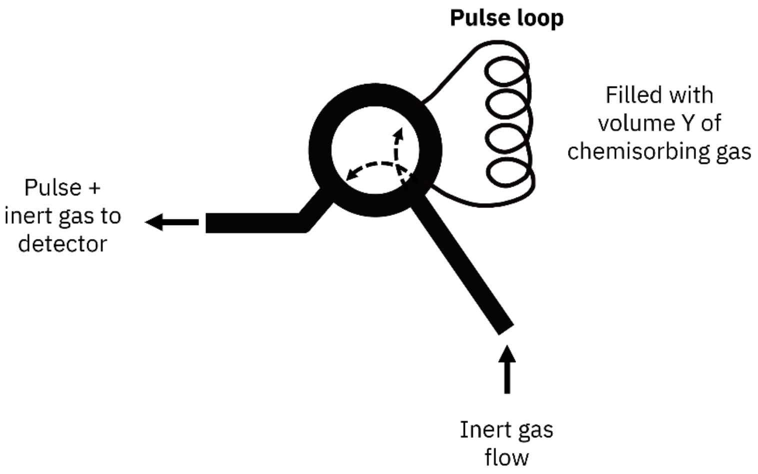

Figure 2: Schematic of uptake calibration for TPD experiment equipped with a GC loop

to volume Y of chemisorbing gas. This gas volume is in turn converted to micromoles using the ideal gas law.

3. Calculating Metal Surface Area from TPD Data

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 (or weight percent) of the metal catalyst in the total material?
- ✓ What is the molecular weight of the metal?
- ✓ What is the stoichiometric factor (SF) of the chemisorbing molecule on the metal in question?

The SF is defined as the number of adsorbed species per the number of binding sites. For example, the SF of CO can be 1 (linear adsorption, one CO molecule on one binding site) or 0.5 (bridging adsorption, one CO molecule on two binding sites).

$$\mathit{Dispersion}\ (\%) = \frac{\mathit{Gas\ Uptake}\ \left(\frac{\mu mol}{g}\right) \times \left(\frac{10^{-6}\ mol}{\mu mol}\right) \times \mathit{Stoichiometric\ Factor}\ (SF)\ \times \mathit{Molecular\ Weight}\ \left(\frac{g}{mol}\right)}{\mathit{Metal\ Loading}\ (wt\%)} \times 100\% \qquad (1)$$

With this information, we can calculate the dispersion (D) of the supported metal catalyst, which is shown in Eqn. 1. The dispersion is also defined as the number of surface metal atoms divided by the total number of metal 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 or agglomerated in a metal crystallite.(2) 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 $V = (\pi/6)d^3$ and surface area $A = \pi d^2$. 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:

$$\frac{V}{A} = \frac{d}{6} \tag{2}$$

Some physical information about the metal in question is then 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 which we measured in Eqn. 1, we obtain the specific surface area (A_{sp}) of our sample:

$$A_{sp} = S_g \times D \tag{3}$$

- ✓ 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:

$$\frac{V_{sp}}{A_{sp}} = \frac{V}{A} \tag{4}$$

Setting these two quantities equal gives:

$$\frac{d}{6} = \frac{1}{\rho \times S_g \times D} \tag{5}$$

and therefore, the diameter of the metal crystallite is given by:

$$d = \frac{6}{\rho \times S_g \times D} \tag{6}$$

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

Table 1: Maximum surface area and density values for common metal catalysts

Table 1 lists maximum theoretical surface areas of transition metal crystallites calculated based on crystallographic parameters and surface atom density.(3) For a supported Ni catalyst with a dispersion of 33% (D = 0.33) determined by Eqn. 1, the average crystallite diameter is calculated by plugging ρ, S_g, and D into Eqn. 6.

The density of Ni (ρ) is 8.9 g/cm^3 from Table 1, converting from cm^3 to $Å^2$ gives:

$$\rho = \frac{8.9\ g}{cm^3} \times \left(\frac{cm}{10^8\ Å}\right)^3 = \frac{8.9\ \times\ 10^{-24}\ g}{Å^3} \tag{7}$$

The maximum surface area of Ni (S_g) is 667 m^2/g from Table 1, converting from m^2 to $Å^2$ gives:

$$S_g = \frac{667\ m^2}{g} \times \left(\frac{10^{10}\ Å}{m}\right)^2 = \frac{6.67\ \times\ 10^{22}\ Å^2}{g} \tag{8}$$

Now plugging the values of ρ and S_g into Eqn. 6 gives:

$$d = \frac{6\ \times Å^3 \times g}{(8.9\ \times\ 10^{-24}\ g) \times (6.67\ \times\ 10^{22}\ Å^2) \times 0.33} \tag{9}$$

Therefore, d = 31 Å.

Conducting TPD experiments with various metals can show the relationship between the dispersion and the crystallite size of common metal catalysts on support oxides, and this relationship is shown in Figure 3.(2,4)

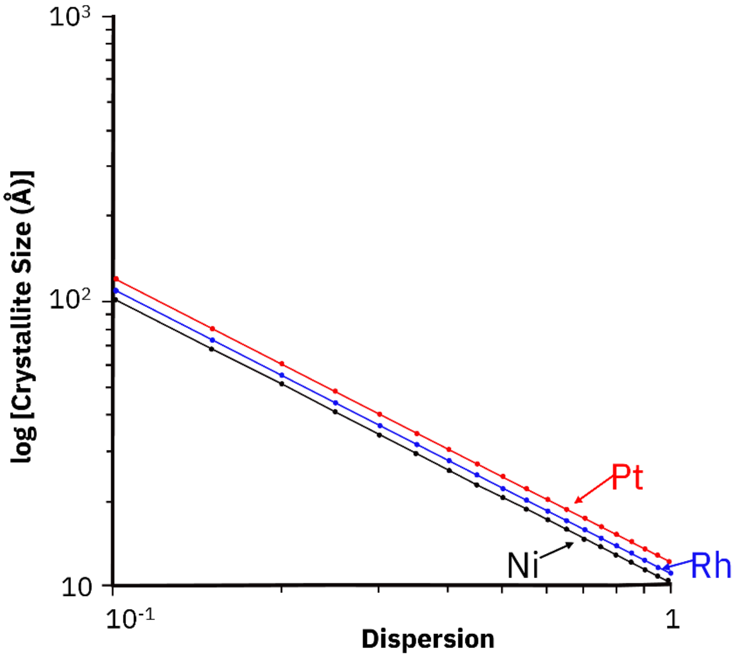

Figure 3: Logarithmic representation of the relationship between metal dispersion and crystallite sizes for Pt (red), Rh (blue), and Ni (black) metals on solid substrates

4. Conclusions

The approaches shown above illustrate the possibilities of TPD analysis and their relevance for analyzing active surface areas for supported transition metal-based catalysts. gives operators and scientists a possibility to evaluate the dispersion of these metal centers and their respective accessible surface for chemical processes. The **AMI 300** and **AMI 400** series of chemisorption analyzers are excellent options for this technique, offering precise temperature control and highly accurate gas sensors. **AMI** chemisorption analyzers are also customizable, making them ideal for combination with external gas analysis instruments.

✓ AMI's flagship model offering fully automated static and dynamic chemisorption in a customizable instrument

✓ Precision gas control with independent mass flow controllers for blending

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✓ Variety of sample holders supporting:
  - ✓ Powders
  - ✓ Pellets
  - ✓ Extrudates
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AMI 300

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✓ Automatic, intelligent gas interface
  - ✓ Software automatically selects appropriate gas for every step

✓ Precision gas control with independent mass flow controllers for blending

✓ Triple thermocouple design for enhanced control and safety

AMI 400

*Figure 4: Highlighted features of **AMI 300** and **AMI 400** chemisorption analyzers*

5. References

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(4) Borodziński, A. and Bonarowska, M. Relationship between crystallite size and dispersion on supported metal catalysts. *Langmuir*, **1997**, *13*, 5613-5620.