

Lecture 9

Chemisorption

In many catalysts, active metals are deposited on the surface of the support such as in Pt/Al₂O₃, Pt/C, Ni/Al₂O₃ etc. These metals act as active sites in various oxidation states including in zero valence state. The location and state of the active metal on the support largely depends on the preparation method of the catalyst. When prepared by impregnation method, more active metals are expected to concentrate on the surface of support, whereas in bulk preparation method active metals are trapped more within the bulk matrix. Further, these metals usually exist as clusters on the support surface and thereby, only a fraction of the total deposited metal is actually exposed to the incoming reactant molecules for participation in a reaction.

The dispersion (D) of metal is defined as
$$D = \left(\frac{N_s}{N_T} \right)$$

where ,

N_s = total no. of exposed surface atoms

N_T = total no. of metal atoms present in the sample

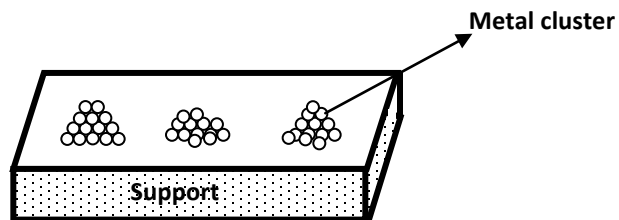


Fig. 1. Metal cluster on support surface

Chemisorption technique gives direct measurement of the number of exposed surface atoms. This method measures quantity of gas adsorbed selectively on the metal at monolayer coverage.

This technique is mainly used to study :

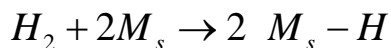
- (1) metal dispersion and
- (2) active metal area.

In this method, the sample is exposed to a gas that can chemisorb on the active metal. At monolayer coverage, the average number of surface metal atoms associated with adsorption of each gas molecule is determined. Accurate determination of metal dispersion and the active metal area is possible if stoichiometry of the chemisorption reaction is known. Pulse method is frequently used to determine the number of gas molecules adsorbed on the catalyst surface.

For a given catalyst, the adsorbate gas is chosen to minimize adsorption on the support and to have an irreversible (or weakly reversible) chemisorptions on the metal. H_2 and CO are the most commonly used adsorbate gases.

Hydrogen Chemisorption

H_2 adsorbs dissociatively on metals according to the equation :



M_s represents a surface metal atom.

The chemisorption stoichiometry n is defined as the number of metal atoms to which one adsorbate gas molecule can attach. In case of hydrogen chemisorption, one hydrogen molecule attaches with two metal atoms; hence $n = 2$.

CO chemisorption

The CO adsorption is considerably more complex. The CO can chemisorb in various forms on metals such as Fe, Ni, Ru, Pt , Pd. The chemisorption stoichiometry varies with temperature, metal dispersion, metal loading and preparation. CO can be chemisorbed :

1. Dissociatively (CO: $n = 2$) or
2. Associatively
 - Linear ($n = 1$)
 - Bridged ($n = 2$)

□ Multi-bonded species ($n = 3$)

The relative proportion of the various forms depends on temperature, pressure and metal particle size.

Adsorbate gas choice

For a given catalyst, the adsorbate gas should be chosen such that it interacts irreversibly with metal or have very weak reversible interaction. The adsorbate should have minimum adsorption on the support. Most commonly used adsorbate for metal characterization is hydrogen and CO. Other gases such as O₂, N₂O, NO, N₂ etc. are also used depending on the specific application. The CO can chemisorb in different forms on metals such as iron, nickel, ruthenium, palladium, rhodium and platinum. Not knowing the exact stoichiometric relation can introduce error. The main difficulty is the formation of metal carbonyl, which are volatile as in case of nickel and rhodium. However, CO chemisorption is better suited when hydrogen can be absorbed into the metal (palladium hydride formation) or significantly adsorbed on support (such as carbon support). Oxygen chemisorption is also used. However, possibility of formation of metal oxides with variable stoichiometry may cause errors. Main application of oxygen adsorption measurement is hydrogen-oxygen titration. For cases, when interaction of metals with H₂ or CO is very low and interaction with oxygen is excessively strong resulting in bulk oxidation, such as for Cu or Ag, the adsorptive decomposition of nitrous oxide can be used.

Working principle and instruments

In pulse chemisorption technique, initially the sample is reduced with hydrogen at elevated temperature to convert the oxide to metallic form (such as NiO to Ni). Then, the sample is flushed with an inert gas at elevated temperature, such as helium, to remove traces of any adsorbed gases. Then, sample is cooled to the analysis temperature, with inert gas flowing. Successive small pulses of adsorbate gas (of known volume) are injected in the flow of inert gas by a syringe or loop at the desired temperature. Pulses of adsorbate gas are continued to be injected until the catalyst surface is saturated. The Fig 2 shows a typical plot of peak area of adsorbate gas as function of number of pulse injected. As the figure shows, the first pulse corresponds to negligible peak area

suggesting that most of the injected gas is adsorbed. For second pulse the peak area increased compared to the first suggesting lesser amount of gas adsorbed compared to first injection. As the number of pulse increases peak area gradually increases corresponding to decreased amount of gas being adsorbed. Finally the peak area becomes constant corresponding to the area of pulse volume. The constant areas are shown by pulse number 6 and 7 in the Fig 2. The amount of gas adsorbed is obtained by calculating the difference between the volume of each pulse and the fraction of H₂ not adsorbed. The total amount of gas chemisorbed can be obtained from the number of consumed pulses. The schematic diagram of equipment for pulse chemisorption is given in Fig. 3.

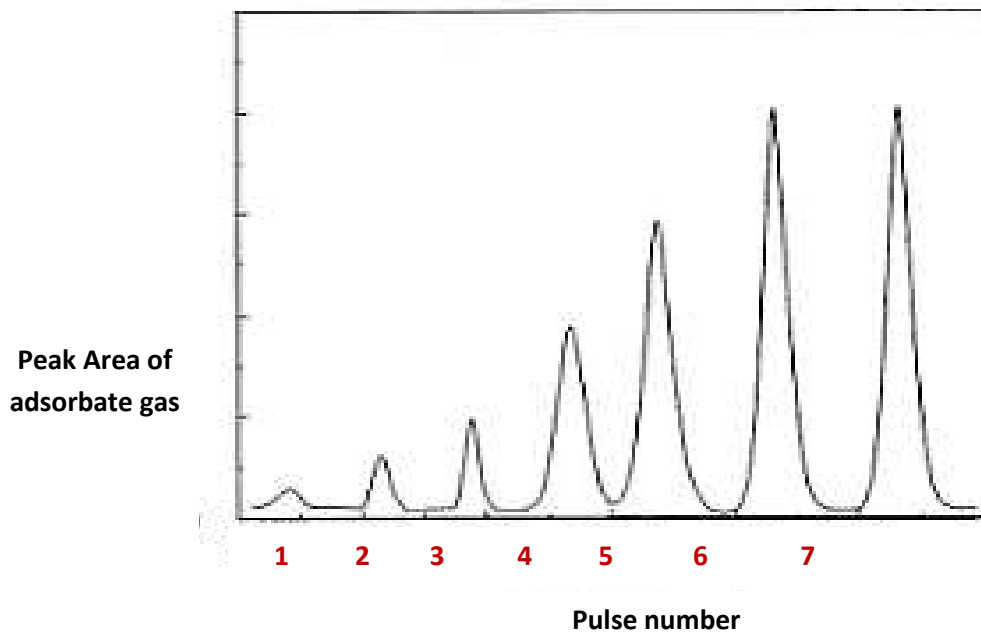


Fig. 2. A typical plot of peak area vs pulse number of adsorbate gas

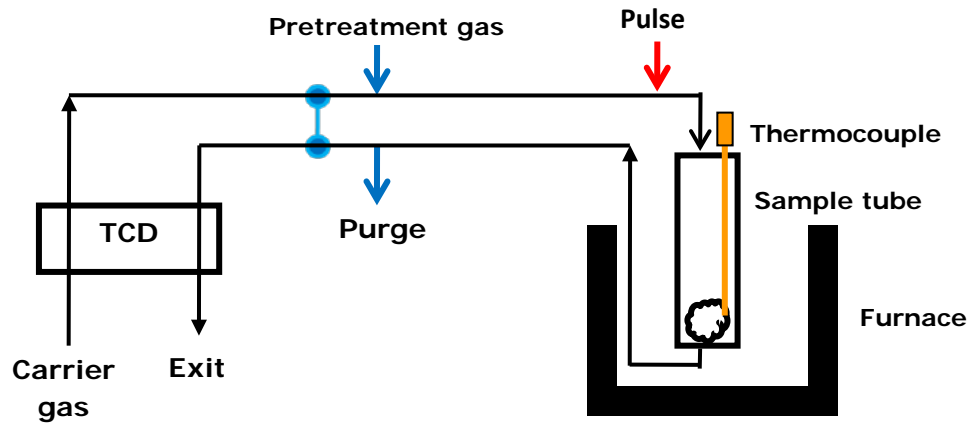


Fig. 3. Schematic diagram of equipment for pulse chemisorption

Calculations for determination of metal dispersion and active metal area :

1. The volume of active gas (CO or H₂) injected, V_{inj} , can be calculated at STP conditions using the equation below. Generally, the active gas is used as a gas mixture, such as 10% CO in helium or 10 % H₂ in argon.

$$V_{inj} \text{ (STP)} = V_{syr} \times \frac{T_{std}}{T_{amb}} \times \frac{P_{amb}}{P_{std}} \times \frac{A}{100}$$

V_{syr} = syringe volume injected, cm³

T_{amb} = ambient temperature, °C

T_{std} = standard temperature = 273K

P_{amb} = ambient pressure, mmHg

P_{std} = standard pressure = 760mmHg

A = % active gas in gas-mixture

2. The volume of active gas chemisorbed is calculated using volume injected V_{inj} and from area under the peaks as follows.

$$V_{ads} \text{ (STP, cm}^3 \text{ / gm)} = \frac{V_{inj}}{m} \times \sum_{i=1}^n \left(1 - \frac{A_i}{A_f} \right)$$

V_{inj} = volume injected, cm³

m = mass of the sample, gm

A_i = area of peak i

A_f = area of last peak

3. Calculation of % Metal Dispersion

$$\text{Moles of metal on surface of sample} = n \times \frac{V_{\text{ads}}}{V_g} \text{ moles/gm}$$

$$\text{Moles of total metal present in sample} = \frac{M}{\text{m.w} \times 100} \text{ moles/gm}$$

$$D = \frac{\text{Moles of metal on surface of sample}}{\text{Moles of total metal present in sample}}$$

$$D = n \times \frac{V_{\text{ads}}}{V_g} \times \frac{\text{m.w}}{M} \times 100$$

n = stoichiometry factor

V_{ads} = volume adsorbed, cm^3 / gm

V_g = molar volume gas at STP = $22414 \text{ cm}^3 / \text{mol}$

m.w. = molecular weight of the metal

M = % metal loading

$$\text{Or } \%D = \left[n \times \frac{V_{\text{ads}}}{V_g} \times \frac{\text{m.w}}{M} \times 100 \right] \times 100$$

4. Active metal surface area per gram of sample

$$A_m (\text{m}^2/\text{gm}) = [\text{total number of surface metal atoms}] \times [\text{cross section area of active metal}]$$

$$A_m (\text{m}^2/\text{gm sample}) = \left[\left(n \times \frac{V_{\text{ads}}}{V_g} \right) \times N_A \right] \times a$$

n = stoichiometry factor

V_{ads} = volume adsorbed, cm^3 / gm

V_g = molar volume of the gas at STP = $22414 \text{ cm}^3 / \text{mol}$

N_A = Avogadro's number = 6.023×10^{23} molecules / mol

a = cross-sectional area of active metal atom, m^2

Solved examples :

1. Calculate the metal dispersion and active metal area for

0.5 wt % Platinum on Alumina catalysts by CO pulse chemisorption. The areas of the pulses are given in the table. Additional given data are :

Sample amount: 1gm ; Analysis gas: 10%CO/He; Carrier gas: He ; Temperature: 25 °C ; Pulse volume: 0.5 cm^3 ; stoichiometry factor of CO on Pt = 1.

Peak No.	1	2	3	4	5	6	7
Peak area	0.0	0.0	0.0003	0.001	0.005	0.007	0.007

Solution :

i. Calculation of volume of Active Gas Injected From a Syringe 10 %CO /He

$$V_{inj} \text{ (STP)} = V_{syr} \times \frac{T_{std}}{T_{amb}} \times \frac{P_{amb}}{P_{std}} \times \frac{A}{100}$$

$$V_{syr} = \text{syringe volume injected} = 0.5 \text{ cm}^3$$

$$T_{std} = \text{ambient temperature} = 22^\circ\text{C}$$

$$T_{amb} = \text{standard temperature} = 273\text{K}$$

$$P_{amb} = \text{ambient pressure} = 743\text{mmHg}$$

$$P_{std} = \text{standard pressure} = 760\text{mmHg}$$

$$A = \% \text{ active gas} = 10$$

$$V_{inj} \text{ (STP)} = 0.5 \times \frac{273}{(25 + 273)} \times \frac{743}{760} \times \frac{10}{100} = 0.0448 \text{ cm}^3$$

ii. Calculating Volume Chemisorbed:

$$V_{ads} = \frac{V_{inj}}{m} \times \sum_{i=1}^n \left(1 - \frac{A_i}{A_f} \right)$$

$$V_{inj} = \text{volume injected} = 0.0448 \text{ cm}^3 ; m = \text{mass of the sample} = 1 \text{ gm}$$

Table 1. Calculation for volume of CO adsorbed on Pt supported on Alumina

Peak no.	A_i	$\left(1 - \frac{A_i}{A_f}\right)$	$(V_i)_{ads}$ $= \frac{V_{inj}}{m} \times \left[1 - \frac{A_i}{A_f}\right]$	$\Sigma(V_i)_{ads}$ $= \sum_{i=1}^n \frac{V_{inj}}{m} \times \left(1 - \frac{A_i}{A_f}\right)$
1	0	1.0000	0.0448	0.0448
2	0	1.0000	0.0448	0.0896
3	0.0003	0.9571	0.04288	0.1325
4	0.001	0.8571	0.0384	0.1709
5	0.005	0.2857	0.0128	0.1837
6	0.007	0.0000	0	0.1837
7	0.007	0.0000	0	0.1837

From Table 1, A_f = area of last peak = 0.007

Volume of CO adsorbed on Pt supported on alumina = V_{ads} = 0.1837 cm³/gm

iii. % Metal Dispersion:

n = stoichiometry factor, CO on Pt = 1

V_{ads} = volume adsorbed = 0.1837 cm³/gm

V_g = molar volume of the gas at STP = 22414 cm³/mol

m.w. = molecular weight of the metal Pt = 195

M = % metal = 0.5

Moles of metal on surface of sample = $n \times \frac{V_{ads}}{V_g} = 1 \times \frac{0.1837}{22414} = 8.196 \times 10^{-6}$ moles / gm

Moles of total metal present in sample =
 $\frac{M}{m.w \times 100} = \frac{0.5}{195 \times 100} = 2.564 \times 10^{-5}$ moles / gm

$$\%D = \frac{8.196 \times 10^{-6}}{2.564 \times 10^{-5}} \times 100 = 31.96 \%$$

iv. Active Metal Surface Area (per gram of sample)

$$A_m = \left[n \times \frac{V_{ads}}{V_g} \right] \times N_A \times a \quad \text{m}^2/\text{gm sample}$$

n = stoichiometry factor, CO on Pt=1

V_{ads} = volume adsorbed= 0.1837 cm³/gm

V_g = molar volume of the gas at STP= 22414 cm³/mol

N_A = Avogadro's number = 6.023 x 10²³ molecules/mol

a = cross-sectional area of active metal atom = 0.08 nm² = 0.08 × 10⁻¹⁸ m²

$$A_m = \left[1 \times \frac{0.1837}{22414} \right] \times 6.023 \times 10^{23} \times 0.08 \times 10^{-18} = 0.395 \quad \text{m}^2/\text{gm sample}$$