Optimizing Adsorbate Selection, Adsorption Conditions, and Stoichiometry in Chemisorption for Supported Metal Catalysts

1. Background

The choice of adsorbate is critical in temperature-programmed desorption (TPD) experiments on supported metal catalysts. The selected gas should chemisorb selectively on the desired site, either the metal catalyst or the support material. Ideally, the adsorbate should form a stable monolayer and avoid irreversible reactions with either the metal or the support. The most common adsorbates for various metals are listed in Table 1, along with considerations on side reactions and best practices.

Common Adsorbates	Common Adsorbents	Use Cases	Safety Considerations[5]
H_2[1,2]	Ni, Rh, Re, V, Co, Pd, Pt, Fe, Cu, Ag, Au	Used to study metal reduction	Ag, Cu, and Au release significant heat upon reduction, use slower heating rates
CO[1,2]	Ni, Pd, Pt, Fe	Milder reducing agent to assess reducibility and uptake, also an FTIR spectroscopic label	Ni, Fe, Ru, and Co can form toxic, volatile carbonyl complexes
CO_2[1-3]	V, Y, Mg, Fe, Al_2O_3, ZrO_2, TiO_2	Used to study basic sites	Samples must be pre-oxidized, some metallic species (Mg, Al, Ti, Zr) may react with CO_2
O_2[1,4]	Catalysts with deposited carbon (coke), Ag, Au	Used to study coke content by oxidizing C to CO_2; also used with metals to identify oxidation species	Ru, Re, and V can form toxic, volatile oxides
NH_3[1,2]	Al_2O_3, SiO_2, ZrO_2, TiO_2, zeolites	Used to study total acid sites, can reach into small pores	Samples containing Ag must be fully reduced to prevent Ag_3N formation
Pyridine[2]	Al_2O_3, SiO_2, ZrO_2, TiO_2, zeolites	Used to study acid sites in more detail (determines Lewis vs. Bronsted) when paired with IR, bulkier than NH_3	Ensure catalysts are free of trace oxidizing agents and strong acids

Table 1: Commonly used adsorbates and adsorbents, their applications, and potential safety concerns

The adsorbate–metal interaction can be visualized using potential energy diagrams, shown in Figure 1. The initial physisorption step involves a small activation barrier (ΔE_1) and a minor energy release (ΔH_1). Transitioning to a chemisorbed state requires overcoming a second activation barrier, which may be small (ΔE_2) or large (ΔE_3). The heat of chemisorption (ΔH_2) is independent of this barrier.

If the activation barrier is high, the process is classified as **activated chemisorption**, which proceeds slowly and may require higher temperatures or longer adsorption times for full surface coverage. For example, hydrogen chemisorption on supported cobalt metal is has a high activation energy. As shown in Figure 2:

- ✓ Fig. 2a: Room temperature H_2 adsorption yielded minimal H_2 desorption, and;
- ✓ Fig. 2b: Elevated temperature H_2 adsorption, followed by cooling in hydrogen, resulted in full site coverage and a significant TPD signal.

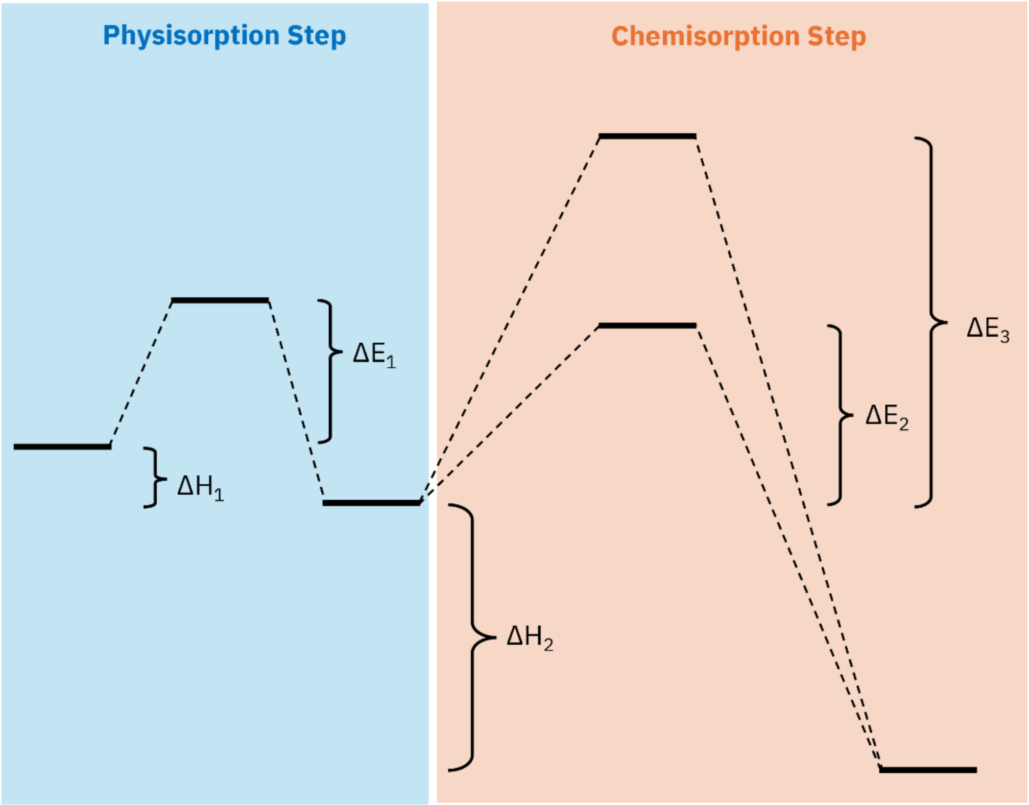


Figure 1: Potential energy diagram for the physisorption (blue) then chemisorption (orange) of an adsorbate

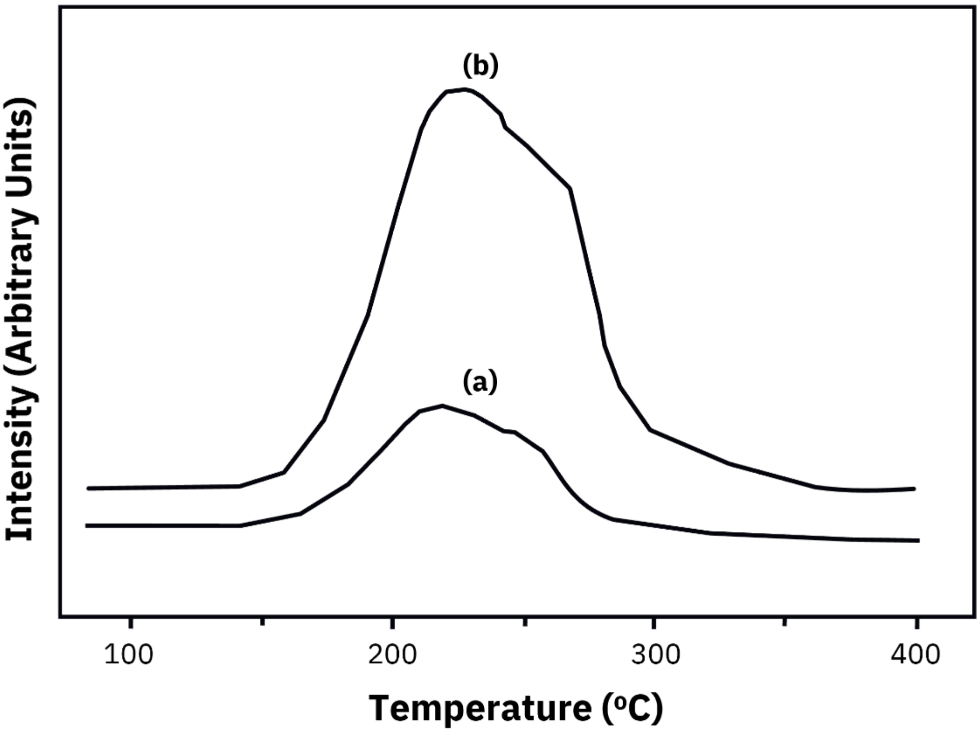


Figure 2: Temperature programmed desorption (TPD) patterns of hydrogen chemisorbed on Co/Al_2O_3 at room temperature (a) and 100 °C (b)

2. Choice of Adsorption Conditions

Adsorption conditions must balance complete surface coverage with minimal side reactions. The typical parameters which can be controlled are temperature, time, and concentration.

- ✓ Temperature: Sufficiently high to ensure adsorption, but below levels that promote undesirable reactions (e.g., CO disproportionation to CO_2 and carbon)
- ✓ Time: Long enough to allow for equilibrium
- ✓ Concentration: Excess adsorbate gas compared to surface sites

It is recommended to start chemisorption at temperatures between 100 – 200 °C for 30 – 90 minutes and then flush with inert gas at lower temperatures to remove weakly held species. TPD can then be utilized to observe the degree of chemisorption, and the parameters can be adjusted accordingly.

However, care must be taken to avoid spillover, where adsorbates migrate from metal crystallites to the support (see Figure 3). This is a kinetically slow process that can distort TPD data if adsorption times or temperatures are too high.

3. Adsorbate Stoichiometry

Interpreting TPD results requires knowledge of the adsorbate-metal stoichiometry (i.e. how many adsorbate molecules are chemisorbed for every surface metal site). While direct measurement is not possible in simple TPD experiments, stoichiometry can be estimated by:

- ✓ Comparing chemisorption surface area to BET surface area
- ✓ Infrared (IR) spectroscopy
- ✓ Crystallite size measurements via TEM or XRD

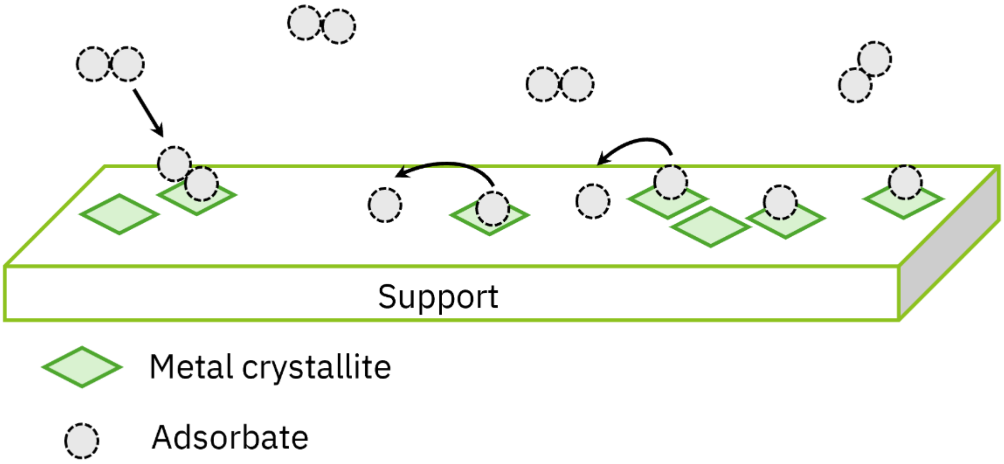


Figure 3: Schematic representation of a dissociative chemisorption process over a supported metal catalyst, including spillover onto the support

<u>General Rules:</u>

- ✓ H_2, O_2: dissociative adsorption, as shown in Figure 3 (stoichiometry = 0.5).
- ✓ CO: Stoichiometry varies widely (0.5 to 2), depending on metal and crystallite size.

4. Advanced Stoichiometry Determination Using the AMI 300IR

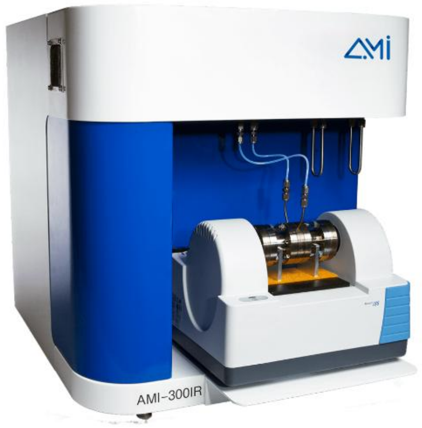
For IR-active adsorbates (such as CO, NO, and selected hydrocarbons), the **AMI 300IR** provides a superior method for stoichiometry determination. By integrating in-situ IR spectroscopy with TPD and chemisorption analysis, the **AMI 300IR** enables:

- ✓ <u>Quantitative analysis</u>: Peak areas correlate directly to adsorbed species concentrations
- ✓ <u>Speciation</u>: Differentiation between linear, bridged, or multidentate adsorption geometries
- ✓ <u>Dynamic monitoring</u>: Real-time observation of adsorbate behavior during adsorption/desorption cycles

During CO adsorption, the **AMI 300IR** can distinguish linear CO on atop sites from bridged CO species, demonstrated in Figure 5. This capability enhances stoichiometric precision and provides deeper insight into adsorption mechanisms. The **AMI 300IR** is particularly valuable for:

- ✓ Validating adsorption models
- ✓ Confirming stoichiometries in complex or supported catalysts
- ✓ Enhancing the accuracy of TPD interpretations

- ✓ TPD paired with real-time catalyst surface analysis using built-in FTIR spectrometer
- ✓ Equipped with proprietary catalyst holder and several heated IR transmission cells



AMI 300IR

*Figure 4: Highlighted features of **AMI 300IR***

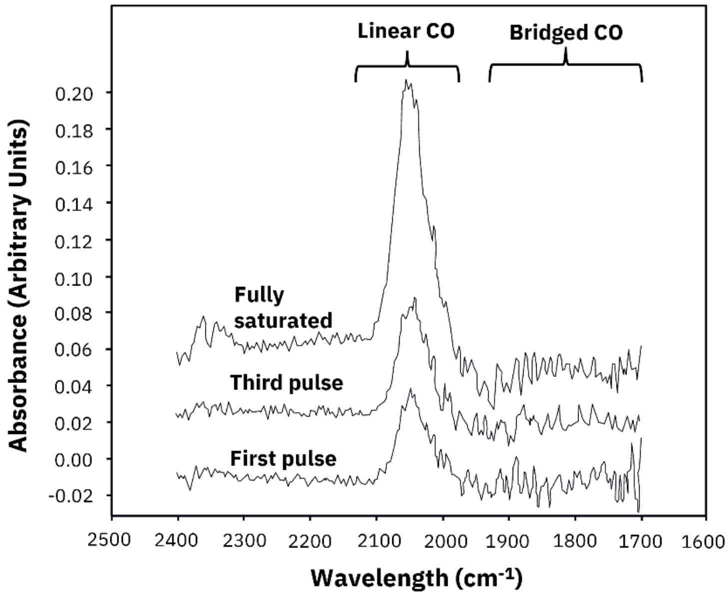


*Figure 5: Pulse chemisorption of CO on Pt catalyst measured by in situ IR with the **AMI 300IR***

5. References

(1) Lv, W.; Zhang, R.; Sun, F.; Guo, Y.; Jiao, W.; Wang, H.; Hou, X.; Qin, R.; Pan, W.; Lv, B. Application of physical adsorption and chemisorption techniques in heterogeneous catalytic research: A review. *Kinet. Catal.* **2025**, *66*, 129-154.

(2) *Calorimetry and Thermal Methods in*

Catalysis; Auroux, A. Ed.; Springer Series in Materials Science; Springer Berlin, 2013.
(3) León, M.; Díaz, E.; Vega, A.; Ordóñez, S. A kinetic study of CO_2 desorption from basic materials: Correlation with adsorption properties. *Chem. Eng. J.* **2011**, *175*, 341-348.
(4) Waterhouse, G. I. N.; Bowmaker, G. A.; Metson, J. B. Oxygen chemisorption on an electrolytic silver catalyst: A combined TPD and Raman spectroscopic study. *Appl. Surf. Sci.* **2003**, *214*, 36-51.
(5) *Bretherick's Handbook of Reactive Chemical Hazards*; 7th ed.; Urben, P. G., Pitt, M. J., Eds.; Elsevier, 2007.