

Optimizing Adsorbate Selection, Adsorption Conditions, and

Stoichiometry in Chemisorption

Choice of Adsorbate

The choice of adsorbate is critical in temperature-programmed desorption (TPD) experiments. The selected gas should chemisorb selectively on the metal, avoiding sorption on the support or other catalytic components. Ideally, the adsorbate should form a stable monolayer and avoid irreversible reactions with either the metal or the support.

Metal	Adsorbate(s)	Comments
Fe	H2, CO	CO may form various carbonyls or carbides
Co	H₂, CO	Activated chemisorption; temperatures above 100°C are necessary for full coverage
Ni	H2	Rapid equilibration; CO forms Ni(CO)4
Cu	N2O, Cl2	Involve surface reactions
Ru	H2	CO forms Ru(CO)5; forms volatile oxide
Rh	H2, CO	H ₂ and CO stoichiometries vary with crystallite size
Pd	СО	H₂ can dissolve into the metal and form the bulk hydride
Re	H2, O2	H₂ uptake can be low; forms volatile oxide
Os	H2, O2	H₂ uptake can be low; forms volatile oxide
Ir	H2, CO	H ₂ and CO stoichiometries vary with crystallite size
Pt	H2, O2, CO	Activated H₂ chemisorption; CO stoichiometry can vary; CO can disproportionate on the metal at high temperatures
Mo, W	O2	Low temperatures required
Ag, Au	O2	High temperatures (420–570 K) required

Table 1: suitable adsorbates

Example: CO can react with nickel to form volatile—and hazardous—nickel carbonyl (Ni(CO)₄), making it unsuitable for certain Ni catalyst systems.



The adsorbate-metal interaction can be visualized using potential energy diagrams (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.



Figure 1. Potential energy diagram for the physisiorption, followed by chemisorption of an adsorbate.

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.

Case Example:

Hydrogen chemisorption on supported cobalt metal is activated. As shown in Figure 2:

- **Curve A**: Room temperature adsorption yielded minimal desorption.
- **Curve B**: Elevated temperature adsorption, followed by cooling in hydrogen, resulted in full site coverage and a significant TPD signal.

Because theoretical guidance is limited, adsorbate selection typically relies on literature precedent and practical experience. *Table 1* provides a summary of suitable adsorbates for common catalytic metals.





Figure 2. TPD patterns of hydrogen chemisorbed on alumina-supported cobalt. A: adsorption at room temperature; B: adsorption at 100° C $\,$

Choice of

Adsorption Conditions

Adsorption conditions must balance complete surface coverage with minimal side reactions.

Key Considerations:

- **Temperature**: Sufficiently high to ensure adsorption, but below levels that promote undesirable reactions (e.g., CO disproportionation to CO₂ and carbon).
- **Time**: Long enough to allow for equilibrium.

Spillover Warning:

Spillover, where adsorbates migrate from metal crystallites to the support (see Figure 3), is a kinetically slow process that can distort TPD data if adsorption times or temperatures are too high.

Recommended Starting Conditions:

- **Temperature**: 100–200°C
- **Time**: 30–90 minutes
- Post-adsorption flush: At low temperature to remove weakly held species.



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



Adsorbate Stoichiometry

Interpreting TPD results requires knowledge of the adsorbate-metal stoichiometry. 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.

General Rules:

- **Hydrogen & Oxygen**: Typically dissociative adsorption (stoichiometry = 0.5).
- **CO**: Stoichiometry varies widely (0.5 to 2), depending on metal and crystallite size.

In some cases (e.g., very small Rh or Ir crystallites), H₂/M stoichiometries of 1 have been reported, but these are rare.

When precise stoichiometry cannot be determined, CO uptake can still be used as a relative basis for comparing catalysts.

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:

- Quantitative analysis: Peak areas correlate directly to adsorbed species concentrations.
- **Speciation**: Differentiation between linear, bridged, or multidentate adsorption geometries.
- **Dynamic monitoring**: Real-time observation of adsorbate behavior during



adsorption/desorption cycles.

Example:

During CO adsorption, the AMI-300IR can distinguish linear CO on atop sites from bridged CO species. 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.

References

- 1. "Chemisorption and Catalysis on Supported Metals", AMI Notes.
- 2. "Temperature-Programmed Desorption of Adsorbed Species from Catalyst Surfaces", *AMI Notes*
- 3. "Measuring Acidity in Zeolites Using TPD", AMI Notes
- 4. "Surface Area Measurement from Temperature-Programmed Desorption Data", *AMI Notes*