Chemisorption and AMI

1. Background

Chemisorption—the formation of chemical bonds between gas-phase molecules and surface atoms—is the foundational step in heterogeneous catalysis. On supported metal catalysts, this process occurs on small metal crystallites, nanoparticles, and single atoms anchored to high surface area oxide materials. These chemisorbed species react with adjacent adsorbed molecules or gas-phase reactants to generate catalytic products.

Figure 1 shows a schematic diagram of the chemisorption step in a typical CO_2 hydrogenation reaction with Pt/TiO_2 catalyst.[1,2] Pt surface sites act as anchors for CO_2 chemisorption until the species react with H_2 and desorb.
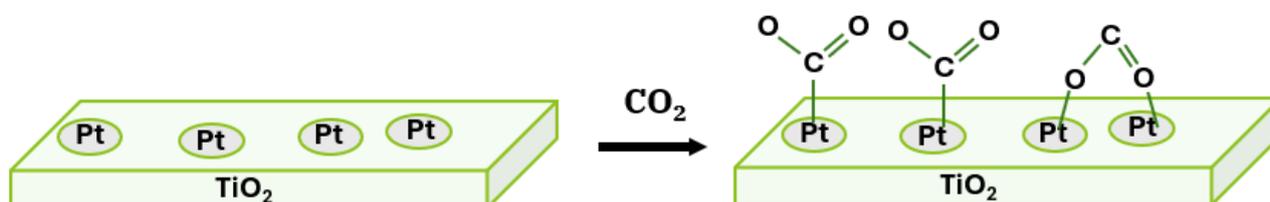

Figure 1: Scheme depicting gas-phase CO_2 chemisorption onto solid Pt/TiO_2 surface

The chemisorption behavior of a catalyst directly impacts both the **reaction rate** and **selectivity** toward desired products. Understanding and quantifying chemisorption is thus essential for both catalyst design and performance optimization.

Optimal catalytic performance requires a balance between the **strength** and **quantity** of chemisorbed species:

✓ **Binding Strength**:
- o Too strong — hinders product formation as molecules adhere too tightly.
- o Too weak — reactants desorb before reacting.
- o Moderate — yields the highest catalytic activity, illustrated by the classic **volcano curve** in Figure 2 for reactions like ammonia synthesis.
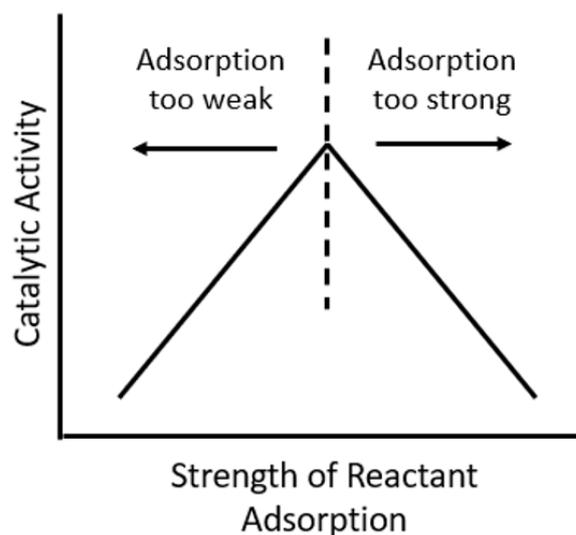

Figure 2: Representative volcano curve showing the relationship between catalytic activity and reactant adsorption strength

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- ✓ **Quantity of Sites**:
  - o The number of chemisorbed species correlates to the number of surface sites available, which can be used to quantify surface chemical properties of the catalyst

2. Measuring Chemisorption

Quantitative assessment of chemisorption requires techniques that can evaluate both the **quantity** and **strength** of adsorption sites, while also describing qualitative **chemical properties**. The broad range of chemisorption methods is shown in Table 1.

Method	Measurement Focus
Static/Volumetric Chemisorption	Equilibrium uptake of gas molecules (closed system)
Pulse Chemisorption	Uptake of calibrated gas pulses
Temperature-programmed esorption (TPD)	Desorption behavior upon heating — provides both site count and adsorption strength
Temperature-programmed reduction (TPR)	Hydrogen consumption under H_2/inert gas flow – provides metal dispersion, metal-support interactions, metal oxidation states
Temperature-programmed oxidation (TPO)	Desorption behavior of oxidized surface species upon heating – quantifies carbon deposits, oxidation states
Temperature-programmed surface reaction (TPSR)	Probe molecules react on surface, product desorption detected upon heating – describes active sites, reaction mechanisms, and kinetics
Steady-state isotopic transient kinetic analysis (SSITKA)	Steady-state conditions achieved with unlabeled reactant gas, then switched to isotopically labeled gas. Desorbed isotopically labeled products detected by mass spectrometry – describes kinetics and reaction intermediates

3. Principles and Procedure

A standard chemisorption experiment involves:

- ✓ **Sample Preparation**:
  - o Catalyst treated to yield clean surface sites.
    - o Introduction of the chemisorbing gas (typically at ambient temperature).
- ✓ **Gas Switching & Flushing**:
  - o Replace chemisorbing gas with inert gas.

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✓ **Controlled Heating**:
- o Linear temperature ramp.
- o Desorption of chemisorbed species occurs at characteristic temperatures.

✓ **Detection**:
- o Quantify desorbed species using calibrated detectors.
- o Calculate site quantity and evaluate adsorption strength.

Example:

H₂ chemisorption was used by Li et al. on Ni/SiO_2 catalysts for ammonia decomposition. TPR and TPD experiments revealed both the number of available Ni sites and the oxidation state of surface Ni species.[3]

4. AMI Solutions: Automated Chemisorption Analysis

AMI Chemisorption Analyzers automate the entire process:
- ✓ Precise flow control and gas switching.
- ✓ Programmable temperature ramps.
- ✓ Quantitative detection and data analysis.
- ✓ Fully customizable experiment parameters via user-friendly software.
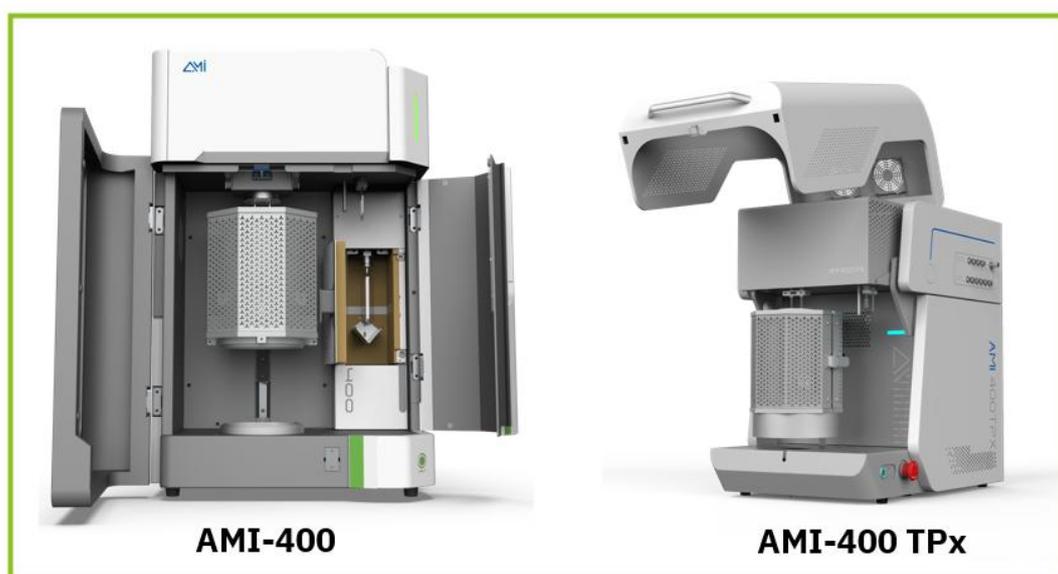
The flagship **AMI-300** platform delivers reproducible, operator-independent measurements, and specialized models are available for advanced chemisorption experiments, empowering researchers to optimize catalysts and advance reaction engineering. The **AMI-300 IR** enables real-time catalyst analysis with Fourier transform infrared spectroscopy (FTIR). The **AMI-300 HP** is engineered for industrially relevant high-pressure conditions up to 100 bar, and the **AMI-300 SSITKA** is integrated with steady-state isotopic transient kinetic analysis capabilities, as well as traditional chemisorption experiments (TPD, TPO/R, TPSR).

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AMI-300 Series	
Unique features	Fully automated, highly customizable
Functions	Pulse chemisorption, temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD), temperature-programmed surface reaction (TPSR), flow BET surface area analysis, steady-state isotopic transient kinetic analysis (SSITKA)
Sample loading	0.1-5g
Temperature range	RT – 1200 ^{o}C with rapid cooling
Ramp rate	0.1-50 ^{o}C/min
Operating pressure	Ambient – 100 bar (**AMI-300 HP**)
Thermocouples	Bed thermocouple, furnace thermocouple
Gas flow rates	2-100 sccm
Reactor types	Quartz U-tubes (6mm, 8mm, 10mm)
Detector	TCD (sensitive tungsten-rhenium filament)
Mass flow controllers	3 (4 optional)
Optional add-ons	FTIR (**AMI-300 IR**), vapor generator, mass spectrometer, FID, methanator reactor, harsh chemistry, SSITKA (**AMI-300 SSITKA**), custom sample holders

The **AMI-400** platform expands on the previous model with improved precision and industry-leading safety features. In addition, the compact **AMI-400 TPx** offers the same automation capabilities with outstanding economic efficiency and space-saving design.

AMI-400   AMI-400 TPx

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AMI-400 Series	
Unique features	Fully automated smart gas interface; integrated safety features including exhaust fan, alarm system, and self-locking door; high precision thermocouples and MFCs
Experiments	Pulse chemisorption, temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD), temperature-programmed surface reaction (TPSR), flow BET surface area analysis,
Sample loading	0.1-5g
Temperature range	RT – 1200 ^{o}C, -130 ^{o}C – 1100 ^{o}C (optional)
Ramp rate	0.1-50 ^{o}C/min
Operating pressure	Ambient
Thermocouples	Bed thermocouple, furnace thermocouple, overtemperature protection thermocouple
Gas flow rates	0-100 sccm (+/- 1% accuracy)
Reactor types	Quartz U-tubes (6mm, 8mm, 10mm)
Detector	TCD (sensitive tungsten-rhenium filament)
Mass flow controllers	1 (2-4 optional)
Optional add-ons	Vapor generator, mass spectrometer, FID, FTIR, methanator reactor

5. Conclusions

Chemisorption is an integral reaction step in heterogeneous catalysis, and it can be employed as a powerful tool for detailed catalyst analysis. Through advanced, automated tools like the AMI Chemisorption Series, scientists can describe the elemental, surface-level interactions driving catalyst performance and use that understanding to implement efficient catalyst design.

6. References

(1) Hu, X.; Xu, D.; Jiang, J. Strong metal-support interaction between Pt and TiO_2 over high-temperature CO_2 hydrogenation. *Angew. Chem. Int. Ed.* **2025**, *64*, e202419103.
(2) Su, G.-X.; Wu, M.-Y.; Wang, W.-W.; Jia, C.-J. Pt nanoparticles supported on hydroxylated TiO_2 as catalysts for the reverse water gas shift reaction. *ACS Appl. Nano Mater.* **2025**, *8*, 9164-6176.
(3) Li, S.; Liu, X.; Guo, Y.; Wang, Y. Highly active and stable $Ni@SiO_2$ catalyst for ammonia decomposition. *Fuel*, **2024**, *368*, 131543.