

## 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<sub>2</sub> hydrogenation reaction with Pt/TiO<sub>2</sub> catalyst.<sup>(1,2)</sup> Pt surface sites act as anchors for CO<sub>2</sub> chemisorption until the species react with H<sub>2</sub> and desorb.

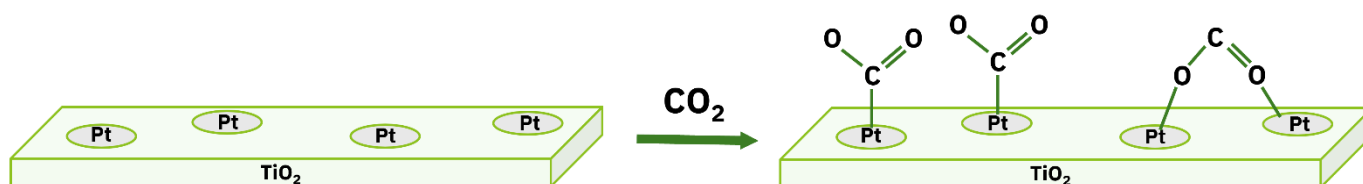


Figure 1: Scheme depicting gas-phase CO<sub>2</sub> chemisorption onto solid Pt/TiO<sub>2</sub> surface

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:

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

#### ✓ Quantity of Sites:

- 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.

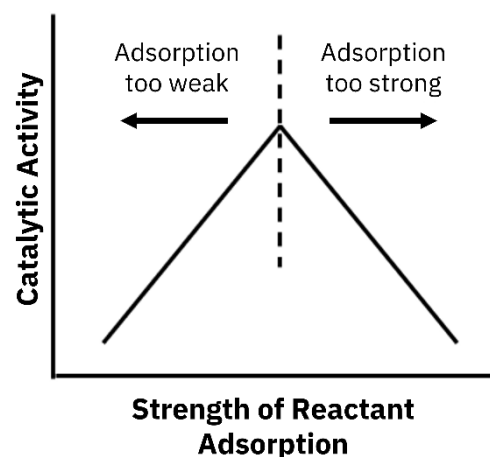


Figure 2: Representative volcano curve showing the relationship between catalytic activity and reactant adsorption strength

## 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 desorption (TPD)	Desorption behavior upon heating – provides both site count and adsorption strength
Temperature-programmed reduction (TPR)	Hydrogen consumption under H <sub>2</sub> /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

Table 1: Comparison between various chemisorption methods

## 3. Experimental Methods

A standard chemisorption experiment involves:

- ✓ **Sample Preparation:**
  - Catalyst treated to yield clean surface sites.
  - Introduction of the chemisorbing gas (typically at ambient temperature).
- ✓ **Gas Switching & Flushing:**
  - Replace chemisorbing gas with inert gas.
- ✓ **Controlled Heating:**
  - Linear temperature ramp.
  - Desorption of chemisorbed species occurs at characteristic temperatures.
- ✓ **Detection:**
  - Quantify desorbed species using calibrated detectors.
  - Calculate site quantity and evaluate adsorption strength.

Example:

H<sub>2</sub> chemisorption was used by Li et al. on Ni/SiO<sub>2</sub> catalysts for ammonia decomposition. TPR and TPD experiments revealed both the number of available Ni sites and the oxidation state of surface Ni species.<sup>(3)</sup>

## 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.

<b>AMI-300 Series</b>	
<b>Unique features</b>	Fully automated, highly customizable
<b>Functions</b>	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)
<b>Sample loading</b>	0.1-5g
<b>Temperature range</b>	RT – 1200 °C with rapid cooling
<b>Ramp rate</b>	0.1-50 °C/min
<b>Operating pressure</b>	Ambient – 100 bar (AMI-300 HP)
<b>Thermocouples</b>	Bed thermocouple, furnace thermocouple
<b>Gas flow rates</b>	2-100 sccm
<b>Reactor types</b>	Quartz U-tubes (6mm, 8mm, 10mm)
<b>Detector</b>	TCD (sensitive tungsten-rhenium filament)
<b>Mass flow controllers</b>	3 (4 optional)
<b>Optional add-ons</b>	FTIR (AMI-300 IR), vapor generator, mass spectrometer, FID, methanator reactor, harsh chemistry, SSITKA (AMI-300 SSITKA), custom sample holders

*Table 2: Specifications and capabilities of the AMI 300 series of chemisorption analyzers*

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).



Figure 3: Complete **AMI 300** line of chemisorption analyzers

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

Table 3: Specifications and capabilities of the **AMI 400** series of chemisorption analyzers

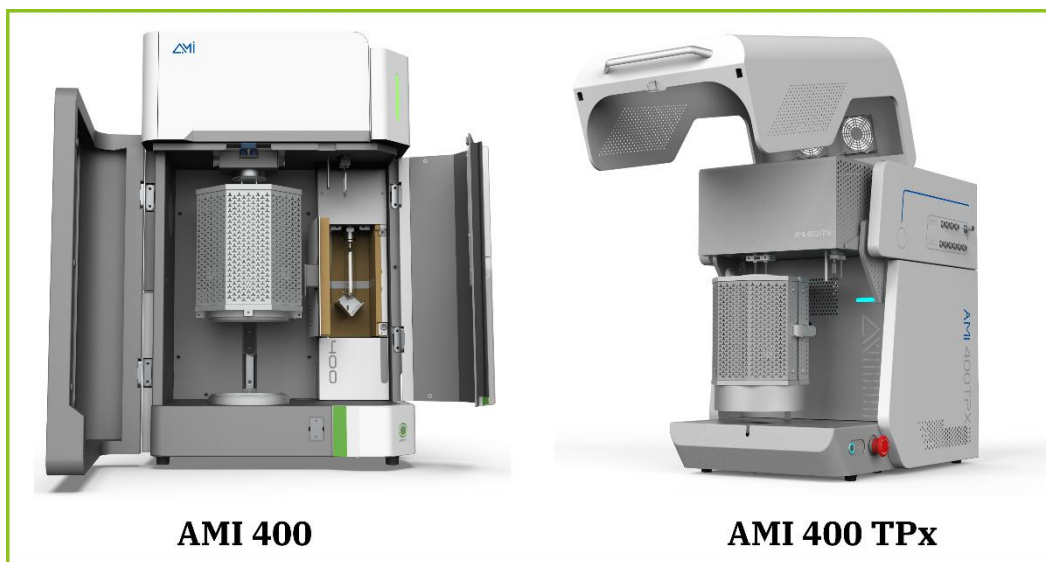


Figure 4: Complete **AMI 400** line of chemisorption analyzers

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.

## 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<sub>2</sub> over high-temperature CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> catalyst for ammonia decomposition. *Fuel*, **2024**, *368*, 131543.