Supported Metal Catalyst Characterization with User-Friendly Chemisorption Techniques

1. Background

Chemisorption, the chemical bonding between gas-phase molecules and surface atoms, is the first step in a catalytic reaction on many heterogeneous supported metal catalysts. Chemisorption takes place on small metal crystallites, nanoparticles, or single atoms, which are typically anchored to a high surface area oxide material. These chemisorbed molecules then react with neighboring surface-adsorbed species or with gas-phase molecules to produce reaction products. Characterization of this chemisorption bond reveals intrinsic chemical properties of the supported metal catalyst which directly relate to the rate and product selectivity of the catalytic reaction.

This relationship between chemisorption and catalytic activity is shown in Figure 1. The theoretical volcano curve shown in Figure 1 (black line) demonstrates the optimum strength of the bond between the chemisorbing species and the surface. Too strong chemisorption can slow down the reaction rate because the molecules are reluctant to leave the surface, and too weak chemisorption can result in desorption of molecules before they have a chance to react. Moderate-strength chemisorption usually results in maximum catalytic activity, as reported by Mehta et al, approximately represented by the dots in Fig. 1.[1]

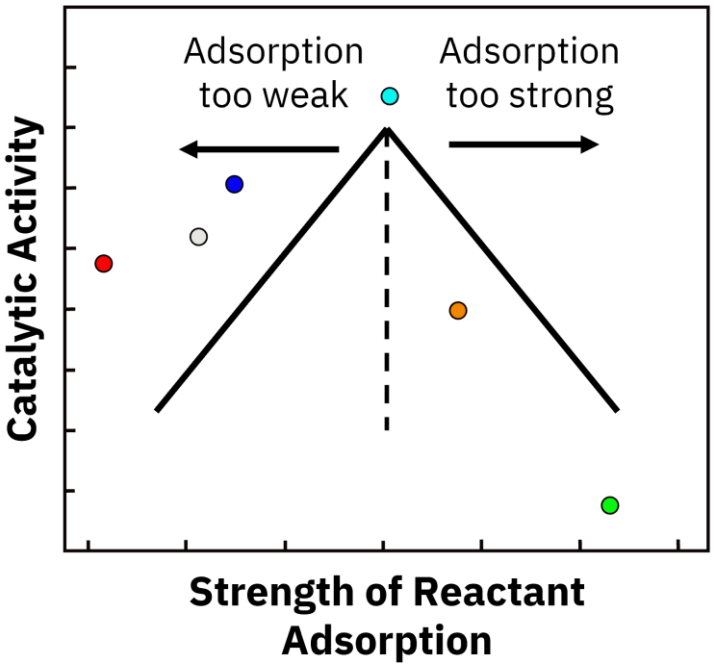

Figure 1: Model volcano plot showing the relationship between catalytic activity and reactant adsorption strength, with colored dots representing approximate data points for various chemical adsorbates reported by Mehta et al.[1]

Strength of chemisorption is only one of the parameters affecting catalytic activity. The number of chemisorbed molecules is also important. It follows that more chemisorbed species result in more reaction product molecules. The number of molecules forming chemisorption bonds with the catalyst surface is related to the number of surface atoms available for bonding. Maximizing the number of these surface sites for chemisorption is a top priority in supported metal catalyst design.

How can we measure these important parameters? We need a technique which can count the number of chemisorption sites and tell us something about how tightly these sites hold onto chemisorbing molecules. A chemisorbing molecule which binds with a known stoichiometry to a surface site can act as a probe of the surface. For supported metal catalysts, this "selective chemisorption" of molecules on metal surface sites can be monitored by:

- ✓ Measuring the equilibrium uptake of gas phase molecules by the surface in a closed system (termed "static" or "volumetric" chemisorption)
- ✓ Detecting how many calibrated pulses of chemisorbing molecules are taken up by the surface (pulse chemisorption)
- ✓ Analyzing chemisorbed molecules as they desorb from the surface upon heating (temperature-programmed desorption)

The first two techniques are performed under isothermal (most often ambient temperature) conditions and hence can offer little information about adsorption strength. The third technique, one in a family of temperature-programmed techniques for catalyst characterization, can provide information about both **strength** and **quantity** of chemisorbing sites.

2. Temperature-Programmed Desorption (TPD)

Quantitative analysis of model surfaces using temperature-programmed desorption (TPD) techniques was developed in the early 1960's, and numerous excellent review articles have since been published.[2,3] While the technique provides quantitative information about the number of metal surface sites, a number of complications often causes information about the strength of adsorption to be limited to a more qualitative treatment for supported metal catalysts.

In a typical TPD experiment, a powder sample of a supported metal is placed in a glass or stainless steel reactor. The reactor is then enclosed in a furnace and is connected to gas delivery lines. The sample is subjected to a pretreatment which generates reduced metal surface sites with clean, bare surfaces. The gas flow is then switched to permit the chosen chemisorbing gas to flow over the catalyst, usually at ambient temperature. After an appropriate time, the flow is again switched to an inert gas and the void volume inside the reactor is flushed. Under inert gas flow, the sample temperature is raised in a controlled manner. This heating provides energy to the chemisorbed species, and when these species gain sufficient energy, they desorb from the surface into the stream of inert gas. This stream is swept

into a detector which has been calibrated to quantify the number of probe gas molecules in the stream. This number, together with the known chemisorption stoichiometry, gives the number of surface sites on the supported metal catalyst. The detector signal is also monitored as a function of the sample temperature, which provides a measure of the strength of adsorption on the surface. Molecules that desorb at low temperatures are only weakly held, while high-temperature desorption indicates a stronger chemisorption interaction. Hence, the TPD experiment describes not only the number and strength of chemisorption sites, but it may also describe the heterogeneous chemistry of the surface sites.

This process is shown schematically in Figure 2 for H_2 chemisorption and TPD on a Ni/SiO_2 catalyst where H_2: Ni = 1:2 for dissociative hydrogen chemisorption. It is easy to see from this brief description that a TPD experiment involves several critical measurements. Gas flow rates must be controlled, and gas switching must be possible. A linear change in temperature with respect to time is required, and an on-stream gas detector should be employed. Typically, highly sensitive thermal conductivity detectors (TCD) are used in tandem with chemisorption

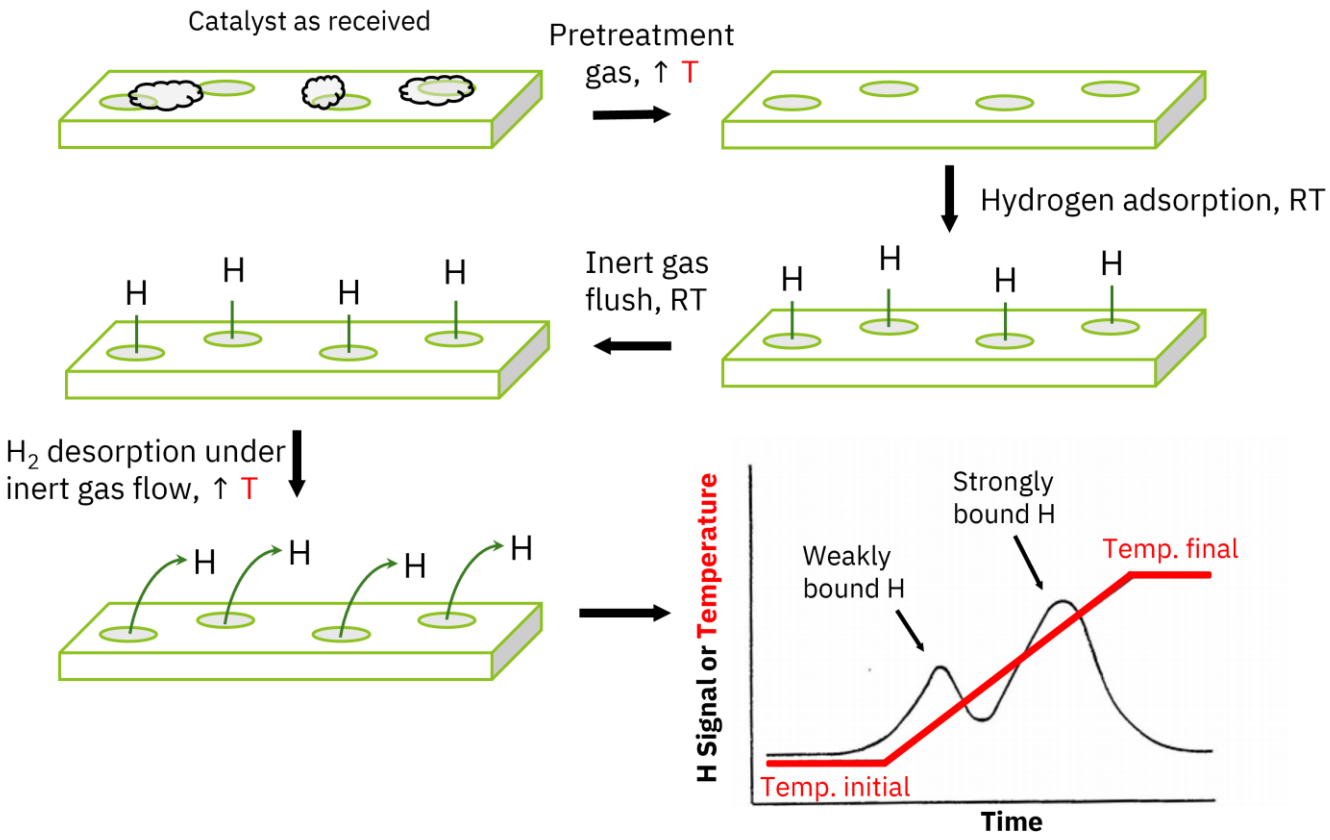

Figure 2: Schematic step-by-step process of H_2 temperature-programmed desorption (TPD) experiment on a Ni/SiO_2 catalyst, with Ni surface sites depicted as green ovals

*Figure 3: Feature comparison of **AMI 300** Series (left) and **AMI 400** Series (right) Chemisorption Analyzers for catalyst characterization*

4. Conclusions

Chemisorption techniques are invaluable for solid catalyst characterization, offering detailed chemical information on the quantity and relative strength of chemical bonds between a gas reactant and surface catalytic sites. With proper instrumentation, these chemisorption techniques can be performed accurately and independently. The **AMI 300** and **AMI 400** offer fully automated operation of a TPD experiment from beginning to end. **AMI Chemisorption Analyzers** perform this task according to parameters and conditions selected by an operator from a menu of instructions in the **AMI software**. After this initial setup procedure, the experiment proceeds in an operator-independent mode while collecting data from a sensitive TCD detector. The unique features of the **AMI 300** and **AMI 400** are highlighted in Figure 3.

5. References

(1) Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. Catalysis enabled by plasma activation of strong chemical bonds: A review. *ACS Energy Lett.* **2019**, *4*, 1115-1133.
(2) Bhatia, S.; Beltramini, J.; Do, D. D. Temperature programmed analysis and its applications in catalytic systems. *Catal. Today*, **1990**, *7*, 309-438.
(3) Herold, F.; Gläsel, J.; Etzold, B. J. M.; Rønning, M. Can temperature-programmed techniques provide the gold standard for carbon surface characterization? *Chem. Mater.* **2022**, *34*, 8490-8516