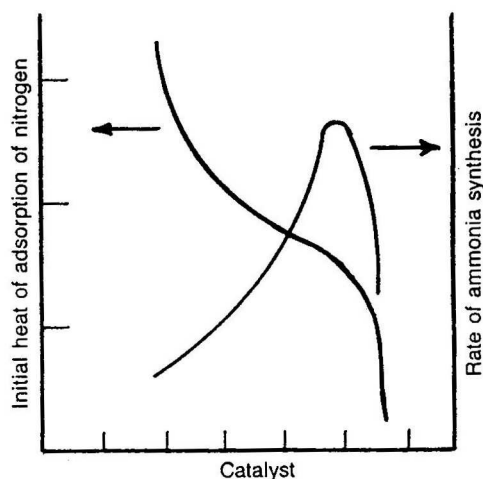
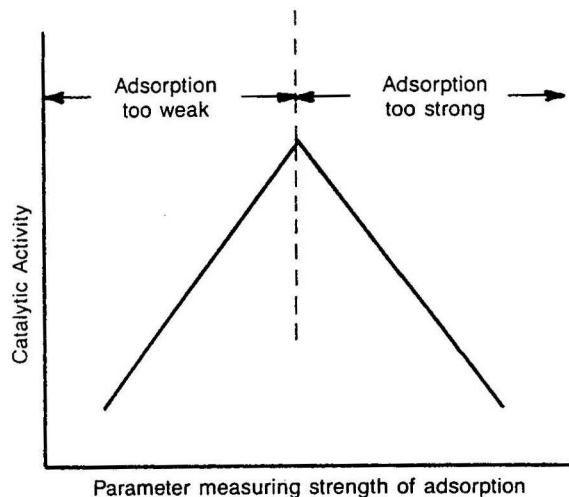




### CHEMISORPTION AND CATALYSIS ON SUPPORTED METALS

Chemisorption, the chemical bonding between gas-phase molecules and surface atoms, is the first and most important step in a catalytic reaction. On supported metal catalysts, chemisorption takes place on small metal crystallites, which are typically anchored to a high surface area oxide material. These chemisorbed molecules then react with other adsorbed species or with gas-phase molecules to produce reaction products. Why is chemisorption so important? The rate of the catalytic reaction as well as its selectivity to desired products is directly related to the chemisorption properties of the supported metal catalyst.

This relationship between chemisorption and catalytic activity can be seen from the figures below. The volcano curve shown on the left demonstrates that there is an 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 means maximum catalytic activity, as shown below for the ammonia synthesis reaction.



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 means 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 good 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 our probe of the surface. For supported metal catalysts, this "selective chemisorption" of molecules on metal surface sites can be monitored by:

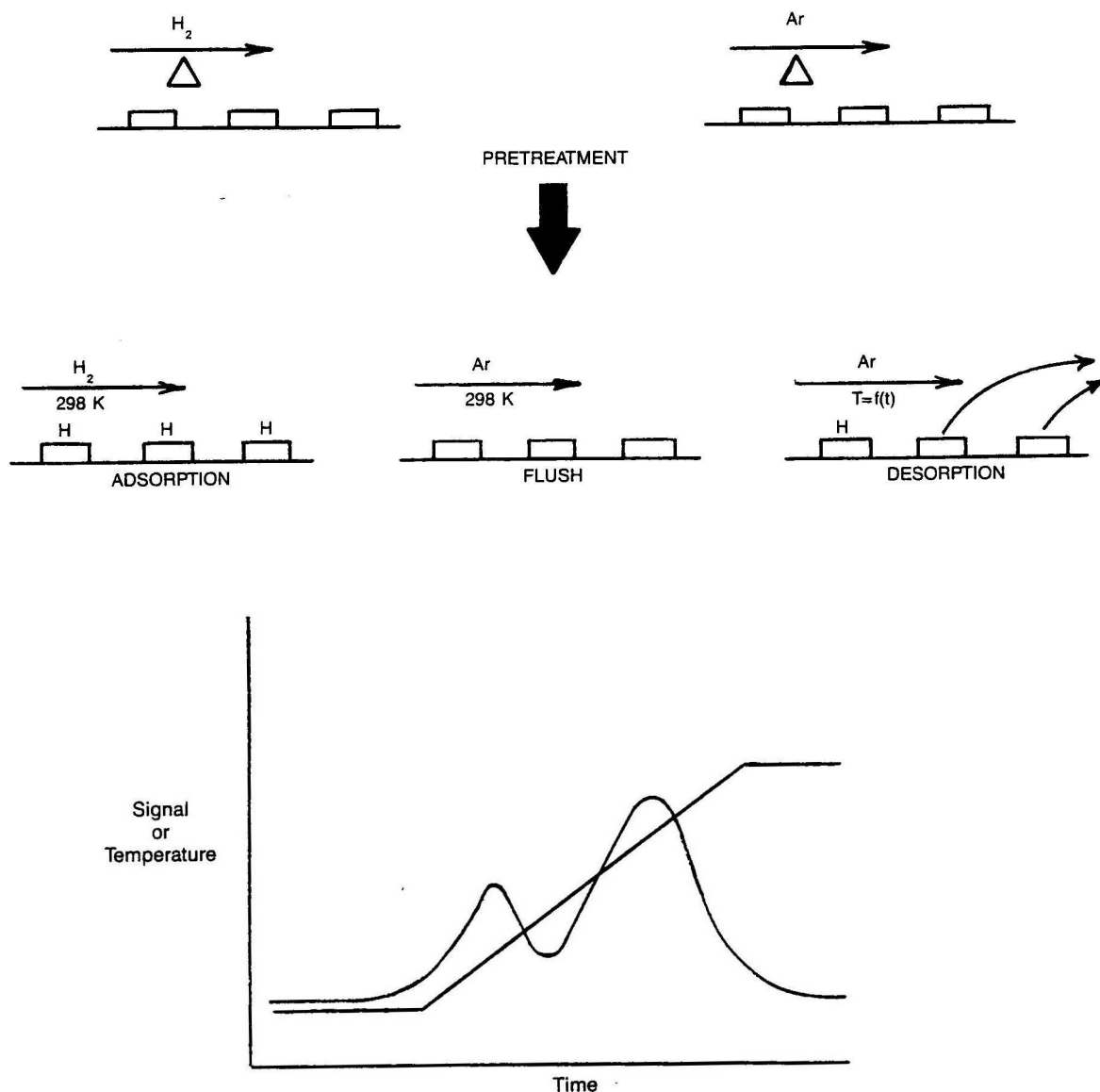
- measuring the equilibrium uptake of gas phase molecules by the surface in a closed system (termed "static" or "volumetric" chemisorption)
- detecting how many calibrated pulses of chemisorbing molecules are taken up by the surface (pulse chemisorption)
- counting chemisorbed molecules as they desorb 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 of the parameters of importance: strength and number of chemisorbing sites.

Quantitative analysis of model surfaces using temperature-programmed desorption (TPD) techniques was developed in the early 1960's and a number of excellent review articles have since been published. 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 provides reduced metal crystallites 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 gas molecules in the stream. This number, together with the known chemisorption stoichiometry, yields the desired quantity---the number of surface sites on the supported metal catalyst. The detector signal monitored as a function of the temperature of the supported metal catalyst provides a measure of the strength of adsorption on the surface: molecules, which desorb at low temperatures are only weakly held, while high-temperature desorption signifies a stronger chemisorption interaction. Hence, the TPD experiment describes not only the number and strength of chemisorption sites, but it may also describe the heterogeneity of the surface sites.

This process is shown schematically below for H<sub>2</sub> chemisorption and TPD on a Ni/SiO<sub>2</sub> catalyst where H<sub>2</sub>:Ni = 1:2 for dissociative hydrogen chemisorption.



It is easy to see from this brief description that a TPD experiment involves a number of 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 a detector which is capable of quantifying the desorbing gas must be employed. The Altamira AMI-1 Catalyst Characterization System can accomplish these tasks and much more. The AMI-1 offers fully automated operation of a TPD experiment from beginning to end. It performs this task according to parameters and conditions selected by an operator from a menu of instructions in the AMI-1 software. After this

initial setup procedure, the experiment proceeds in an operator-independent mode.

September's issue of Altamira Notes describes in more detail how the quantitative calculations are made for counting surface sites using temperature-programmed desorption.