Conditions and Parameters for TPD Experiments:
Supported Metal Catalysis

Previous _Altamira Notes_ have discussed the use of temperature programmed desorption (TPD) for characterizing the surfaces of metallic catalysts[1,2] and acid catalysts[3]. In this note, we discuss the selection of some critical experimental parameters necessary for conducting a successful TPD experiment on supported metal catalysts.

Choice of Adsorbate

The choice of adsorbate is critical in a TPD experiment. The selected gas should chemisorb selectively on the metal without sorbing on other catalytic components or on the support. Additionally, it should easily form monolayer coverage and not react irreversibly with either the metal surface or the support. An example of the latter is the interaction of CO with nickel metal in which volatile (and poisonous!) nickel carbonyl-$Ni(CO)_4$ - can form.

METAL	ADSORBATE	COMMENTS
Fe	H_2, CO	CO may form various carbonyls or carbides
Co	H_2, CO	Activated chemisorption; temperatures above 100°C are necessary for full coverage
Ni	H_2	Rapid equilibration; CO forms $Ni(CO)_4$
Cu	N_2O, Cl_2	Involve surface reactions
Ru	H_2	CO forms $Ru(CO)_5$; forms volatile oxide
Rh	H_2, CO	H_2 and CO stoichiometries vary with crystallite size
Pd	CO	H_2 can dissolve into the metal and form the bulk hydride
Re	H_2, O_2	H_2 uptake can be low; forms volatile oxide
Os	H_2, O_2	H_2 uptake can be low; forms volatile oxide
Ir	H_2, CO	H_2 and CO stoichiometries vary with crystallite size
Pt	H_2, O_2, CO	Activated H_2 chemisorption; CO stoichiometry can vary; CO can disproportionate on the metal at high temperatures
Mo, W	O_2	Low temperatures required
Ag, Au	O_2	High temperatures (420 - 570 K) required

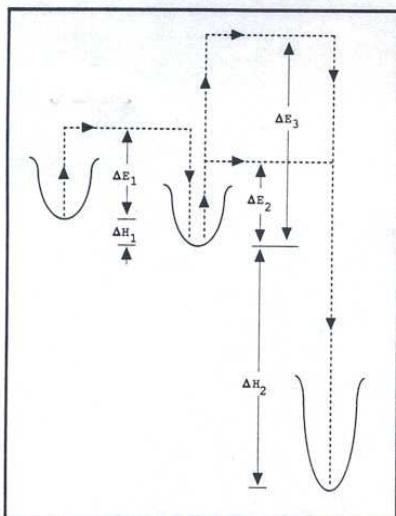Table 1: Useful adsorbates for Commonly Used Catalytic Metals

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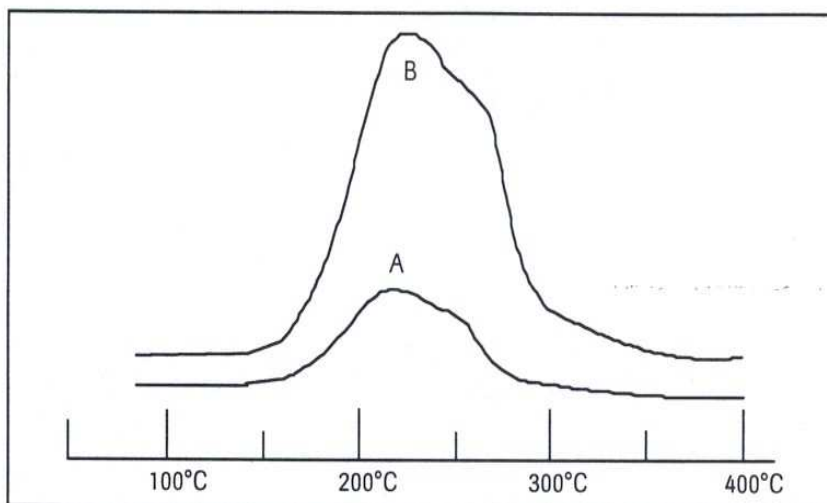

Figure 2. TPD patterns of hydrogen chemisorbed on alumina-supported cobalt. A: adsorption at room temperature; B: adsorption at 100° C

The interaction of the adsorbate with the metal during a TPD experiment can be viewed in terms of potential energy diagrams, as depicted in Figure 1. The first step in the experiment involves the collision of an adsorbate molecule with the surface and subsequent physisorption. This process involves a small activation barrier (ΔE_1), and energy loss (ΔH_1), a few kcal/mole. The physisorbed molecule then transfers to a chemisorbed state. This transfer requires the adsorbate to overcome a second activation energy barrier which may be small (ΔE_2) or large (ΔE_3). It should be noted that the heat of chemisorption, depicted as ΔH_2 in Figure 1, is independent of the activation energy barrier. In cases where the activation energy barrier is large, the chemisorption process is said to be activated, meaning that it will be kinetically slow, thus requiring either long equilibration times, higher adsorption temperatures, or possibly both, for complete surface coverage. In choosing an adsorbate, it is important to recognize those that may exhibit activated chemisorption and to adjust the temperature or time of chemisorption accordingly.

An example of activated chemisorption is that of H_2 on supported cobalt metal. Figure 2 shows TPDs of H_2 from such a catalyst for two sets of adsorption conditions. Curve A shows a TPD pattern in which the adsorption was conducted at room temperature. Only a small desorption signal was observed since few chemisorption sites were filled. In contrast, curve B shows a similar TPD in which the adsorption was carried out at an elevated temperature and the sample then cooled in hydrogen. Such a procedure allowed all the chemisorbing sites to fill and resulted in a meaningful TPD pattern.

Unfortunately, there is little theoretical basis for choosing an adsorbate and, thus, one must rely on previous experience and the literature. Table 1 summarizes some suitable adsorbates of for a variety of transition metals. This list is by no means all-inclusive and does not take into account the effect of supports or additives to the catalyst, which can markedly affect their chemisorptive properties. As such, this table should be considered a starting point for choosing an adsorbate.

2

Choice of Adsorption Conditions

The choice of adsorption conditions is just as important as the choice of adsorbate. Adsorption should be carried out at temperature sufficiently high and for a period of time sufficiently long to ensure complete surface coverage. At the same time one must prevent the reaction of certain adsorbates with the surface, such as the disproportionation of CO to CO_2 and C, which can occur at elevated temperatures. An additional possible complication is the occurrence of spillover in which a selective adsorbate can chemisorb on a metal crystallite and move onto the support (see Figure 3). Spillover is a kinetically slow process and is primarily observed at high temperatures. Thus, the adsorption temperature and time must be optimized to ensure complete coverage without the on set of spillover. As a rule of thumb, one can start with adsorption temperatures of 100-200°C and adsorption times of 30-90 minutes. Test experiments, however, must be conducted to ascertain that these conditions are suitable. A flushing step, at low temperature, is typically used after adsorption in order to clean the surface of any weakly-held species.

Figure 3. Schematic representation of a dissociative chemisorption process over a supported metal catalyst, including spillover onto the support.
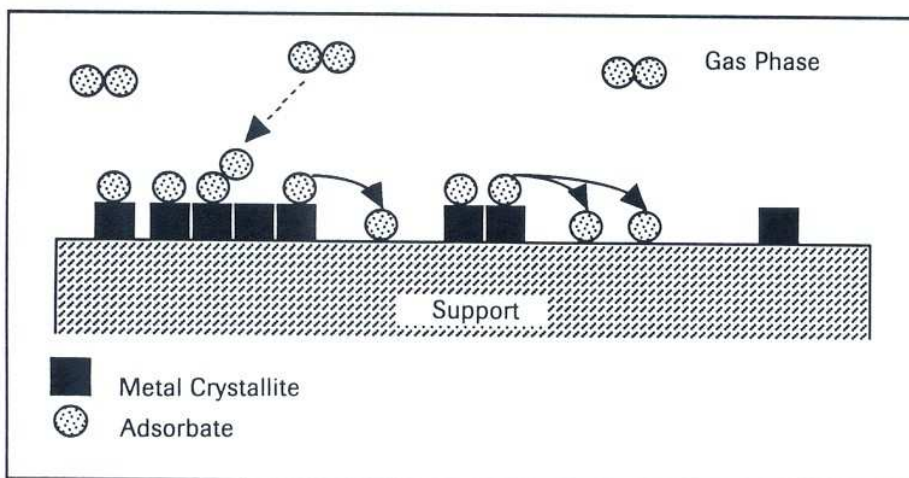
References
1. "Chemisorption and Catalysis on Supported Metals", Altamira Notes, July 1989.
2. "Temperature-Programmed Desorption of Adsorbed Species from Catalyst Surfaces", Altamira Notes, November 1989.
3. "Measuring Acidity in Zeolites Using TPD", Altamira Notes, July 1991.
4. "Surface Area Measurement from Temperature-Programmed Desorption Data", Altamira Notes, September 1989.

Adsorbate Stoichiometry

In order to effectively interpret the results of a TPD experiment, it is necessary to know the adsorbate-metal stoichiometry. Adsorption stoichiometries cannot be directly obtained from a simple TPD experiment of a powder catalyst, but can be obtained by comparison of chemisorption surface areas[4] with BET surface area for a metal powder or metal foil, determined in some cases by

3

interpretation of IR spectra, or by independent measurement of metal crystallite size using techniques such as TEM or XRD.

Again, some rules-of-thumb can be applied to Stoichiometric factors. Hydrogen and oxygen will typically adsorb dissociatively, i.e. a H_2 (or O_2) molecule will dissociate and form an H-M (or 0-M) adsorbate-adsorbent pair. Thus, its stoichiometry is adsorbate/metal=0.5. There are some instances where oxygen will adsorb associatively $O_2/M=1$, particularly at low temperatures. For Rh and Ir, it has been reported that the hydrogen adsorption stoichiometry can vary with crystallite size and, for very small crystallites, stoichiometries of $H_2/M=1$ have been reported. These, however, are rare cases.

The stoichiometries for CO adsorption are less well-defined. CO can adsorb with varying stoichiometries depending on the metal and the crystallite size. CO/M Stoichiometries between 0.5 and 2 are routinely reported. In such cases it is sometimes best to assume an average stoichiometry (say, 1) or simply use the CO uptake as a basis of comparison between catalysts.