Altamira Instruments

Altamira Application Note

Chemisorption Experiments on Pt Based Catalysts

Platinum has been utilized as a catalyst since the early 19th century, when platinum powder was used to catalyze the ignition of hydrogen. Pt's most famous and arguably most important application is in catalytic converters for combustion engines, where it promotes the complete combustion of exhaust hydrocarbons into water and carbon dioxide. Pt is also a major catalyst found in petroleum applications and is highly valued in catalytic reforming of straight-run naphthas into higher-octane fuels, rich in aromatics.

An important variation of platinum is PtO2, which is used as a hydrogenation catalyst. The use of PtO2 most recently can be found in the biofuel industry, breaking down vegetable oils into useable fuels.

To help evaluate the applicability of a particular catalyst, Temperature Programmed Desorptions (TPD's) are commonly performed. But one additional technique providing similar information is pulse chemisorption. This method is one of the simplest, most straightforward ways to measure adsorbate uptake by a metal surface and has the big advantage of generally being a much quicker test then a TPD.

To begin a pulsed chemisorption test, one must first apply an appropriate pretreatment to provide a clean, reduced metal surface. A reducing agent, commonly hydrogen in argon, is used. What follows is an inert gas flow, while heating the sample to remove any residuals and hydrogen absorbed on active sites.

The sample is then ready for the pulsed chemisorption tests. An inert gas, such as argon, is flowed over the sample while a small amount of chemisorbing gas (like hydrogen or carbon monoxide) is injected into this argon stream as it flows over the catalyst. Using a small sample loop, the volume of the absorbing gas is known and can be used in the calculations later. The composition of the stream exiting the sample cell is monitored quantitatively by a thermal conductivity detector or similar device, and this signal is compared to that produced by the injected pulse of chemisorbing gas flowing direct to the TCD. If the amount of chemisorbing gas in the injected pulse is known, the uptake by the catalyst may be calculated.

In the beginning pulses, little or no signal is detected after the pulse of adsorbate passes over a clean catalyst surface. This indicates that the catalyst surface has adsorbed all or most of the chemisorbing gas in the pulse. This pulse procedure may be repeated many times over the same sample. As the catalyst surface becomes saturated with adsorbate, less and less of the gas in each pulse is taken up by the sample. With each pulse, the size of the detector signal increases until it becomes constant and equal to the blank cell pulse signal. The total chemisorption uptake by the sample is then given by the sum of the uptakes from all of the pulses prior to saturation.

What follows is an example of a Pt catalyst characterization by a pulsed experiment. The results, like a TPD, will tell us uptake, dispersion, surface area and crystallite size.

Experimental: A .095-gram sample of 5% Pt on Alumina was run in an AMI-300 chemisorption instrument where a pulsed chemisorption experiment was performed. The sample was first preconditioned (10% H2 in Ar) to reduce it. A purge gas of Ar followed to eliminate any contaminates, and lightly bound gases.

For the final pulse steps, a gas of 10% H2 in Ar was selected and the sample was exposed to each pulse followed by analysis from the built-in TCD. The pulse gases were fed into a continuous flow of carrier gas from a 500 uL loop. Pulses were applied until no further H2 gas was absorbed.

The programmed conditions are noted below.

Programmed Conditions:

Treatment Flow Rate: 20 cc/min

Treatment Heat Rate: 20C/min

Treatment Maximum Temperature: 350C

Treatment Hold Time: 60 minutes

Sample Purge: 20cc/min

Sample Purge Time: 120 minutes

Sample Purge Maximum Temperature: 375C

Pulse Flow Rate: 20cc/min

Number of Pulses: 10

Pulse Sample Temperature: 40C

TCD Programming: current of 75 mA and gain of 5

Results:

From the experiment, figure one shows the series of pulses with progression towards sample saturation, when the pulse heights show no more change. By adding the area differentials from each pulse, we can use this to calculate absorbate uptake, or the amount of gas absorbed onto the active sites. The AMI-300 software does these calculations (figure 2) and shows the results and conversion into micromoles absorbed/gram of sample.

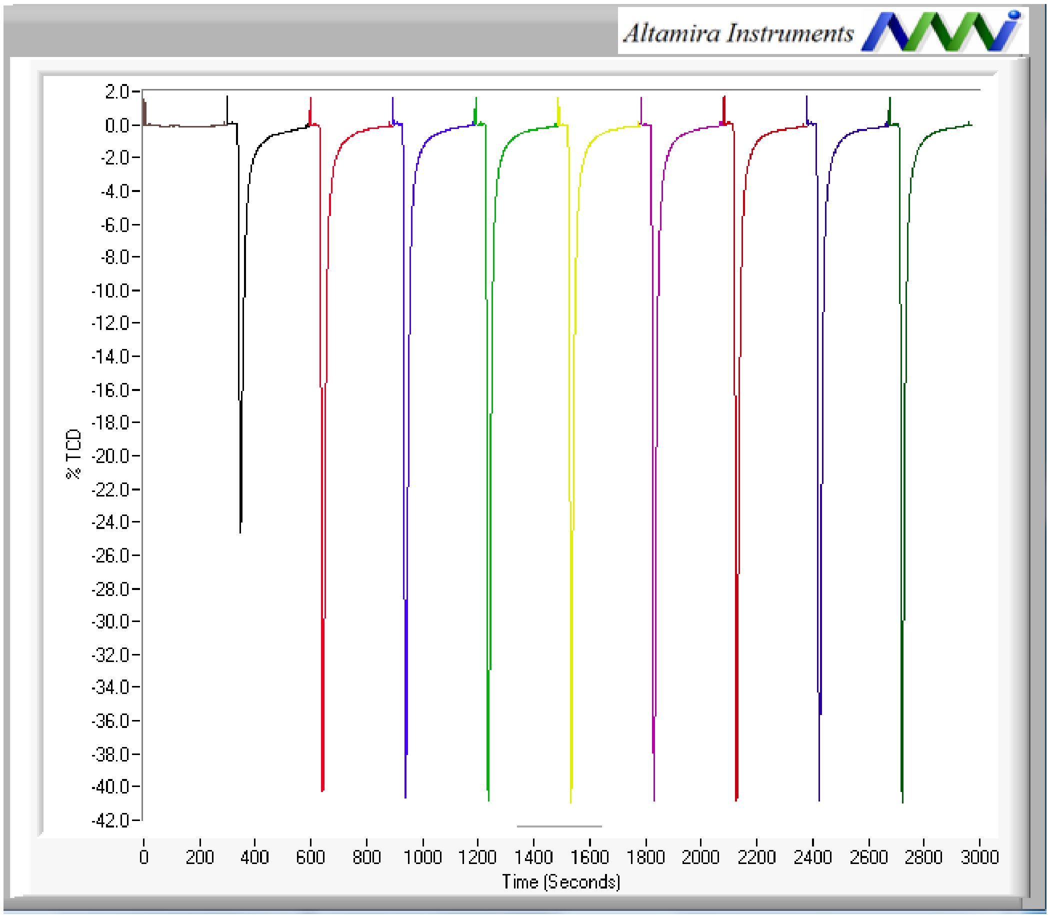

Figure 1

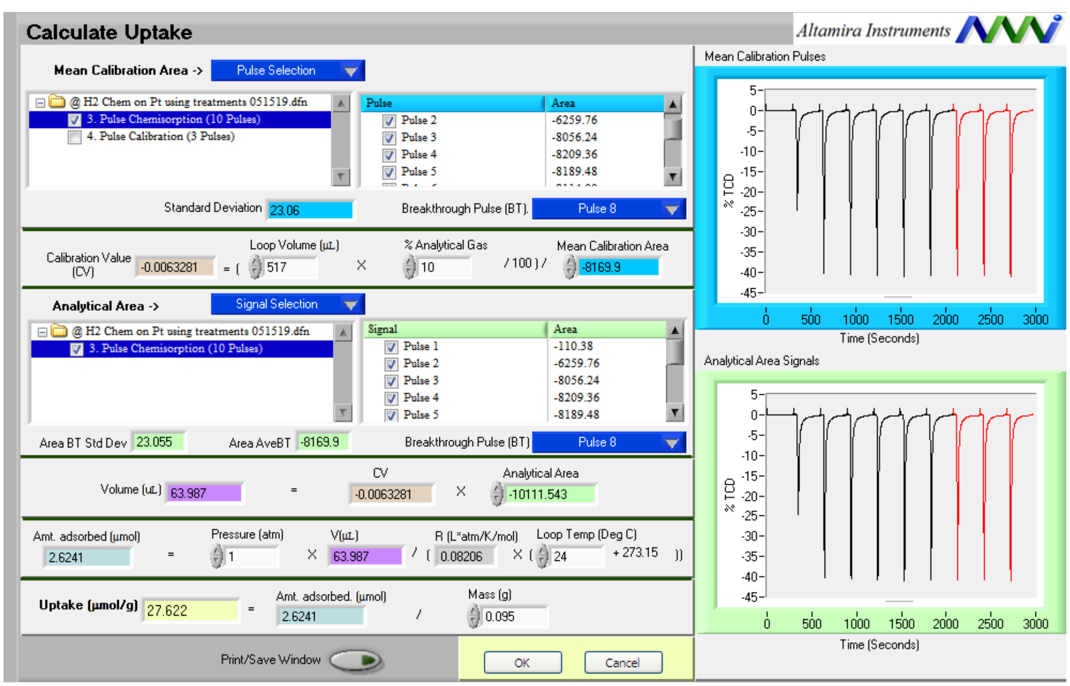

Figure 2

From the uptake calculations, we can determine the percent dispersion, which is the ratio of surface atoms of the catalyst to total atoms (figure 3). The percent dispersion number is important when comparing different catalyst types and manufactured lots, as it is relevant in how effective it is when used in process. In this case, % dispersion was calculated at 21.5 %.

Other factors that can be determined is the specific surface area, by using the % dispersion and with a few assumptions, the crystallite dimensions of the surface catalyst (Pt) on the support (Alumina).

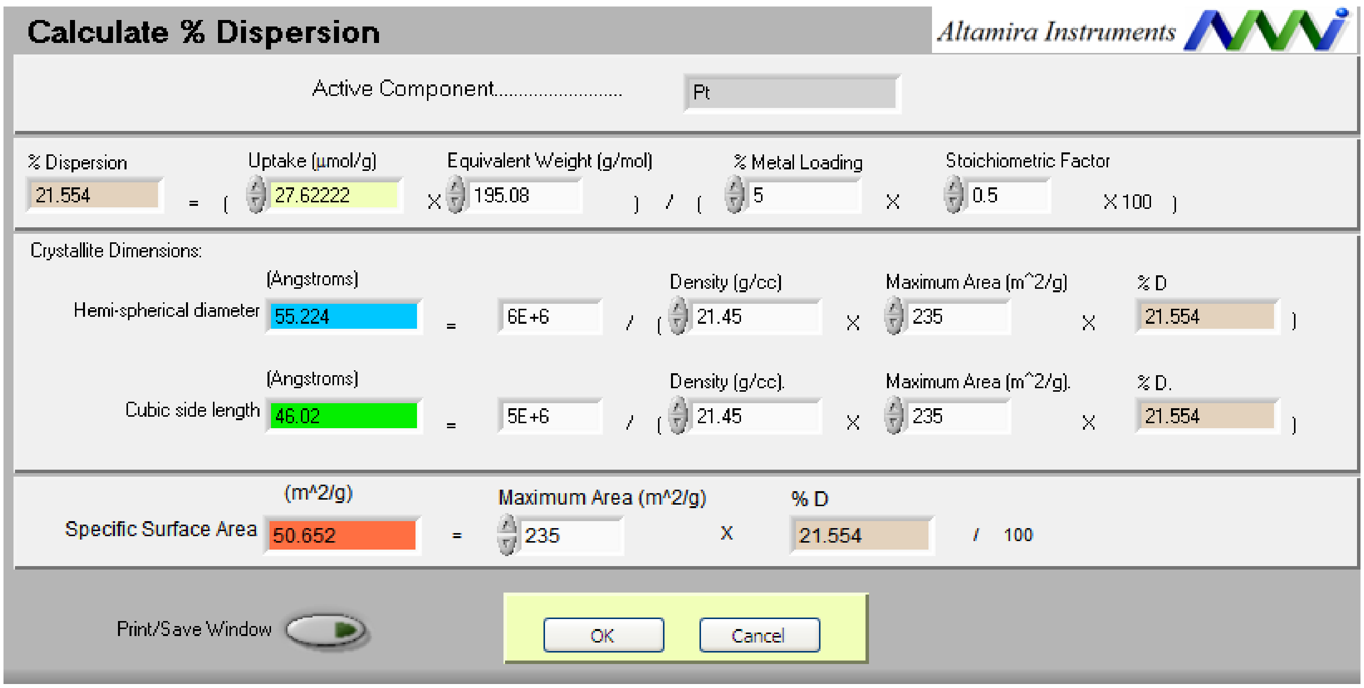

Figure 3

Pulse chemisorption experiments provide a quick and easy way of determining the same parameters of a longer TDD experiment. But it is important to remember that each new catalyst-adsorbate combination must be studied to ascertain its applicability to the technique. Any system in which a large fraction of the adsorbed species are weakly held makes calculating complete surface coverage difficult. Also, systems in which the adsorption kinetics are slow compared to the residence time of the adsorbate pulse presents similar complications.   Pulse chemisorption experiments have been carried out with a wide variety of catalysts though, and when used properly, the technique can become a routine and useful method of catalyst characterization.

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