Altamira Instruments

Altamira Application Note

Chemisorption Experiments on Ni Based Catalysts

Over a century ago, nickel was first used as a hydrogenation catalyst. Since then, its use has evolved into one of the most highly used catalyst materials, either in a pure composition, or in combination with other compounds and supports. In the 1970s, nickel was utilized not only for cross-coupling reactions of alkenes/alkynes, but also for C/H activation, oxidative cyclidation and basic reduction reactions.

During the 1990s through today, Ni based catalysts, including Ni/SiO2, Ni-Alumina, and NiO can be commonly found in biofuel research. Since they can promote various hydrogenation reactions, they are useful in breaking down the lignin and cellulose found in biomass as well as the longer-unsaturated hydrocarbons which are the majority of the composition in waste or plant-based bio-oils.

Although these catalysts are far from what we would consider the latest innovation in catalysis, they represent the backbone of many processes and they are being investigated in newer areas. Most recently, they have been used in the formulation of catalysts assessing important environmental issues, such as CO2 chemical utilization, a dopant of molybdenum, and sulfide-containing catalysts for desulfurization processes.

Several key properties of nickel, such as its thermal stability and redox behavior, mean that nickel-containing catalysts are still challenging for a very large range of innovative reaction developments and industrialization. To help ascertain some of these limitations or physical limits, chemisorption experiments are commonly performed to determine what conditions are best suited for a given application. What follows is an example of common catalyst characterization experiment that will tell us surface area, dispersion, activation energies and basic desorption temperature profiles for a nickel based catalyst.

Experimental: A .120-gram sample of 10% Ni on Alumina was run in an AMI-300 chemisorption instrument where a Temperature Programmed Desorption (TPD) was performed. The sample was first preconditioned to eliminate any contaminates, including moisture, oils, and lightly bound gases.

A treatment gas of 10 % H2-90% Ar was selected and the sample was purged at the conditions noted below. After treatment, the sample was heated at a rate of 50C/min and a carrier gas of Argon was used to desorb the treatment gas to a built-in Thermal Conductivity Detector (TCD).

After the analysis, a pulsed calibration was performed for use in calculating the results. A built-in calibration loop of 535 microLiters filled with10% H2-90% Ar and then pulsed onto the TCD to determine a known area count, which could be adjusted with the sample results. For better accuracy, a 5-pulse calibration was performed and the area count was averaged over the 5 pulses.

Programmed Conditions:

Treatment Flow Rate: 30 cc/min

Treatment Heat Rate: 10C/min

Treatment Maximum Temperature: 550C

Desorption Heat Rate: 10C/min

Desorption Flow Rate: 50cc/min

Desorption Maximum Temperature: 400C

Hold Time: 15 minutes

TCD Programming: current of 75 mA and gain of 5

Results:

From the experiment, figure one shows a single point in the desorption isotherm. The TPD experiment describes not only the number and strength of chemisorption sites, but it may also describe the heterogeneity of the surface sites.

From the analysis software we can determine the peak temperature of 113C, using the thermocouple inserted above the catalyst bed. We can use this to calculate the activation energy, which was determined to be 1.2038×10^5 J/mol.

Activation Energy= R (Tmax + 273.15) x ln (1E13x (Tmax + 273.15)/B – 3.64)

R= Ideal gas constant, 8.3145
Tmax= Temperature with highest desorption rate (113C in this case)
B= C/sec (calculated by TPD results)

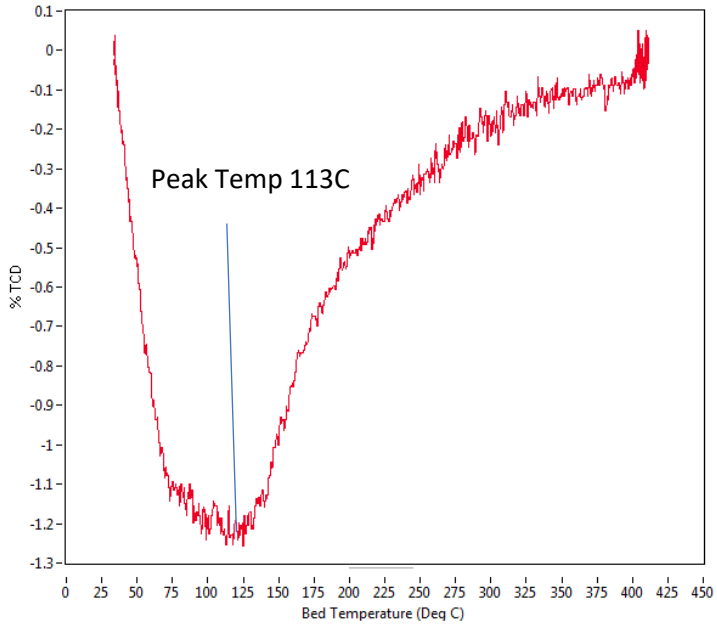

Figure 1

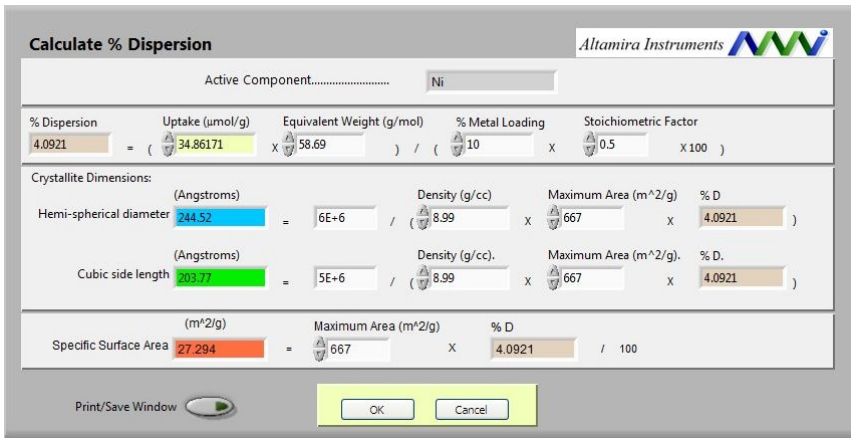

Figure 2

Figure two, shows how the percent uptake (treatment gas absorbed in micromoles) was calculated and how this is used to calculate the percent dispersion, in this case 4.09%. The percent dispersion is the ratio of surface atoms of the catalyst to total atoms. 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.

Why is it important to have information about the number of chemisorbing sites or the size of metal crystallites on a given catalyst? This information provides a basis for comparing the performance of different catalysts. Different catalyst preparations may vary significantly in characteristics such as composition, density of the material or metal weight loading. The chemisorption characteristics of a catalyst may be more closely related to the catalyst's chemical activity than are these other physical characteristics. Knowledge about sites for chemisorption may be used to develop catalytic rate expressions based on the number of adsorption sites rather than the gross catalyst weight or volume. Catalyst activity given on a per site basis makes comparison of the true efficiency of different catalysts more meaningful.

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