Altamira Instruments

Altamira Application Note

Chemisorption Experiments on Co Based Catalysts

From the early days of catalysis, cobalt has been one of the most frequently used transition metals to promote chemical processes. The oxidation-reduction properties of cobalt allow for different valences of I, II or III to be demonstrated. Electrons can be easily transferred between these states, speeding up reactions. Also, its ability to activate CO and CH reactions has made it a critical component to many manufacturers. Several industrial processes and synthetic routes utilize this metal, either in pure form or in combination. A few examples are CoThO, CoFe and Co-Alumina, among many others.

Most famously, cobalt based catalysts are used in the Fischer-Tropsch reaction where hydrocarbons are produced from CO and H2. But other common processes include desulphurization of petroleum and hydroformylation for the production of aldehydes.

The end result is a vast number of materials being produced from these processes, including oil, lubricants, waxes, diesel, hydrogen (e.g., fuel cell applications), gasoline, rubbers, plastics, alcohols, pharmaceuticals, agrochemicals, feed-stock chemicals and other alternative materials. However, given the true complexities of the variables involved in these processes, many key mechanistic issues are still not fully defined or understood. To help better evaluate cobalt based catalysts, chemisorption experiments can be a valuable tool in learning how to best apply and optimize each individual variety.

What follows is an example of common catalyst characterization experiment using a Temperature-Programmed Reduction (TPR) technique that can yield direct information on the reducibility of a catalyst and catalyst precursors. As such, it is an excellent technique for characterizing a variety of catalysts. The technique consists of exposing the sample to a flowing mixture of a reducing agent, such as hydrogen, in an inert gas while linearly ramping the temperature. The rate of consumption of the reducing agent is monitored and related to the rate of reduction of the sample.

Experimental: A .1240-gram sample of 10% Co+1% Re on Alumina was run in an AMI-300 chemisorption instrument where a Temperature Programmed Reduction (TPR) was performed.

A treatment gas of Ar was selected and the sample was purged at the conditions noted below. This treatment gas helps assure that we are starting with a catalyst surface free of water, contaminants or other reducing gases. After treatment, the sample was flushed with a gas of 10% H2 in Ar at a heated rate of 30cc/min. Upon the gas exiting the sample, it flows through the built-in Thermal Conductivity Detector (TCD) to determine how much of the Hydrogen gas is being consumed.

After the analysis, a pulsed calibration was performed for use in calculating the results. A built-in calibration loop of 535 microLiters was filled with10% H2-90% Ar and then pulsed onto the TCD to determine a known area count, which is used to adjust 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: 350C maximum

TPR Flow Rate: 30cc/min

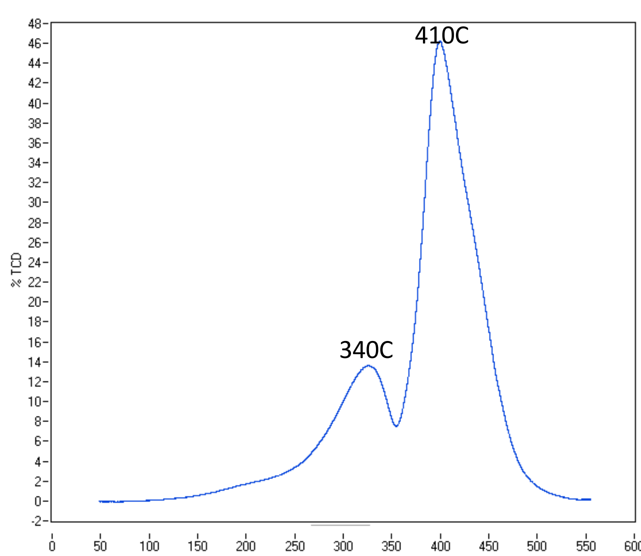
TPR Maximum Temperature: 550C

TCD Programming: current of 75 mA and gain of 5

Results:

From the experiment, figure 1 shows a TPR comparing the catalyst bed temperature vs % TCD response. Such a signal gives information concerning the ease of reducibility (temperature at maximum) as well as the extent of reducibility (TCD signal area) of the material being studied.

Figure 1



From the analysis graph two clearly defined, but overlapping, peaks are displayed. The first peak has a maximum temperature of 340C. The second peak's maximum is at 410C. However, it should be noted that the peak position can vary depending on the exact placement of the bed thermocouple and the exact composition of the H2-Ar mixture.

This graph ultimately gives information concerning the ease of reducibility (maximum temperature) as well as the extent of reducibility (signal area) of the material being studied. From the AMI-300 analytical software, you can see in figure 2 how we the % reduction of the catalyst is calculated. The uptake number, which is the amount of micromoles of H2 absorbed/gram of catalyst, is a key measurement from the TPR and is used in calculating the % reduction number, in this case 55.3%.

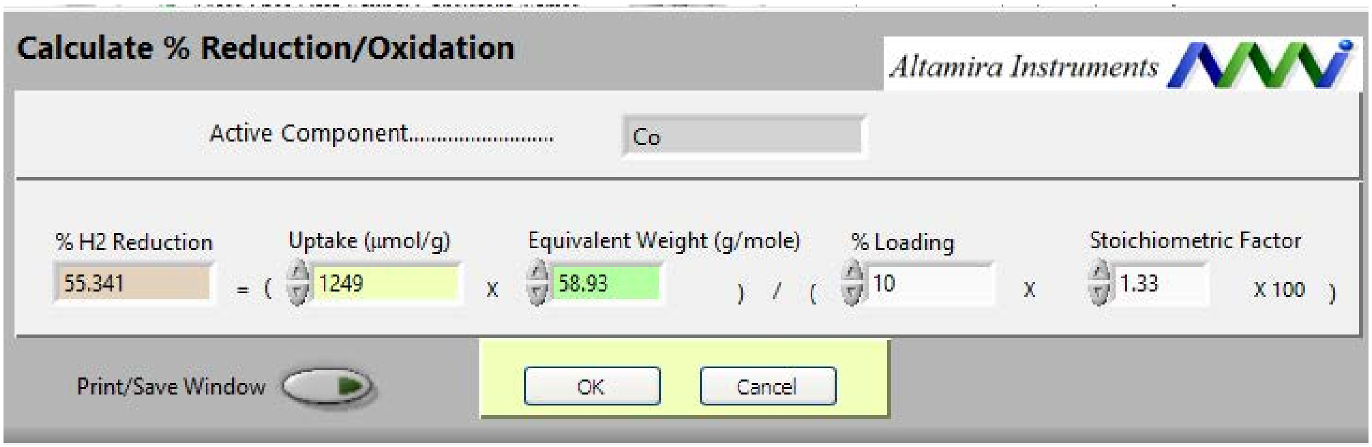


Figure 2

However, it is sometimes difficult to compare results obtained in different laboratories or reported in literature. There exist no optimum experimental parameters for conducting TPR experiments and parameters such as the rate of heating, the composition of the reducing mixture, gas flow rates, and particle size can all greatly affect the rate of reduction. So, it is important for the user to have some understanding of the physical characteristics of their sample and to establish some consistent baselines in programming when comparing in house samples.

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