Surface Science
Application Note 276

CATLAB

Dispersion Measurement By CO Pulse Chemisorption

Dispersion Measurement

In the characterisation of a catalyst sample it is important to quantify the total amount of metal available for reaction. The amount of available metal is usually expressed as a percentage of the total number of surface metal atoms compared with the total number of metal atoms in the sample. This is known as dispersion. The equation for this is shown below:

Dispersion, % = (No. Surface Atoms / Total No. Atoms) x 100

When using supported metal catalysts, there are several molecules that can be selected to use as adsorbates. These include carbon monoxide, oxygen, hydrogen and nitric oxide. In all these cases, it is important to know:

- What is the metal atom to adsorbate gas stoichiometry?
- Does the molecule adsorb associatively or dissociatively?
- Does the support material play any part in the adsorption, i.e. is there spillover, or does the support play an active role in adsorption?

Here, we describe the use of CO pulse chemisorption to determine the dispersion of a 5 % Pd/Al_2O_3 catalyst.

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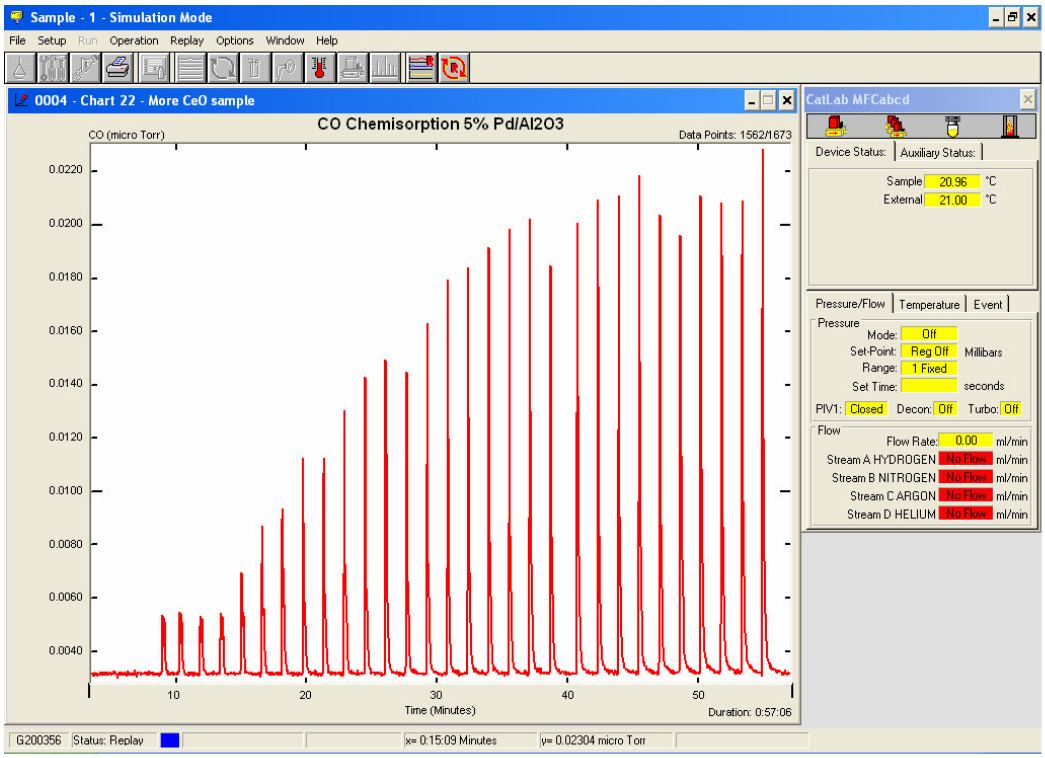

Figure 1 Pulse Adsorption Profile

Experimental

In order to perform the pulsed chemisorption, the sample surface must be clean from oxygen. Heating the sample in a reducing atmosphere performs this.

Approximately 0.150g of 5% wt Pd/Al_2O_3 catalyst pellets was accurately weighed and loaded into the CATLAB microreactor. The sample was flushed with 60 $mlmin^{-1}$ of He (purified by passing through O_2 and H_2O traps) for 30 mins. The flow was then switched to 5 % H_2 in He, 60 $mlmin^{-1}$ (purified as before). The sample was flushed for 30 mins before the temperature was increased to 473 K at 3 $Kmin^{-1}$. The sample was held at this temperature for 2 hours before the flow was switched to He, 60 $mlmin^{-1}$ to remove excess H_2 from the system. The sample was maintained under these conditions before cooling to room temperature under flowing He.

After activation the sample was exposed to 30 pulses of a 5 % CO in He mix. The pulse sample loop volume is 100 µl of which 5 % is CO.

The *QIC* -20 mass spectrometer was set to record on the data for CO (m/z 28) during the pulse experiment. The resulting adsorption plot is shown in Figure 1.

The data in Figure 1 shows that there has been adsorption of significant amounts of CO for the first 20 pulses, after which the peak areas begin to become more similar, suggesting the sample has reached it's saturated coverage.

In order to quantify the amount of gas adsorbed and therefore the dispersion, the data was exported to the Hiden TPD Analysis Software

TPD Analysis Software

The TPD Analysis program is a standalone software package supplied as standard with the Hiden CATLAB.

This software package allows calculations including:

- Total Uptake Measurements
- Adsorption Isotherms
- Dispersion

The CO pulse adsorption profile in the TPD Analysis Software is shown in Figure 2 below:

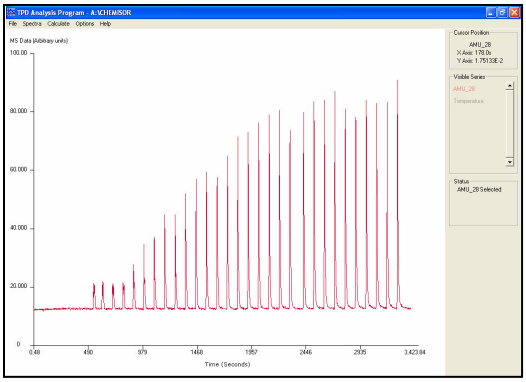

Figure 2 Pulse Profile in TPD Analysis Software

Dispersion Calculation

The TPD Analysis Software automatically integrates the area under the curve for each pulse. It then subtracts this from the average area of calibration pulses. Calibration pulses are defined as pulses that pass through the catalysts with no uptake, generally the last 3 or 4 pulses. From this difference the amount of gas adsorbed on the catalyst surface at each pulse is quantified. Using this information and data input by the user (mass of sample, metal details etc.) the software can calculate the percentage of metal dispersion. Figure 3 shows the dispersion calculation screen in the TPD Analysis Software.

In order to calculate the metal dispersion, the ratio of adsorbate gas to metal sites must be known. It is known that CO can coordinate to one, two or three Pd atoms upon adsorption. The exact ratio depends upon the experimental conditions used. A typical ratio for the type of experiment described here is CO:Pd = 1:2.

The ratio can be confirmed by other analysis techniques

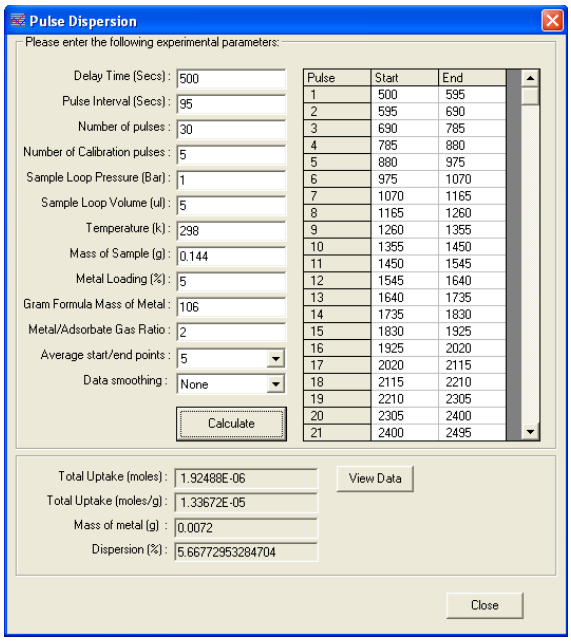

Figure 3 Dispersion Calculation Screen

Therefore, for the 5 % wt Pd/Al_2O_3 catalyst analysed here a dispersion of **5.7 %** was calculated.

Pulse Adsorption Isotherm

Using the same experimental data a pulse adsorption isotherm can also be plotted. The adsorption Isotherm relates the surface coverage of an adsorbate gas to the exposure of the sample to an adsorbate gas. Figure 4 shows the TPD Analysis Software screen for the adsorption isotherm of CO on the Pd catalyst described above. The resulting Isotherm can be seen in Figure 5.

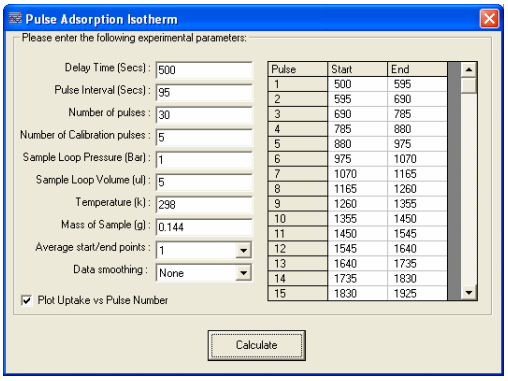

Figure 4 Pulse Adsorption Isotherm Screen

Conclusion

This application note demonstrates how the close-coupled QIC-20 mass spectrometer within the PCS CATLAB microreactor system provides high quality time resolved data enabling routine accurate measurement of fundamental catalyst properties.

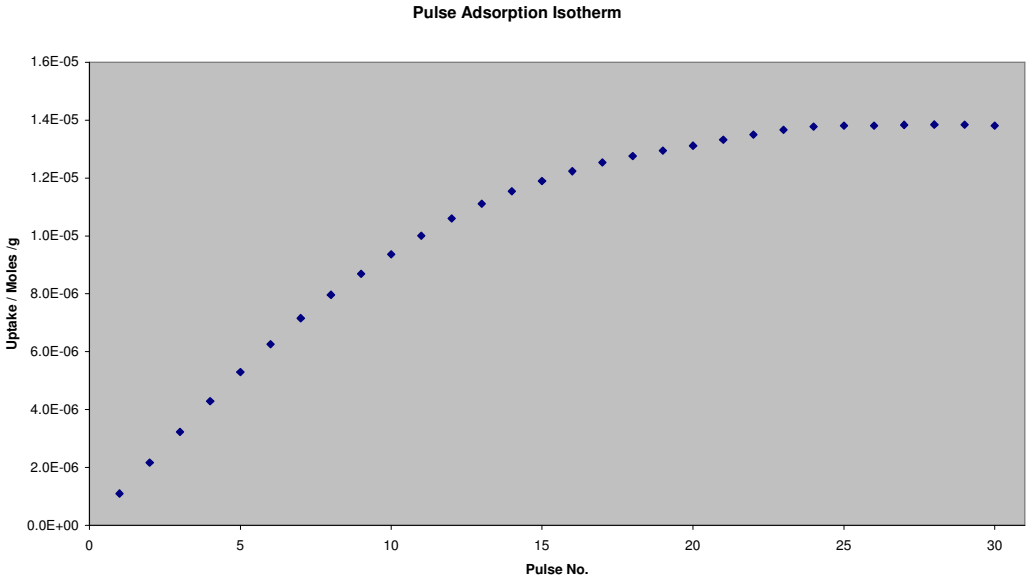

Figure 5 Pulse Adsorption Isotherm