micromeritics®
Effective Solutions for Material Characterization

APPLICATION NOTE 185

DEMONSTRATING THE CONSISTENT PERFORMANCE OF THE *IN SITU* CATALYST CHARACTERIZATION SYSTEM (ICCS) WITH DIFFERENT REACTOR SCREENING SYSTEMS.

Researchers screen catalyst performance using a wide variety of different experimental units and test rigs. A substantial proportion of these are constructed in-house by, or to the design, of individual scientists though commercial solutions are available, as exemplified by the Micromeritics Microactivity Effi reactor. Prior to a screening trial, physisorption, chemisorption, and temperature programmed analyses are applied to rigorously characterize the catalyst. Application of such techniques during, or post-reaction reveals any changes, and more specifically insight into the mechanisms of deactivation; catalyst regeneration can be studied in an analogous way. However, post-reaction characterization typically involves removal of the catalyst from the test reactor. This is widely recognized as compromising data integrity, since exposure to the environment can change the catalyst.

The ICCS enables the integration of catalyst characterization with reaction screening tests, allowing it to be carried out with the catalyst in the test reactor. A defining feature of the system is that it can connect to most existing test units. The capabilities of the ICCS are therefore accessible to any researcher using a flowing system unit with appropriate temperature control. This application note demonstrates this feature with reference to experimental data illustrating the consistency of results obtained with two different units.

Characterizing catalysts

Heterogeneous catalysts often consist of metal dispersed across a high specific surface area support. Their performance depends on the efficient mass transfer of reactants and products to and from the

active catalytic site, in addition to the activity of the site itself. A wide variety of established techniques are used to characterize these complex systems including:

- Physisorption – which quantifies physical characteristics of the catalysts and supports via metrics such as surface area and porosity, total pore volume, and pore size distribution.

- Chemisorption – which quantifies parameters that often relate to reactivity, crucially the number of accessible active sites on the catalyst along with other variables including: the active surface area of the catalyst; metal dispersion (the ratio of the number of active metal atoms to the total amount of metal in the catalyst); and the percent metal (the quantity of active metal per unit mass of catalyst, including support). Given an active particle or crystallite with regular geometry it is also feasible to estimate the size of the active site.

- Temperature programmed analyses – which enable the quantification of critical reactions, principally reduction and oxidation - temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) respectively. The traces produced act as a fingerprint for the catalyst and elucidate performance, providing insight into, for example, the influence of support materials, pretreatment procedures and promotors.

These techniques all support the differentiation of candidates for an application, highlighting a higher performance support, for example, a catalyst that offers more accessible active sites, or a system in which the active sites are more effectively dispersed. A promising candidate typically proceeds to screening trials which involve testing very small quantities for the reaction of interest, preferably under representative conditions of temperature and pressure. Screening trials generate a mass balance for the reaction enabling the determination of crucial metrics such as turnover frequency - the number of moles of reactant converted into the desired product by each active site per hour - and selectivity. This is the point at which researchers can reliably differentiate high performance catalyst for a specific reaction, from a catalyst that simply offers high but less specifically defined activity.

However, the value of characterization techniques extends beyond this point. One of the issues assessed in screening trials is deactivation. As a catalyst proceeds towards commercial use it is crucial to assess how long activity remains economically sustainable, and how to regenerate the catalyst once activity is lost. The characterization tools used to select a catalyst are valuable for elucidating deactivation, and regeneration, and integrating characterization tools with screening trials is therefore highly advantageous.

The ICCS meets this requirement. Attaching it to a screening system makes it possible to apply chemisorption and temperature programmed analyses, without removing the catalyst from the reactor; there is also an optional capability for physisorption, for the post-reaction measurement of surface area. This enables a workflow whereby, for example, the catalyst is rigorously employed for a period of time, recharacterized to assess the impact of reaction, run for a further period of time, recharacterized and so on. The same catalyst can be tested repeatedly with no requirement to remove it from the reactor. The resulting data provide highly representative insight into the mechanisms associated with changing catalyst performance, providing a secure foundation for exerting control over that change.

A defining feature of the ICCS is that it can be attached to any existing screening reactor system such that researchers can access these capabilities easily, simply by adding to their existing equipment. The following data were collected via the integration of the ICCS with two different representative systems to demonstrate this feature and the consistency of data generated.

Experimental study 1: Testing the ICCS with the Micromeritics Microactivity Effi reactor

Figure 1 shows a TPR trace for a silver oxide reference material measured by an ICCS connected to a Microactivity Effi; the catalyst is held in the Microactivity Effi, the TPR analysis is performed using the ICCS. The Microactivity Effi is a fully automated, compact system for the measurement of catalyst activity, for the study of yield and catalyst kinetics. The ICCS utilizes some of the same technology as this system and was designed to complement it.

The experiment was carried out with a total gas flow rate through the reactor system of 100 ml/min; the flowing gas is a carrier with a known concentration of hydrogen. In a TPR the temperature is ramped as a function of time and the quantity of hydrogen consumed is monitored, in this case by the thermal conductivity detector (TCD) of the ICCS. The observed peak is associated with a triggering of the reduction reaction at a defined temperature. Analysis of the data showed that the quantity of hydrogen consumed was in line with the specification for the material validating the calibration of the TCD and the performance of the overall system.

A pulse chemisorption experiment was also carried out with the same system, this time using a Pt supported on alumina reference catalyst. Again, the results obtained are consistent with published data.

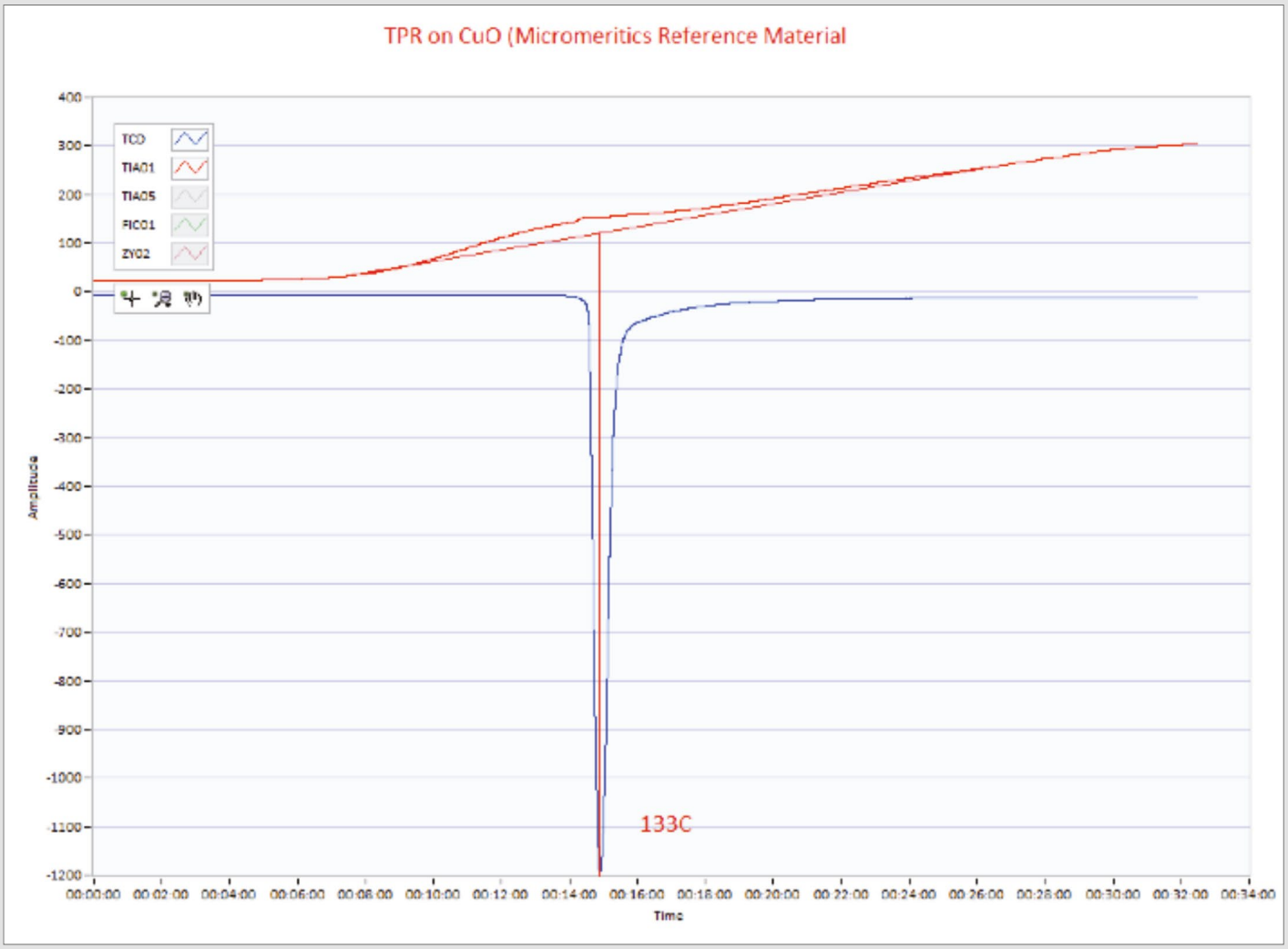

Figure 1: A TPR analysis for a reference silver oxide material measured by connecting the ICCS to a Microactivity Effi produces results that are consistent with published data.

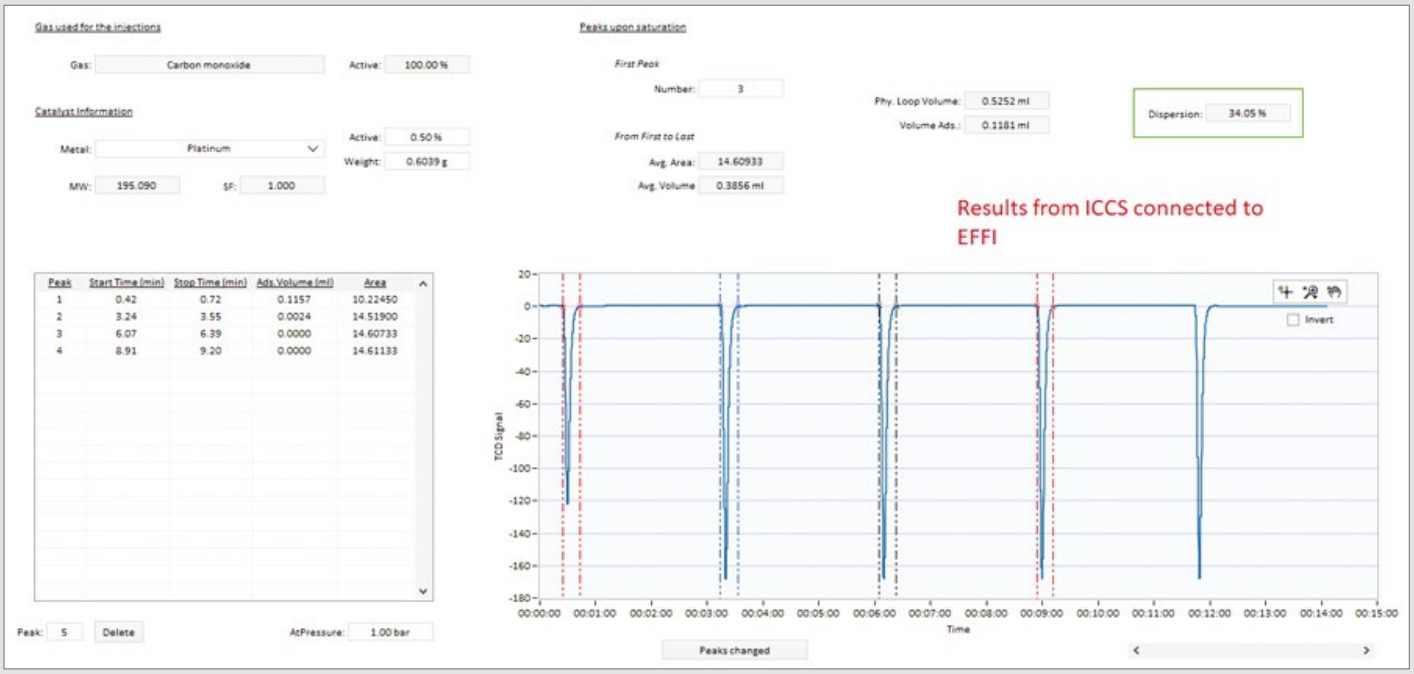

Figure 2: Pulse chemisorption results for a reference Pt/alumina reference catalyst, measured by connecting the ICCS to a Microactivity Effi, are consistent with published data for the material.

Experimental study 2: Testing the ICCS with the ASAP 2020C

The previously described experiments were repeated using the same reference materials and test conditions with a system consisting of a Micromeritics ASAP 2020C connected to the ICCS. The ASAP 2020C is a gas adsorption system that can be used to apply physisorption and chemisorption. It has 12 gas inlets, providing facility for multiple probe gases, and a dedicated exhaust port to which detectors can be connected. However, it has no integral TCD or alternative detector and by extension no facility to perform temperature programmed analyses. A high temperature furnace provides accurate temperature control up to 1100°C. Here, the ASAP 2020C therefore provided a good approximation of the capabilities of a typical screening test rig; the catalyst was loaded into the ASAP 2020C for the tests and analyses were conducted using the ICCS. Figure 3 shows the TPR results measured with this system; figure 4 shows the pulse chemisorption data.

The results for both the TPR and the pulse chemisorption are closely comparable to those generated with the Microactivity Effi, and, as before, consistent with the published data for the reference materials. These results therefore demonstrate the flexibility of the ICCS with respect to its ability to produce identical data when attached to different 'reactor' systems. The flow rate of 100 ml/min was the same for both the Microactivity Effi and ASAP 2020C but it is worth noting that for in-house systems with dead volumes the flow rate of the carrier gas can be increased to improve the responsiveness of the overall system and measurement accuracy.

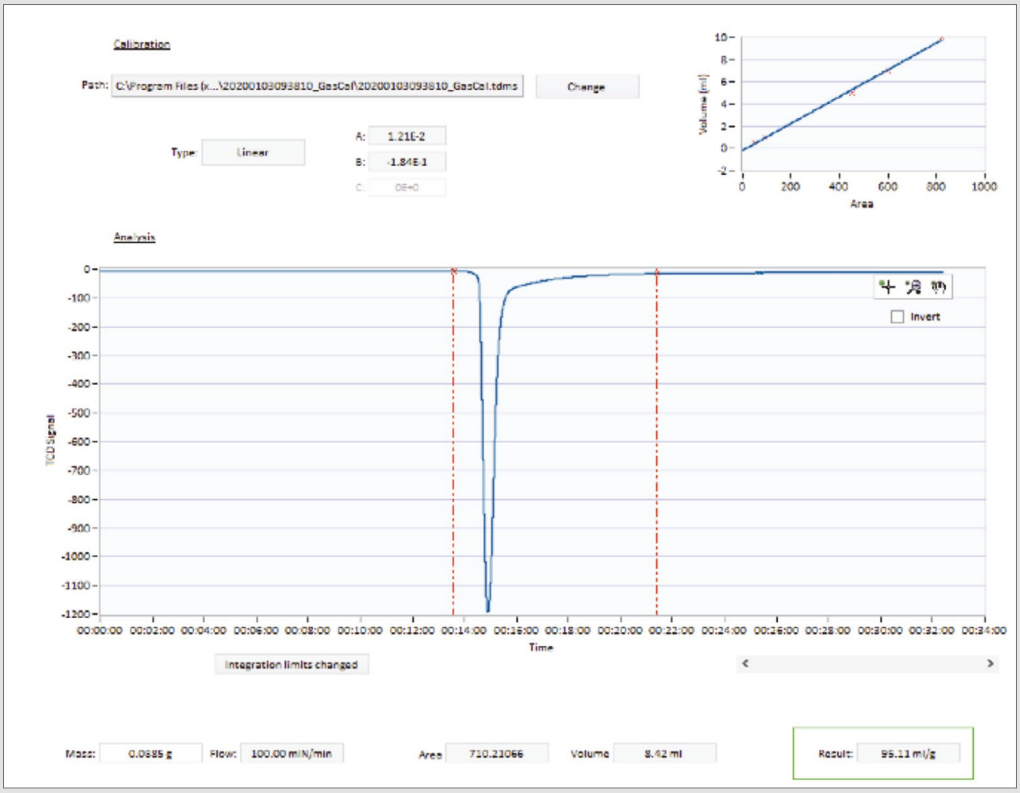

Figure 3: A TPR analysis for the reference silver oxide material measured by connecting the ICCS to an ASAP 2020C produces results that are consistent with previously measured and published data.

Figure 4: Pulse chemisorption results for a reference Pt/alumina reference catalyst, measured by connecting the ICCS to an ASAP 2020C, are consistent with previous results and published data for the material.

In conclusion

A key feature of the ICCS is that it enables the integration of chemisorption and temperature programmed analyses with a very wide range of heterogeneous catalyst screening reactors. The data presented here demonstrates this capability and the consistency of results generated when the ICCS is attached to two quite different reactor systems.

Micromeritics Instrument Corp.
4356 Communications Drive
Norcross, GA 30093 • USA

Tel.: +1 770 662-3636

info@micromeritics.com
micromeritics.com

880/42702/00