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Effective Solutions for Material Characterization

WHITEPAPER

CHARACTERIZING CATALYSTS *IN SITU*: TECHNOLOGY, APPLICATION AND VALUE

Learn how to elucidate reaction, deactivation and regeneration mechanisms by testing used heterogeneous catalysts in situ to generate representative characterization data.

Catalyst characterization is usually performed using a test apparatus separate from that used to screen catalysts under process-representative conditions. Measuring critical properties of a fresh catalyst provides a baseline for comparative studies and information that can be used to rationalize performance. Catalyst characterization post-reaction elucidates reaction, deactivation, and potentially regeneration mechanisms but typically involves removing the catalyst from the screening reactor and transferring it to an alternative system for analysis. This introduces the risk of environmental contamination, compromising data integrity.

This white paper introduces the Micromeritics *In Situ* Catalyst Characterization System (ICCS), a novel apparatus for applying chemisorption, temperature-programmed analyses, and other established characterization techniques to a catalyst in a reactor. It explains how the technology works and the data that can be generated; experimental studies highlight the value and application of the results in the development of heterogeneous catalysts.

Applying catalyst characterization techniques

Heterogeneous catalysts commonly take the form of metal dispersed across a high specific surface area support; reaction proceeds via the following steps:

- Bulk diffusion of the reactants to the catalyst surface
- Reactant adsorption at the catalyst surface
- Reaction
- Desorption of the product
- Bulk diffusion of the product away from the catalyst surface

The development of productive and selective heterogeneous catalytic systems, therefore, extends beyond optimization of the active catalyst site to precise mass transfer control. By controlling the ease with which reactant molecules access an active site, and products diffuse from it, it is possible to manipulate the localized environment in which reaction takes place, thereby optimizing the speed of reaction and selectivity to the required product.

The techniques used to characterize heterogeneous catalysts are well-established and reflect the need for detailed knowledge to support the manipulation of interactions at a molecular level and robustly optimize the complete catalyst. These techniques include:

- Physisorption – which utilizes reversible adsorption to quantify internal structure and texture, especially of the support, via variables such as porosity (total pore volume and pore size distribution) and surface area. These characteristics can be manipulated to control mass transfer within the catalyst, and dispersion of the active catalyst.
- Chemisorption – which characterizes parameters relating to the reactivity of an active catalyst such as the number of accessible sites and parameters 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
  - Active particle or crystallite size – using cubic or hemispherical geometries.
- Temperature programmed analyses – which are used to quantify the response of the catalyst, for example, to reduction (temperature-programmed reduction (TPR)) and oxidation (temperature-programmed oxidation (TPO)); temperature-programmed desorption (TPD) is also common. These are crucial reaction steps in many catalytic cycles and the traces associated with such analyses provide a "fingerprint" for a catalytic system. TPR analyses are extremely useful for probing the influence of support materials, of pretreatment and promotors while TPO can be especially relevant when determining how to regenerate a fouled or deactivated catalyst. TPD analysis provides insight into binding strength and the number of active sites.

The development of a heterogeneous catalyst, within a laboratory, typically involves materials in powder form, the use of 'research' catalysts consisting of a single bulk or supported active phase. Applying the techniques previously outlined allows researchers to robustly assess libraries of well-characterized options for a specific reaction to develop the knowledge required to move efficiently towards higher performing candidates.[1] Such candidates subsequently become subject to screening trials, where the catalyst is tested under process conditions to produce a mass balance for the reaction system, to assess yield, conversion, and selectivity. It is at this point that researchers can reliably differentiate a high-performance catalyst for a specific reaction, from a catalyst that simply offers high but less specifically defined activity. Screening trials determine productivity, a defining metric, which can be quantified via the term turnover frequency (TOF). TOF is the number of moles of reactant converted into the product of interest by each active site, per unit time and is determined from mass balance (rate of reaction) and chemisorption data (number of active sites), in combination. Beyond TOF, such trials generate information about catalyst stability and lifetime, critical attributes of heterogeneous systems, and offer capability for the investigation of regeneration strategies.

Researchers use a wide variety of different systems or experimental rigs for screening trials, from simple glassware units to sophisticated, fully automated units capable of operating at substantially elevated pressure. These can be bought off-the-shelf – notably the Micromeritics Microactivity Effi – or built to a customized design, in-house or again by an external supplier.

The application of characterization techniques does not cease as catalysts proceed to screening trials. Rather, characterization techniques are needed to elucidate the behavior of the catalyst as it undergoes more advanced testing. For example, rigorous characterization of a catalyst that has been used for reaction studies for a prolonged period and is starting to deactivate can reveal whether all sites are simultaneously losing activity or whether deactivation is associated with the complete loss of a fraction of the sites. The post-reaction measurement of surface area may provide insight into deactivation by revealing whether sintering of the catalyst, which can occur at high temperatures, is a contributory factor. These same analyses are equally valuable for the determination of appropriate regeneration strategies, which similarly necessitates post-treatment characterization.

Routine practice is to remove a catalyst from a screening reactor system for post-reaction characterization in an alternative system, but this introduces the risk of environmental contamination, the potential for moisture ingress or for oxidation due to the action of air. Such practice also complicates the workflow. The ICCS resolves this issue by enabling characterization of the catalyst in a reactor screening system, any reactor screening system that allows gas flow.

Introducing the ICCS

The ICCS is a self-contained accessory that connects to a reaction screening system to enable the application of pulse chemisorption and temperature-programmed analyses (TPR, TPD and TPO). The ICCS:

- Allows the testing of a catalyst *in situ* with no requirement to remove it from the reaction screening system
- Enables characterization, and further testing, of the same aliquot of catalyst
- Can test catalysts at elevated temperature and pressure, depending on the constraints associated with the screening unit
- Can be attached to almost any existing reactor screening unit with the provision for gas flow and an automated oven, to apply the temperature ramping protocols associated with temperature-programmed analyses
- Offers optional physisorption capability for post-reaction testing

The ICCS enables a streamlined and productive workflow wherein a catalyst is tested by a combination of temperature-programmed analyses and chemisorption to generate a description of the unused catalyst under reaction (or alternative screening) conditions. The reactor can then be operated for a defined period of time and the catalyst can then be re-characterized, *in situ*, using the same techniques to precisely determine the impact of the reaction on, for example, the number of active sites or the TPR profile, with no risk of external contamination. Following characterization, the same aliquot of the catalyst may then be subject to further reaction, and again retested, to develop further understanding.

These capabilities of the ICCS offer significant potential to boost the integrity of catalyst assessment and the capacity of researchers to gain representative insight into the mechanisms that govern reaction, deactivation, and regeneration.

In practical terms, the ICCS is highly automated and easy to use, utilizing high-performance equipment and designs from the Microactivity Effi. It incorporates two gas mass flow controllers for fully automated precise gas flow metering and an integrated pressure controller for real-time control. A cold trap, cooled by a Peltier system, removes condensibles and can be controlled at temperatures from -20 to 60 °C. A precision thermal conductivity detector (TCD) monitors changes in the concentration of gases flowing into and out of the sample reactor and there is a calibrated loop for pulse chemisorption analyses. The software for the system is particularly advanced and makes it easy to make measurements, for example, automatically determining the:

- Amount of hydrogen consumed to quantify the amount of reducible species present in a sample, for TPR analysis
- T_m, the temperature at maximum signal, for each peak on a TPR profile.
- Amount of oxygen consumed to quantify the extent of oxidation for TPO analysis
- The acidity of a catalyst site and the strength of acid sites via desorption testing with a basic molecule at different ramping rates

The following example studies illustrate the performance of the ICCS and the relevance of the information generated.

Experimental study 1: Exploring the benefits of TPR analysis at elevated pressure

Figure 1 shows a series of hydrogen TPR traces for a copper oxide catalyst, measured at elevated pressure, up to 15 bar. These measurements were made by connecting an ICCS to a Microactivity Effi which can operate at pressure up to 100 bar. The ICCS can operate up to 20 bar enabling characterization at significantly elevated pressure, provided the associated reaction screening system is rated accordingly.

In a TPR experiment, the catalyst is subject to a flowing gas of defined composition, to maintain a reductive atmosphere, and the change in gas composition is monitored in response to a well-defined temperature ramp. At a certain temperature, reaction(s) take place changing the composition of the flowing gas. This change in composition is observed as a pulse in the TCD which is used to produce the TPR plot.

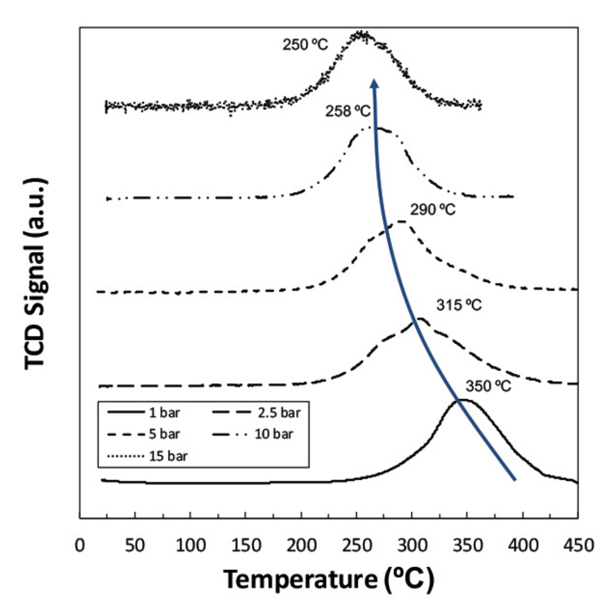


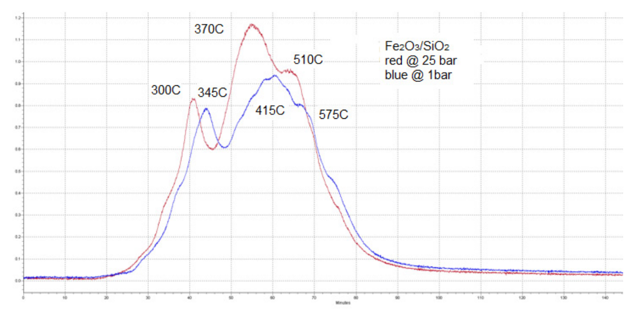
Figure 1: TPR traces indicate that the temperature associated with copper oxide reduction decreases with increasing pressure across the range 1 to 15 bar.

The results show a shift in reduction temperature as a function of pressure, with the temperature at which reduction takes place decreasing progressively as pressure is increased. This is an important trend to quantify since higher temperatures are associated with an elevated risk of the catalyst sintering which reduces the surface area of a catalyst and is a primary cause of loss of activation. These trends quantify the benefit of increasing pressure to reduce the temperature of any reduction cycle and, by extension, the potential to lose activity via this mechanism. Clearly, such observations are not possible with TPR analysis at atmospheric pressure; the ability to characterize at elevated pressure is essential. Via the connection to a reactor screening system rated for high-pressure operation, the ICCS delivers this capability in a highly efficient way.

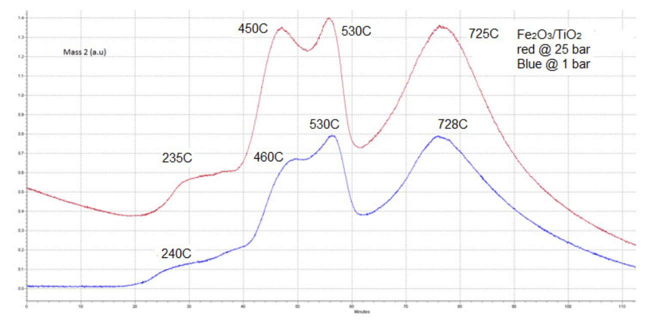
Figure 2 shows a further study that capitalizes on the high-pressure characterization capabilities afforded by the ICCS. Here, the change in the TPR profile of three different catalyst systems was assessed as a function of pressure to evaluate the performance of different supports: SiO_2, TiO_2 and Al_2O_3. The active catalyst used in each case was Fe_2O_3 and testing was carried out at 1 and 25 bar using a comparable test setup to that described for the previous study.

The results clearly differentiate the behavior of the supports in terms of their ability to stabilize the Fe_2O_3. These traces exhibit multiple peaks, which is commonplace, with each peak corresponding to the reduction of a specific component within the sample. The signal indicates changes in concentration, as a result of gas consumption due to the reduction process, and the area under the curve is therefore related to the quantity of each component in the catalyst. Looking first at the results for SiO_2, these show that elevated pressure significantly reduces reduction temperature, by around 45 – 65 °C depending on which peak is compared. With TiO_2, in contrast, there is only a minor shift in the reduction profile as H_2 pressure is increased.

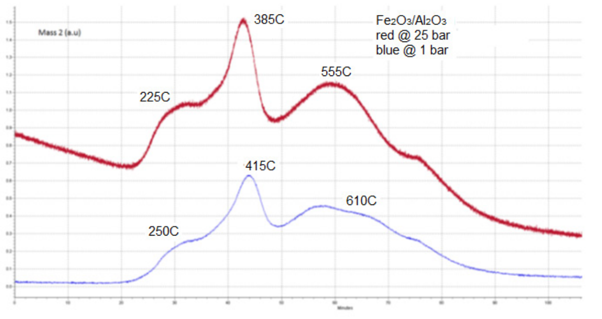
These data suggest that TiO_2 more effectively stabilizes the Fe crystallites. With the SiO_2 increasing pressure enhances reaction, reducing the temperature at which it occurs. A rationale for this is that higher pressure boosts concentration, thereby enhancing the rate of transfer of reactants to the active site. The lack of this trend with the TiO_2 indicates that conversely, with this support, the catalyst is more optimally dispersed with no mass transfer limitations compromising reaction. Al_2O_3 exhibits intermediate behavior, temperature shifts in the region of 30 – 50 °C that show stronger surface interactions than the SiO_2 but less effective stabilization than the TiO_2.



Effect of the high pressure of H_2 over the reduction of Fe_2O_3/SiO_2



Effect of the high pressure of H_2 over the reduction of Fe_2O_3/TiO_2



Effect of the high pressure of H_2 over the reduction of Fe_2O_3/Al_2O_3

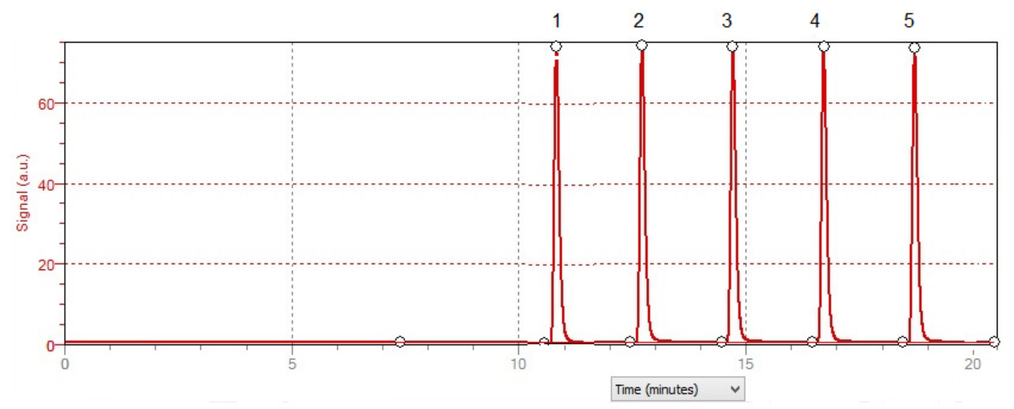
Figure 2: Clear differences between the impact of pressure on the TPR traces associated with different supports (a)SiO_2 (b) TiO_2 and (c) Al_2O_3 highlight the superior performance of the TiO_2 for stabilization of the Fe_2O_3 catalyst.

In summary, in this case, the high-pressure testing capability of the ICCS is valuable because it elucidates the strength of the interactions between the catalyst and different supports, ranking their ability to stabilize the catalyst.

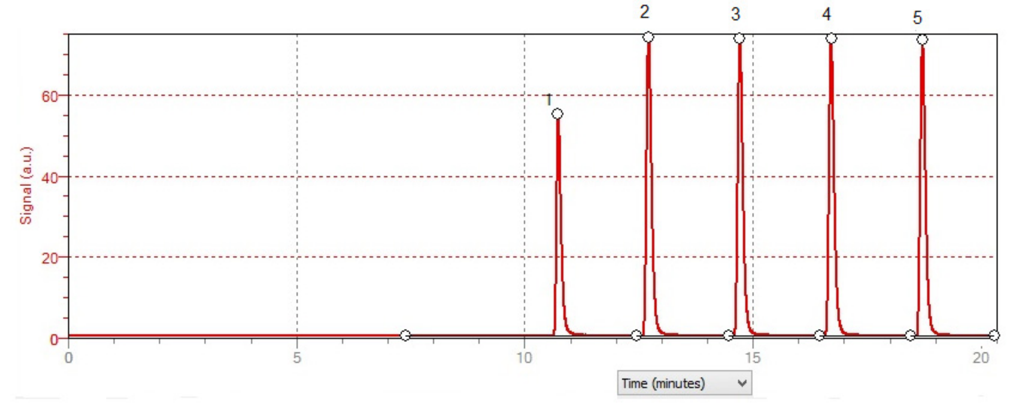
Experimental study 2: Exploring the information generated by high-pressure pulse chemisorption data

Figure 3 shows data from an experiment designed to assess the impact of pressure on pulse chemisorption data; the catalyst under test is Co_3O_4 on Al_2O_3. With this dynamic chemisorption technique, pulses of a chemically active sorbent are introduced in an inert gas flow. Measuring uptake of the reactive gas by compositional analysis allows determination of the number of active sites on the sample and other metrics associated with chemisorption. In this experiment, pulse chemisorption has been carried out at atmospheric and elevated pressure (15 bar) using CO as the probe gas to contrast the results observed. CO bonds strongly and selectively to many of the metals used for catalysis and is often selected for chemisorption.

In this experiment, the dispersion measured for the catalyst is higher at elevated pressure – 18% c.f. 4%. Dispersion is the ratio of the number of active metal atoms to the total amount of metal in the catalyst, so the results indicate that at higher pressure more active metal becomes accessible. This difference can be attributed to enhanced diffusion of the CO into the structure of large particles of Co_3O_4 at elevated pressure and further illustrates the potential for more relevant information gathering if characterization can be carried out at high pressure.



Pulse chemisorption of CO at 35C and AP, Dispersion 4%



Pulse chemisorption of CO at 35C and 15 bar, Dispersion 18%

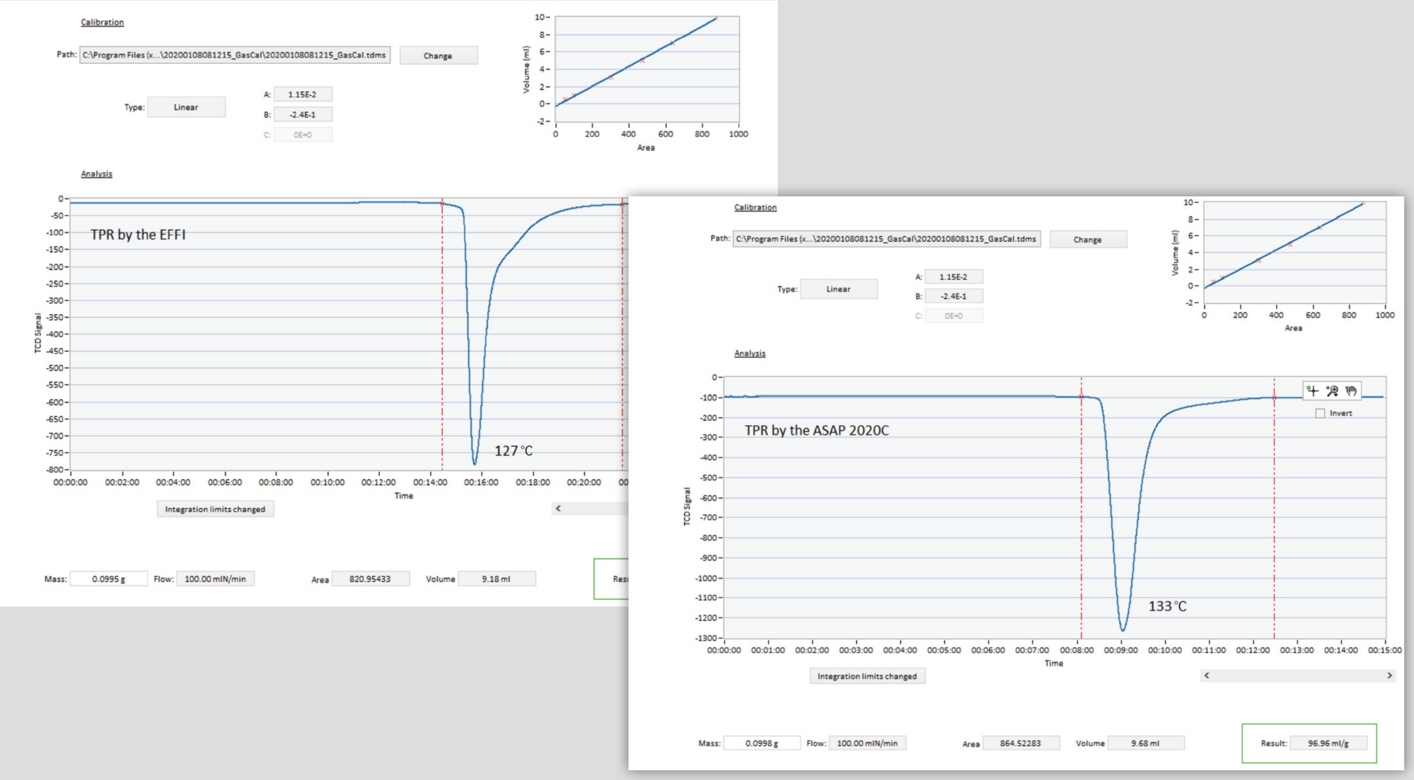
Figure 3: Pulse chemisorption data at 1 and 15 bar shows a significant difference between the measured dispersion at each pressure, illustrating the importance of characterizing the catalyst under representative conditions.

Experimental study 3: Demonstrating data consistency when the ICCS is attached to alternative reactor screening systems.

Figure 4 shows comparative TPR traces for a silver oxide reference material measured by an ICCS connected to a) a Microactivity Effi and b) a Micromeritics ASAP 2020C. The ASAP 2020C is a gas adsorption system with a dedicated exhaust port and a high-temperature furnace for precise temperature control up to 1100 °C. With no integral, online detector, it does not have the capability to perform temperature programmed analyses. In this experiment, it provides a good approximation of a catalyst screening rig, for comparative testing. Total gas flow rate – carrier dosed with a known concentration of hydrogen – was 100 ml/min with both systems.

The results produced with each system are closely similar; a hydrogen consumption of 92.23 ml/g is measured with the Microactivity Effi set up compared with 96.96 ml/g with the ASAP 2020C setup; T_m values are 127 and 133 °C respectively. This similarity illustrates the consistent performance of the ICCS in both experiments, providing evidence of its suitability for connection to different screening units. The results are also consistent with the specification for the material, validating the calibration of the TCD and the performance of both systems.

In a further experiment, the same test setups were used to carry out a pulse chemisorption experiment, using a Pt/alumina reference catalyst. Figure 5 shows the resulting datasets. With the Microactivity Effi set up, Pt dispersion is quantified as 34.05%. The comparable figure with the ASAP 2020C is 30.17%. Consistency between the results provides further evidence of the reproducible performance of the ICCS with different reactor screening units while agreement with published data again validates the system performance. The flexibility of the ICCS to produce closely similar data with alternative reactor systems is extremely valuable since it allows researchers to simply add functionality to existing equipment, rather than investing in completely new test systems.



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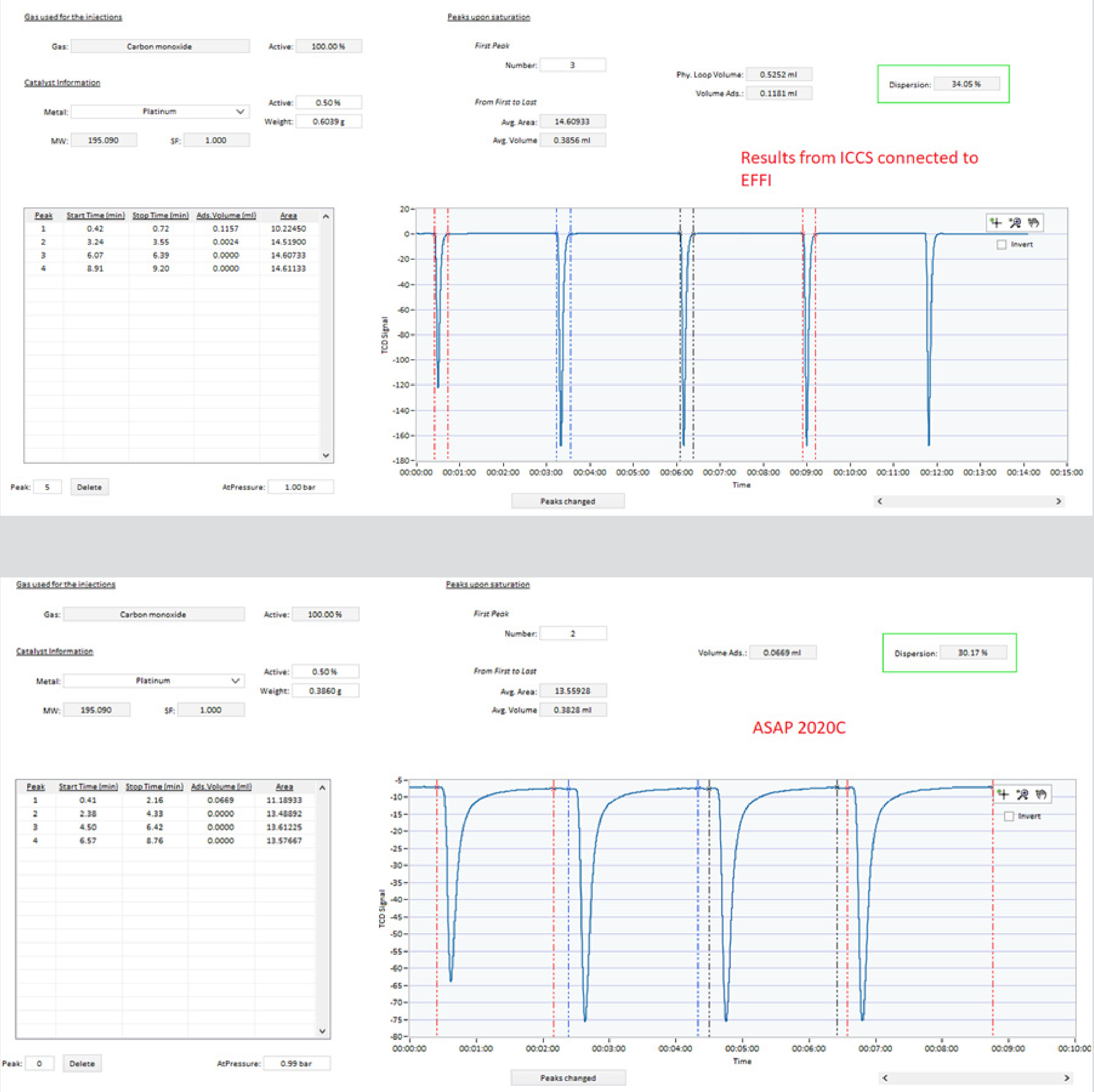
A: 1.15E-2
B: -2.4E-1
C: 0E+0
Mass: 0.0995 g
Flow: 100.00 mlN/min
Area 820.95433
Volume 9.18 ml

Path: C:\Program Files (x...\20200108081215_GasCal\20200108081215_GasCal.tdms
Type: Linear
A: 1.15E-2
B: -2.4E-1
C: 0E+0
Mass: 0.0998 g
Flow: 100.00 mlN/min
Area 864.52283
Volume 9.68 ml
Result: 96.96 ml/g

Figure 4: TPR traces for a reference silver oxide material measured by connecting the ICCS to a) a Microactivity Effi and b) a Micromeritics ASAP 2020C are closely similar and consistent with published data.



Gas used for the injections

Gas: Carbon monoxide
Active: 100.00 %

Catalyst Information

Metal: Platinum
Active: 0.50 %
Weight: 0.6039 g
MW: 195.090
SF: 1.000

Peaks upon saturation

First Peak

Number: 3

From First to Last

Avg. Area: 14.60933
Avg. Volume 0.3856 ml

Phy. Loop Volume: 0.5252 ml
Volume Ads.: 0.1181 ml

Dispersion: 34.05 %

Results from ICCS connected to EFFI

Peak	Start Time (min)	Stop Time (min)	Ads. Volume (ml)	Area
1	0.42	0.72	0.1157	10.22450
2	3.24	3.55	0.0024	14.51900
3	6.07	6.39	0.0000	14.60733
4	8.91	9.20	0.0000	14.61133

Peak: 5
AtPressure: 1.00 bar

Gas used for the injections

Gas: Carbon monoxide
Active: 100.00 %

Catalyst Information

Metal: Platinum
Active: 0.50 %
Weight: 0.3860 g
MW: 195.090
SF: 1.000

Peaks upon saturation

First Peak

Number: 2

From First to Last

Avg. Area: 13.55928
Avg. Volume 0.3828 ml

Volume Ads.: 0.0669 ml

Dispersion: 30.17 %

ASAP 2020C

Peak	Start Time (min)	Stop Time (min)	Ads. Volume (ml)	Area
1	0.41	2.16	0.0669	11.18933
2	2.38	4.33	0.0000	13.48892
3	4.50	6.42	0.0000	13.61225
4	6.57	8.76	0.0000	13.57667

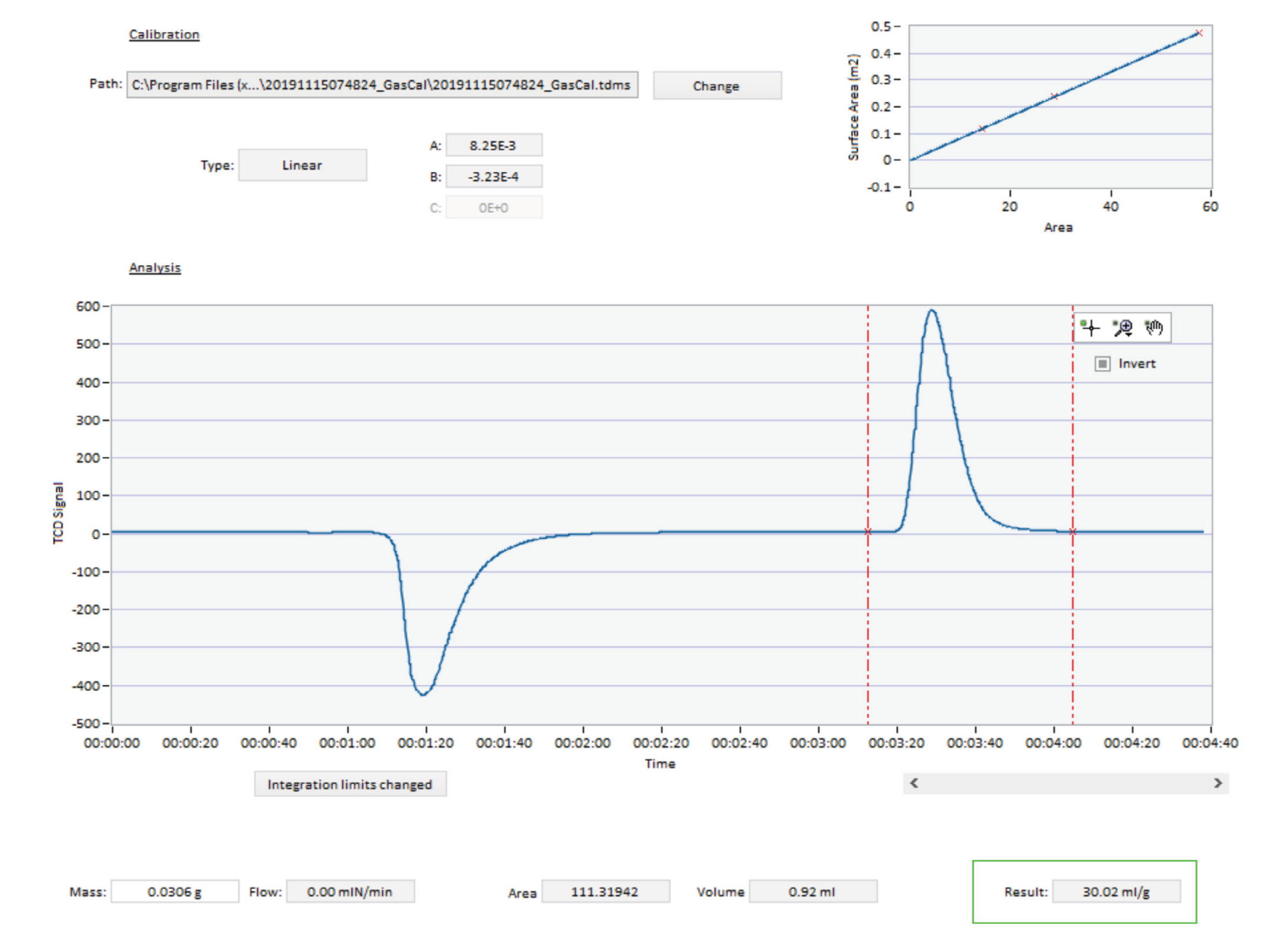
Peak: 0
AtPressure: 0.99 bar

Figure 5: Pulse chemisorption results for a reference Pt/alumina reference catalyst, measured by connecting the ICCS to a) a Microactivity Effi and b) a Micromeritics ASAP 2020C, further demonstrates the suitability of the system for connection to different reactor screening systems; consistency with published data validates the performance of both systems.

Experimental study 4: Demonstrating the potential for surface area measurement

Figure 6 shows surface area data measured with the ICCS for a carbon black reference material. Gas adsorption, the gold-standard technique for the quantification of surface area, involves measurement of the amount of inert gas absorbed by a sample as a function of pressure. Optional functionality for the ICCS includes the ability to apply a single point surface area method to assess changes in the catalyst, especially in the support, induced by reaction. Assessing the texture of a catalyst in this way can be useful for estimating the amount of active species that a given support will stabilize in the dispersed state, at defined temperature and pressure, and for the detection of sintering, a process routinely associated with catalyst deactivation. Sintering is associated with the collapse of support porosity, an associated loss of surface area, and compromised reaction as a result of sub-optimal mass transfer to active sites.

In this experiment, the sample was saturated with a mixture of 30% N_2 in helium at a defined pressure. The sample was then allowed to desorb and the amount of N_2 released was quantified by the TCD of the ICCS system. These data were used to determine the surface area of the sample, producing a value of 30.58 m²/g. The quoted value for the sample is 29.9 ±0.75 m²/g. These results, therefore, provide confirmatory evidence of the performance of the ICCS for surface area determination.



Calibration

Path: C:\Program Files (x...\20191115074824_GasCal\20191115074824_GasCal.tdms

Type: Linear

A: 8.25E-3

B: -3.23E-4

C: 0E+0

Analysis

Mass: 0.0306 g

Flow: 0.00 mlN/min

Area 111.31942

Volume 0.92 ml

Result: 30.02 ml/g

Figure 6: Data from a single point surface area measurement for a carbon black reference material show close agreement with published results for the material.

Conclusion

The ICCS is a powerful catalyst characterization system that attaches directly to existing reaction screening units to boost informational output and data integrity. It allows catalysts to be characterized post-reaction, in the reactor, without the risk of exposure to air or moisture. It also enables characterization at elevated pressure to generate more representative data. The established techniques of chemisorption, notably pulse chemisorption, temperature-programmed analyses – TPR, TPO and TPD – and physisorption can all be applied to gather vital, relevant insight into catalyst reaction, deactivation and regeneration.

Utilizing elements of the technology that underpins the highly successful Microactivity Effi, the ICCS is a perfect complement to this highly automated, off-the-shelf reaction screening system. However, the ICCS demonstrates highly reproducible performance with alternative reaction screening units. The capabilities of the ICCS are therefore easily accessible to any catalyst researcher, who can add this valuable system directly to existing test setups to integrate catalyst characterization and reaction screening and develop catalysts more quickly and efficiently.

Reference

1. S. Mitchell et al "From powder to technical body: the undervalued science of catalyst scale up" Chem Soc Rev, 2013, DOI: 10.1039/c3cs60076a

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About Micromeritics Instrument Corporation

Micromeritics Instrument Corporation is a global provider of solutions for material characterization with best-in-class instrumentation and application expertise in five core areas: density; surface area and porosity; particle size and shape; powder characterization; and catalyst characterization and process development.

The company is headquartered in Norcross, Georgia, USA and has more than 400 employees worldwide. With a fully integrated operation that extends from a world class scientific knowledge base through to in-house manufacture, Micromeritics delivers an extensive range of high-performance products for oil processing, petrochemicals and catalysts, to food and pharmaceuticals, and works at the forefront of characterization technology for next generation materials such as graphene, metal-organic-frameworks, nanocatalysts, and zeolites. Under its premium brand Particulate Systems, Micromeritics discovers and commercializes innovative material characterization technologies that are complementary to core product lines. Cost-efficient contract testing is offered via its laboratory Particle Testing Authority (PTA).

The strategic acquisitions of Freeman Technology Ltd and Process Integral Development S.L. (PID Eng & Tech) reflect an ongoing commitment to optimized, integrated solutions in the industrially vital areas of powders and catalysis.

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