WHITEPAPER

Developing Nanocatalyst Performance: Analytical Techniques for a Knowledge-Led Approach

Micromeritics Instrument Corp.

The science of heterogeneous catalysis continues to see exciting advances particularly in computational modelling and microfabrication techniques and our understanding of how to design and manufacture optimized catalysts for specific applications is becoming increasingly secure. Developments at the nanoscale, in nanoparticles and in nanostructured materials, have a defining role to play in the advancement of heterogeneous catalysis and the synthesis of more efficient and selective processes. In this whitepaper we look at the suite of analytical technologies that Micromeritics offers to support catalyst development and manufacture highlighting their application to nanoscaled materials. These complementary technologies enable the optimization of catalyst preparation processes, precise and detailed characterization of the material made, and the robust assessment of catalytic activity under representative conditions. In combination they deliver a comprehensive information set for catalyst development, evaluation and use.

Trends in catalysis

The use of heterogeneous catalysts allows easy separation of the products and any unreacted reagents from the catalyst, simplifying overall process design. Furthermore, heterogeneous catalysts can usually be regenerated and re-used, to achieve considerable lifetimes. These are significant advantages, but they come at some cost. Compared with their homogeneous counterparts, heterogeneous catalysts tend to offer lower reaction rates and selectivity. Mechanistically they are, in general, more complex, and the understanding required for full optimization is often hard to establish. Developing heterogeneous catalysts that offer reaction performance approaching that achievable with a homogeneous system, to combine the advantages of both, has long been the focus of catalytic endeavor.

Heterogeneous catalysts are frequently used as fine particles and contacted with liquids and gases in fluidized or packed bed reactors, or in the form of pellets or larger structures such as those found in catalytic converters. They may be formed primarily of catalyst, with binder to promote mechanical stability, but are often dispersed on to a high specific surface area support to enhance access to active catalyst sites. For most catalysts in industrial use the particle size of deposited active crystallites typically lies in the range 0.3-0.4 nm to 9 nm; the porosity of supports, synthetic or natural, has historically been poorly controlled.

An examination of how heterogeneously catalyzed reactions proceed highlights the potential benefits of our growing ability to exert greater control at the nanoscale. The first step is diffusion of the reacting molecules to active centers. Structure at the nanometer to micrometer scale impacts this process of mass transfer influencing the rate of transport and the local concentration of reactants, and of products, that develops. Once the reactants reach the active site their conversion proceeds via physical/chemical adsorption and reaction. The chemical nature of the active center and its local environment influence this behavior which is governed by processes occurring at the nanometer scale. Localized hydrophilicity, hydrophobicity and acidity along with stereochemical effects impact both the activity and the selectivity observed [1].

Current trends with respect to catalyst supports are towards synthetic, uniform materials, with well-defined mesoporous and microporous structure at the nanoscale. Metal organic frameworks (MOFs) exemplify the highly tuned materials that can now be manufactured. Such materials deliver exceptionally high specific surface area and offer the flexibility to tailor the size and ‘stickiness’ of pores to control the flow of both reactants and products and optimize localized concentrations towards higher selectivities [2].

With respect to deposited actives the correlation between activity and metal particle size is widely recognized, although quantified relationships can be difficult to establish [3]. Manipulating particle size at the nanoscale to achieve desirable performance is established practice with important changes in reaction rate typically occurring as metal particle size is reduced below 5nm [4]. In recent years the focus has shifted to the potential benefits of using even smaller crystallite sizes to more effectively expose sites for interaction and exert greater control over the electronic interactions that underpin reaction. Transitioning to a single or three-site cluster structure changes the properties of the metal crystallite, inducing ion-like behavior closely similar to that observed in homogeneous catalysis [5,].

The use of strategies such as these to drive heterogeneous catalysis to new levels of performance relies on detailed catalyst characterization, with innovative methods and high-performance instrumentation delivering the precise information required.

Refining preparation: nanoparticle sizing and deposition

As previously discussed, controlling the size of catalyst particles, supported or otherwise, is essential to achieve desirable reaction performance. As used in a process, catalysts typically have a particle size that is optimally measured by laser diffraction. The particle size of fluid catalytic cracking (FCC) materials, for example, typically lies in the region of 10 - 150µm, comfortably within the range of laser diffraction which extends from ~0.04 to 2500µm. However, there is also a need to measure finer nanoparticles, in colloidal suspension, and/or in the preparation of supported/impregnated catalysts. Dynamic light scattering (DLS) efficiently meets this need measuring particle size and particle size distribution on the basis of light scattering intensity across a particle size range that extends from 10µm to less than 1 nm. Furthermore, well-specified instrumentation for DLS also permits the determination of zeta potential by electrophoretic light scattering (ELS). This capability can be used to determine the point of zero charge (PZC) an important parameter for the effective preparation of supported catalysts.

Particle sizing by DLS

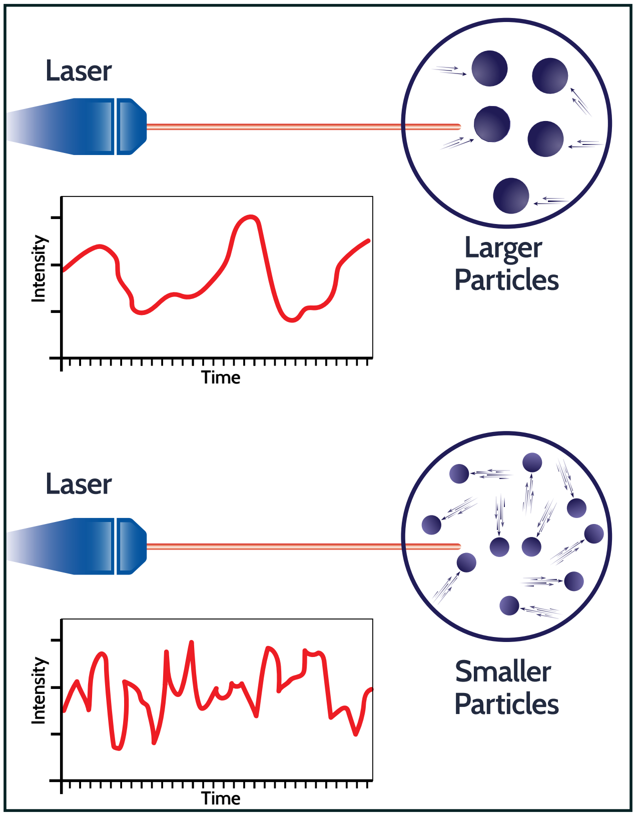


Figure 1: DLS determines particle size in the nanoregion from measurements of fluctuations in light scattering intensity.

Fine particles in a liquid dispersion exhibit Brownian motion, moving at a speed that is directly proportional to their size, as a result of collisions with liquid molecules. Illuminating such particles with a coherent light source produces a light scattering pattern which exhibits short-term intensity fluctuations. These correlate with the speed of movement of the particles (see figure 1). In a DLS measurement particle size is calculated via the Stokes-Einstein relationship, following the determination of particle velocity from a detected light scattering pattern. The detector set-up directly influences the concentration and size range over which measurements can be made with features such as Non-Invasive Back-Scatter (NIBS) detection and Multi-Angle-DLS significantly enhancing the utility of the technique.

Zeta potential by ELS

Figure 2 shows the layers of charged particles that form around a particle with a surface charge in solution. The Stern layer is an immobile layer of particles, of opposite charge to the particle surface. Beyond this is a mobile layer influenced by the charged particle, the edge of which is the shear plane for the particle; this plane can be thought of as marking the boundary of influence of the charged particle. The technique of ELS is used to determine zeta potential, the charge at the shear plane. A suspension with a large absolute value of zeta potential will exhibit electrostatic stability since the particles are sufficiently charged to repel one another. Lower absolute values of zeta potential are, conversely, associated with flocculation, aggregation and potentially separation. The PZC is the point at which zeta potential is zero, the point of minimum system stability.

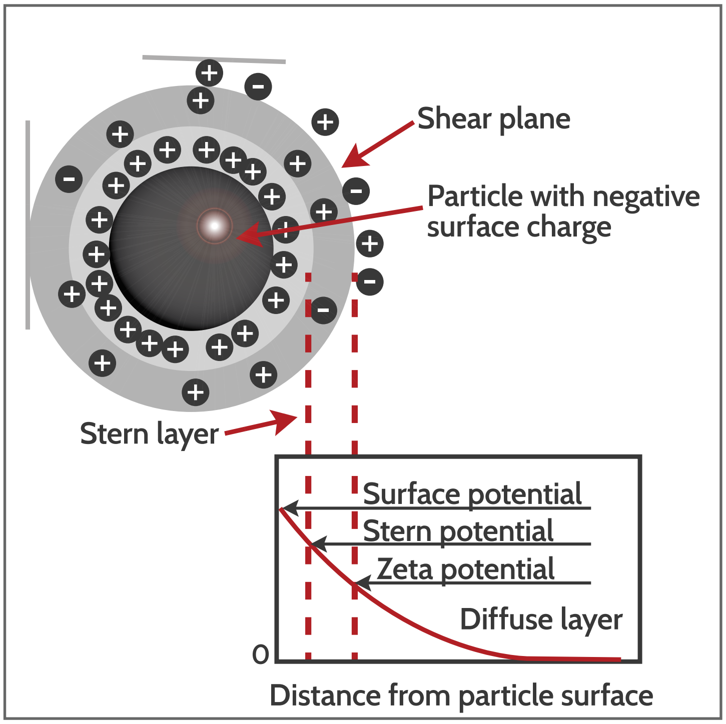


Figure 2: Zeta potential is the charge at the edge of the shear plane and can be measured to determine whether a suspension will be electrostatically stable.

In an ELS measurement sample is placed between two charged electrodes (see figure 3). Positively charged particles in the sample move towards the cathode while those that are negatively charged attract to the anode. The velocity at which particles move is dependent on the field strength applied, the viscosity and dielectric constant of the medium through which the particles are moving and the zeta potential of the particles. In ELS, particle velocity is detected from the light scattering pattern, using a Laser Doppler method and the resulting values are then used to determine zeta potential.

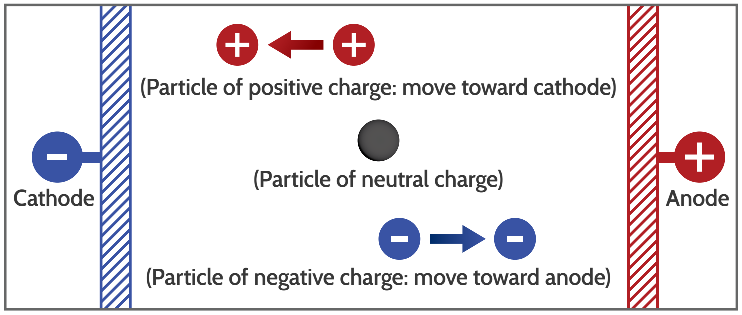


Figure 3: ELS determines zeta potential from measurements of the speed at which particles move in an electric field.

Since zeta potential is zero at the PZC, zeta potential measurements are one way of determining the pH associated with the PZC to identify optimized conditions for the preparation of supported catalysts. This is a simple experiment, essentially a pH titration, in which zeta potential is measured as a function of pH for a solution containing the catalyst support. Carrying out catalyst preparation at a pH close to the PZC encourages effective and controlled deposition – since the catalyst carrying solution is at a point of maximum instability – and has been shown to be an effective way of boosting catalyst performance (see case study).

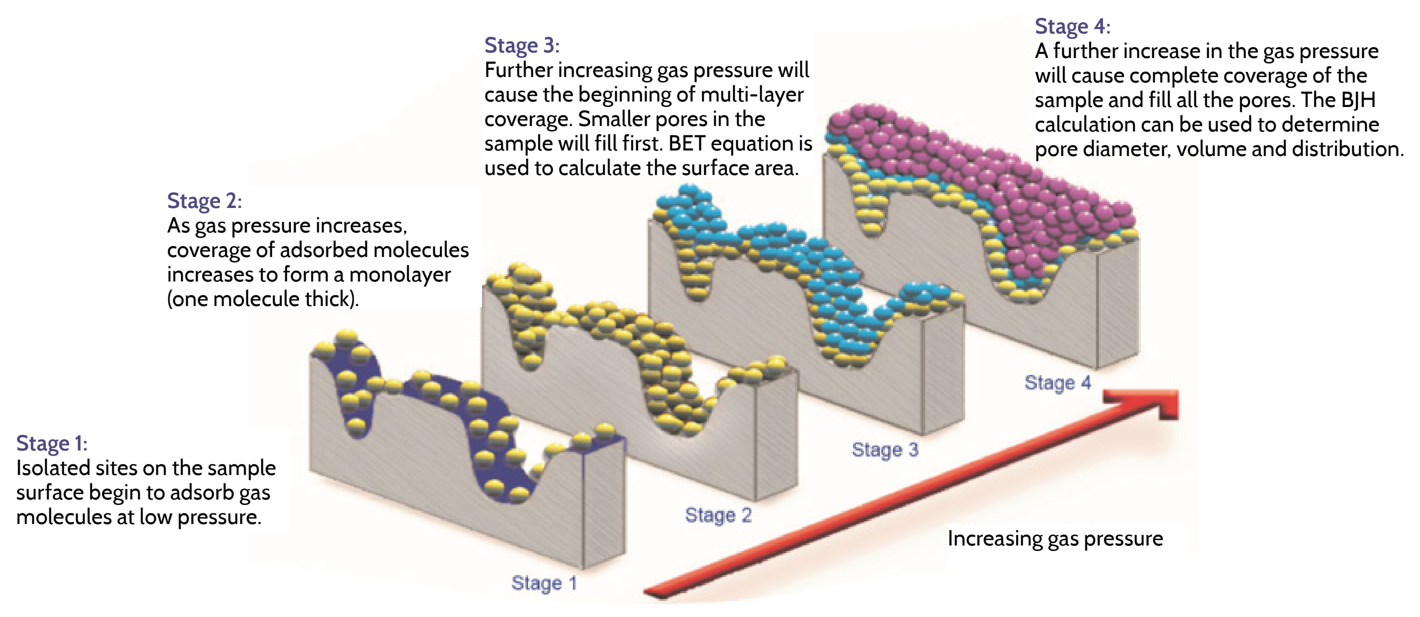
Precise characterization into the nano-region: quantifying surface area and active sites

When it comes to characterizing a prepared catalyst, or indeed one that has become damaged or deactivated with use, gas adsorption is the gold standard technique. In physical gas adsorption, or physisorption, an inert adsorptive gas is used to measure specific surface area, total pore volume and pore volume distribution by pore size, from the macropore region down through the mesoporous to the microporous, to a minimum pore size of around 0.3 nm. Chemical adsorption, or chemisorption, on the other hand involves the use of an adsorptive gas that interacts with the surface of the sample to quantify percentage metal dispersion, active metal surface area, the size of active particles, and the surface acidity of catalytic materials.

Physisorption

Physical adsorption is the result of relatively weak interactive forces (van der Waals and electrostatics) between the solid surface and the gas and occurs on all surfaces exposed to the adsorptive gas. It results in the formation of multiple layers and is easily reversed, by reducing pressure or increasing temperature. Figure 4 shows what happens at a molecular level in a physical gas adsorption measurement as the sample is exposed to an adsorptive gas at progressively higher pressures.

In a gas adsorption apparatus, a precisely defined volume of gas, at known temperature and pressure, is allowed to equilibrate with the surface of a decontaminated sample. The number of moles of gas adsorbed is calculated, by difference, using the gas law once an equilibrium pressure has been reached; effective temperature control and an accurate measurement of system volume is essential. Charging the apparatus to a higher pressure and repeating this measurement process produces a plot of number of moles of gas adsorbed as a function of equilibrium pressure, an adsorption isotherm that is a unique fingerprint for the material. Desorption behavior can be studied in a closely analogous way, by reducing pressure. This is not usually necessary for surface area measurement but can be valuable for detailed porosity characterization.



Stage 1:
Isolated sites on the sample surface begin to adsorb gas molecules at low pressure.

Stage 2:
As gas pressure increases, coverage of adsorbed molecules increases to form a monolayer (one molecule thick).

Stage 3:
Further increasing gas pressure will cause the beginning of multi-layer coverage. Smaller pores in the sample will fill first. BET equation is used to calculate the surface area.

Stage 4:
A further increase in the gas pressure will cause complete coverage of the sample and fill all the pores. The BJH calculation can be used to determine pore diameter, volume and distribution.

Figure 4: Increasing pressure in a physisorption analyses results in the build up of multiple layers of molecules on the surface of the material and the progressive filling of accessible pores.

The surface area of the sample is calculated directly from an adsorption isotherm, typically using the Brunauer, Emmett and Teller (BET) theory [6] which correlates monolayer capacity, the quantity of gas associated with the adsorption of a monolayer across the surface of the sample, with measured parameters. The surface area of the sample is easily calculated from monolayer capacity since the surface area occupied by one molecule of adsorptive is a known quantity. Porosity is quantified from the same isotherm via a procedure developed by Barrett, Joyner and Halenda (BJH) [7] using the Kelvin model of pore filling.

	Chemisorption	Physisorption
Temperature Range:	Unlimited	Near or above dew point of gas
Enthalpy of Adsorption:	Typically (80 - 800 kJ/mol)	Typically (5 - 80 kJ/mol)
Nature of Adsorption:	Irreversible	Reversible
Saturation:	Limited to one layer	Multilayer formation
Adsorption Kinetics:	Variable. Activated process	Fast non-activated process

Figure 5: Physisorption and chemisorption are different processes, each revealing valuable information about a catalyst.

Chemisorption

Chemical adsorption is quite different from physisorption, involving a much stronger, irreversible interaction between the adsorptive gas and the solid surface (see figure 5). During this irreversible interaction the adsorbing gas or vapor molecule splits into atoms, radicals or ions, electrons are shared, and chemical bonds form. As a result, chemisorption is localized, occurring only on clean, active sites and ceasing when the adsorbate can no longer directly contact the surface; it is a single layer process (see figure 6).

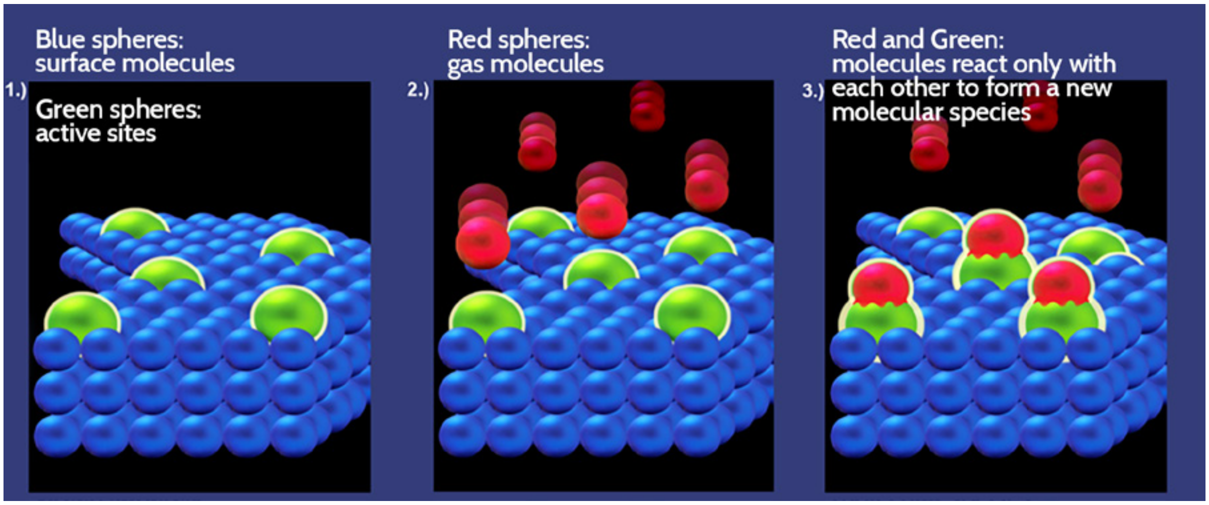


Figure 6: Chemisorption is an irreversible process that only occurs at clean active sites, making it a single layer process.

While physisorption decreases with temperature chemisorption exhibits the opposite trend. Indeed, it may not occur at all to any detectable degree below certain temperatures and is typically associated with an activation energy. The apparatus used for chemisorption is often identical to that for physisorption but clearly these differences have an impact on the equipment and techniques used.

Chemisorption measurements can be carried out using a static volumetric technique analogous to that described for physisorption or using a dynamic or pulsed technique which effectively titrates the active surface. This latter technique is enabled by the addition of a thermal conductivity detector (TCD) which senses and quantifies changes in gas concentration. With this set-up it becomes possible to carry out temperature programmed analyses to gain further insight into catalytic performance. These include temperature programmed oxidation (TPO), temperature programmed reduction (TPR), temperature programmed desorption (TPD) and temperature programmed surface reaction (TPSR).

In a temperature programmed analysis, a TPR, for example, the behavior of the catalyst is tracked through the application of a specific temperature profile. For a reduction an appropriate gas mixture would be hydrogen (high thermal conductivity) in argon (low thermal conductivity). The analysis is started at a temperature that is low enough to preclude reduction to gain a baseline conductivity measure for the gas. As temperature is ramped up, hydrogen is adsorbed, reacting with oxygen to form water which then desorbs and is removed from the system via a cold trap. The non-condensible gas stream becomes less conductive as hydrogen concentration falls relative to that of argon. The TCD detects this change in hydrogen concentration allowing the rate of reaction to be determined (see case study).

Chemisorption analyses can be a cost-efficient way to investigate catalyst behavior, to determine whether surface modification results in more or fewer active sites, for example, to assess the oxidation state of the catalyst and to see under what conditions it becomes more or less oxidative/reductive, more or less reactive. What such analyses cannot provide is the key metric of turnover, the mass of a specific product that will be made per number of active sites. These parameters can only be determined by knowing the number of active sites and testing under representative conditions, using a microreactor or pilot plant.

Case study: Preparing and characterizing Co/Al_2O_3 catalysts for the dry reforming of methane

In a study carried out by researchers at the Georgia Institute of Technology (Atlanta, Georgia) and Pacific North West Laboratory (Richland, WA) Co/Al_2O_3 catalysts prepared by two different techniques were characterized and evaluated for the dry reforming of methane. Their study was published in Green Chemistry [8] and the discussion here is limited to a brief description of the preparation techniques used and their impact as quantified primarily by physisorption, chemisorption, and TPR studies. The two preparation methods used were controlled adsorption (CA) and direct impregnation (DI).

Catalyst preparation

The PZC of the Al_2O_3 was determined using the technique of potentiometric titration, to optimize conditions for Co^{2+} deposition, and was found to occur at a pH of 7.7. Precipitation studies were also carried out to support optimization of the deposition process. Based on these results a pH of 8.5 was selected for CA, just above the PZC but below the point at which bulk precipitation was observed. Cobalt was deposited on the Al_2O_3 support using a cyclical 2-hour procedure during which pH was periodically re-adjusted (every 30 minutes) back to 8.5. The resulting 2 wt% Co/ Al_2O_3 (2CoCA) catalyst sample was filtered and washed twice with de-ionized water.

DI is a standard impregnation method routinely implemented to synthesize industrial catalysts that involves exposing the support to a volume of solution matched to its pore volume. Here, the weight loading for catalysts prepared by DI was matched to that of the 2CoCA catalyst and the pore volume of the support was determined by nitrogen physisorption. The precursor solution and support were mixed for 1 hour at room temperature to produce a 2 wt% Co/ Al_2O_3 catalyst designated 2CoDI.

Both prepared catalysts were dried and calcined for 3 hours.

Catalyst characterization and performance

Samples of the calcined catalysts were characterized using a range of techniques including nitrogen physisorption (Micromeritics ASAP 2020), TPR (Micromeritics AutoChem II 2920 with TCD detector) and hydrogen chemisorption (Micromeritics Chemisorb 2750).

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)	Elemental Analysis (wt% Co)	Average Metal Particle Diameter (nm)	Dispersion (%)
2CoCA	88	0.35	14.7	2.01	19.4	5.1
2CoDI	84	0.31	16.0	2.02	28.0	3.5

Table 1: Physisorption and chemisorption data for the two catalysts highlight similarities and differences resulting from the preparation methods used. Note: Elemental analysis was carried out by ICP.

Physisorption data reveal that the surface area of the two catalysts is similar with both exhibiting a slightly lower surface area and larger pore volume and pore diameter than that of the fresh support (data not shown). However, the hydrogen chemisorption data show that the 2CoCA catalyst has a higher dispersion and a smaller particle size. TEM images elucidate the size differences indicating that while Co particles on the 2CoDI catalysts lie in the 10 to 40 nm size range, most of those on the 2CoCA samples are just 6 – 8 nm. The presence of a few relatively large particles on the CA samples boosts the average.

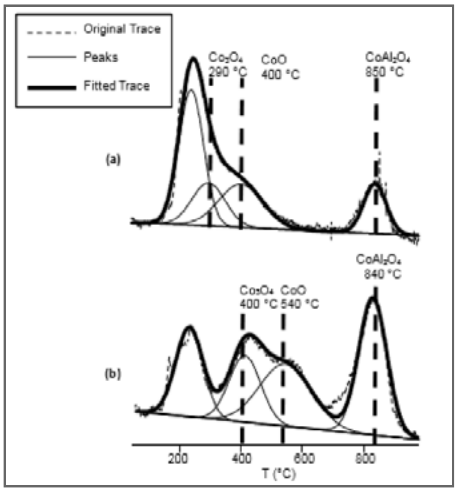


Figure 7: TPR profiles for (a) 2CoDI and (b) 2CoCA highlight clear differences in the reductive behavior of the two catalysts.

Peak Assignment	-NO3[a]	Co_3O_4 --> CoO	CoO --> Co^0	$CoAl_2O_4$
2CoDI ($\mu molH_2/g_{cat}$)	-	79	105	61
2CoCA ($\mu molH_2/g_{cat}$)	-	93	141	168
[a] Hydrogen consumption omitted due to volatilization of nitrate species that affect TCD response				

Table 2: Hydrogen consumption per gram of sample, for each TPR peak, indicates the 2CoCA proceeds further to complete reduction than the 2CoDI sample.

Data from TPR studies further differentiate the two catalysts (Figure 7, Table 2). The four peaks are assigned to: decomposition of the residual nitrate (~200°C); reduction of Co_3O_4 to CoO; reduction of CoO to metallic Co; and the reduction of surface $CoAl_2O_4$. The recorded hydrogen consumption figures correspond to a total reduction of 60% for the 2CoCA catalyst and 40% for the 2CoDi catalyst.

The peaks relating to the reduction of Co_3O_4 to Co^0 are more distinct in the trace for the 2CoCA catalyst than for the 2CoDi catalyst and occur at higher temperature indicating that the controlled method leads to stronger metal – support interactions. The ratio of the areas of these peaks should be 1:3 for complete reduction but are, instead, 1:1.3 for the 2CoDi catalyst and 1:1.5 for the 2CoCA catalyst. Neither sample is fully reduced to the metallic state but the reduction proceeds furthest to completion with the 2CoCA catalyst. The relative magnitude of the fourth peak is attributed to a greater amount of spinel phase material in the 2CoCA sample. A rationale for this is that strong metal-support interactions promote surface spinel formation by bringing the metal and support into intimate contact.

Full details of the reaction trials carried out are not included here but in methane dry reforming tests the catalysts were also clearly differentiated with the 2CoCA samples exhibiting superior performance – higher methane and carbon dioxide conversion and slower deactivation. In summary, this study illustrates how controlling adsorption conditions with reference to the PZC results in more highly dispersed catalysts, with smaller particle sizes, that have higher catalytic activity and superior reaction performance.

Establishing performance: quantifying activity and selectivity under representative conditions.

Testing the performance of a catalyst in a specific reaction calls for an experimental unit capable of handling liquid and gas feeds, of operating at closely controlled temperature and pressure, and of delivering products and unreacted reagents for timely analysis. Pilot scale units can be expensive to build and costly to run so smaller lab-scale units are preferable for the majority of catalyst studies. Such systems can be built in-house, but the time and effort required to design, build and optimize a unit that delivers sufficiently sensitive performance should not be under-estimated. Efficient ongoing operation relies not just on the mechanical design of the unit but on effective control and automation with a user-friendly interface/integral software significantly boosting ease of operation and data processing. A more cost-efficient option can be to purchase an ‘off-the-shelf’ system with the required features, as exemplified by the Microactivity EFFI (PID Eng & Tech), an advanced, fully automated, customizable lab system for measuring catalyst performance (see figure 8).

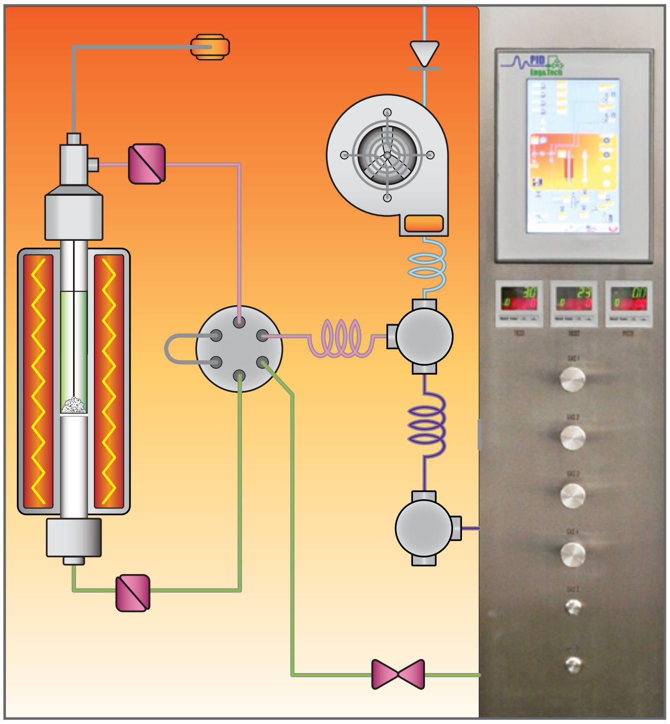


Figure 8: A schematic of the Microactivity EFFI, a customizable laboratory system that enables representative catalyst assessment with just a few grams of material.

At the heart of the Microactivity EFFI is an interchangeable stainless steel (316) cylindrical reactor with an internal diameter of 9 mm and length 300 mm; catalyst sits on a 20μm porous support plate. The reactor is encased by ceramic fiber furnaces with a very low thermal inertia that ensure responsive temperature control, up to 1100°C, with minimal overshoot. Gas(es) are fed into the reactor using mass flow control, with both feed pipework and the reactor sitting in a temperature controlled hot box, a key design feature, which is maintained at up to 200°C to avoid condensation in the system. An HPLC pump delivers liquid feeds to the hot box which are vaporized and mixed with reactant gases prior to entering the reactor.

Patented, high-precision micrometric servo-controlled valves are used to achieve automated pressure control, up to 100 - 200 bar, and in combination with a patented capacitance level sensor to maintain a liquid seal in the liquid/gas separator of less than 1 ml. This separator runs at around 4°C, splitting condensable and gaseous products (or unreacted feeds) for analysis typically by liquid and gas chromatography (LC and GC) respectively; online mass spectrometry is the faster, more responsive alternative. The quasi-zero dead volume of the whole system allows almost real-time product analysis which can be essential to detect, and change, conditions that are causing deactivation of the catalyst, before it is lost. The entire system is fully automated with experimental control and data processing driven from a streamlined user interface.

Systems such as these allow the representative testing of catalysts with very small quantities of material making them far more accessible in terms of cost and logistics than pilot scale trials that may need around 5 to 20 kg of catalyst. Their use enables the detailed scoping of catalyst performance to provide data for catalyst selection and optimization. Microreactors can be operated singly or in dual configurations – parallel or series – to, for example, study a reaction/regeneration system. With the Microactivity EFFI (ICCS - In-situ Catalyst Characterization System) it is also possible to carry out pulse chemisorption experiments making it feasible to characterize the catalyst in situ before and after reaction to, for example, determine reaction conditions that will help to maintain activity and to elucidate deactivation mechanisms. The scale-up of multiphase systems is always complex, and heterogeneously catalyzed reactions are challenging in this regard but there are established pathways to use measurements made at this scale to design pilot/commercial scale processes, making these systems a powerful tool for advancing an understanding of catalytic performance.

Case study: Assessing the performance of bifunctional zeolite supported silver catalysts for the conversion of glycerol to allyl alcohol.

In a study carried out by researchers at ETH Zurich (Switzerland), catalysts composed of silver (Ag) nanoparticles supported on a modified hierarchical ZSM-5 zeolite (H-Z40-haw) were optimized for the gas phase hydrogen mediated conversion of glycerol to allyl alcohol. Glycerol is the main byproduct from biodiesel production and its efficient conversion to chemicals such as allyl alcohol that can be used to synthesize other, more valuable products is an issue of considerable industrial interest. The study is described in full in a paper in ChemCatChem [9] with the discussion limited here to experiments carried out using a Microactivity EFFI reactor to optimize Ag loading and operating conditions to enhance productivity and to assess catalyst stability.

In the set-up used nitrogen and hydrogen were fed into the reactor on mass flow control; glycerol was pumped into the system as a 20 wt% in water solution using a high-performance liquid chromatography (HPLC) pump. A catalyst charge of 0.1g was used (particle size in the range 0.2 to 0.4 mm), loaded into a tubular reactor design with an internal diameter of 6 mm. The post-reactor separator was maintained at 273K.

To assess each catalyst, the reactor was charged, and the system was then heated to 673K under nitrogen (100cm^{3}min-1). The catalyst was then reduced by being subject to a gas flow with a composition of 20 vol% hydrogen (balance nitrogen) for two hours. Reaction conditions were subsequently changed to the required temperature, pressure and gas composition and allowed to equilibrate prior to introduction of the liquid feed at a rate of 0.1 cm3min-1. As the reaction proceeded liquid samples were periodically collected from the separator and analyzed by HPLC to assess performance via the following metrics:

- **Conversion** – the ratio of moles of glycerol reacted to moles of glycerol fed
- **Selectivity** - the number of moles of a specific product formed per mole of glycerol reacted
- **Yield** – the product of glycerol conversion and selectivity to a specific product, under defined conditions.

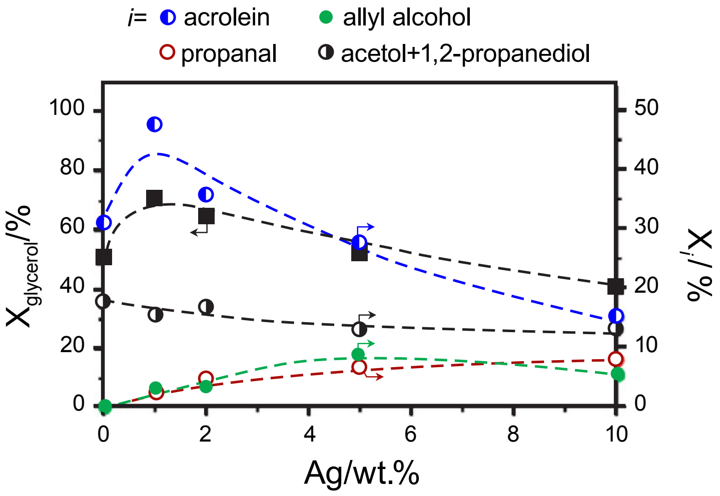


Figure 9: Glycerol conversion and the selectivity of the reaction to acrolein and allyl alcohol varies significantly with Ag loading.

A carbon balance was also carried out by calculating the ratio of the number of moles of carbon in the condensate to the number of moles in the feed; experimental error determined on the basis of three repetitions was within 5%.

Figure 9 shows data from experiments carried out to optimize Ag loading with tests carried out with catalysts containing 0, 1, 2, 5 and 10% wt% Ag. These identify an Ag loading of 5% as optimal in terms of allyl alcohol yield. The conversion of glycerol to allyl alcohol is a two-step process requiring a bifunctional catalyst capable of exhibiting both acid and redox behaviors (see figure 10). At lower Ag loadings the conversion of acrolein to allyl alcohol is relatively inefficient, a result attributable to a lack of redox centers, while at Ag loadings in excess of 5% the rate of dehydration to acrolein is limiting with respect to allyl alcohol production. Please see the original paper for further details on how catalyst loading changes the size of catalyst particles and how loading and particle size, in combination, give rise to these effects.

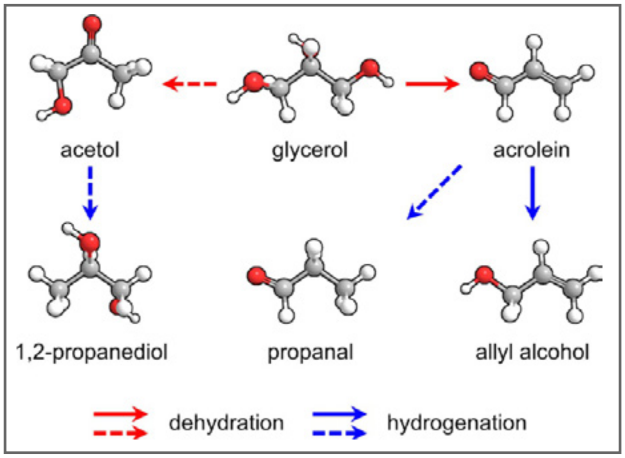


Figure 10: A simplified reaction scheme for the conversion of glycerol to allyl alcohol showing the desired reaction pathway (solid lines) and pathways leading to key by-products (dashed).

The performance of the 5 wt% Ag catalyst was optimized with respect to temperature (in the range 523 to 773K), hydrogen pressure (in the range 0 to 40 bar) and weight hourly space velocity (WHSV) (see figures 11 a to c). Performance was also assessed as a function of time to investigate the potential lifetime of the catalyst (see figure 11d). The results show that while higher temperatures drive up glycerol conversion, selectivity to allyl alcohol falls markedly at temperatures in excess of 673K. Higher temperatures are also associated with an observed increase in coking and the formation of undesirable solid deposits on the catalyst surface. Conversion and selectivity to allyl alcohol both increase with hydrogen pressure up to 40 bar. Higher values of WHSV, shorter contact times, are associated with a decrease in conversion with selectivity passing through a maximum, at a WHSV of around 12 (1000 h-1). Under fully optimized conditions selectivity to allyl alcohol is around with a glycerol conversion of 80%; the stability of the catalysts is relatively high over 100 hours under these conditions, following an early, minor loss of activity (see figure 11 d).

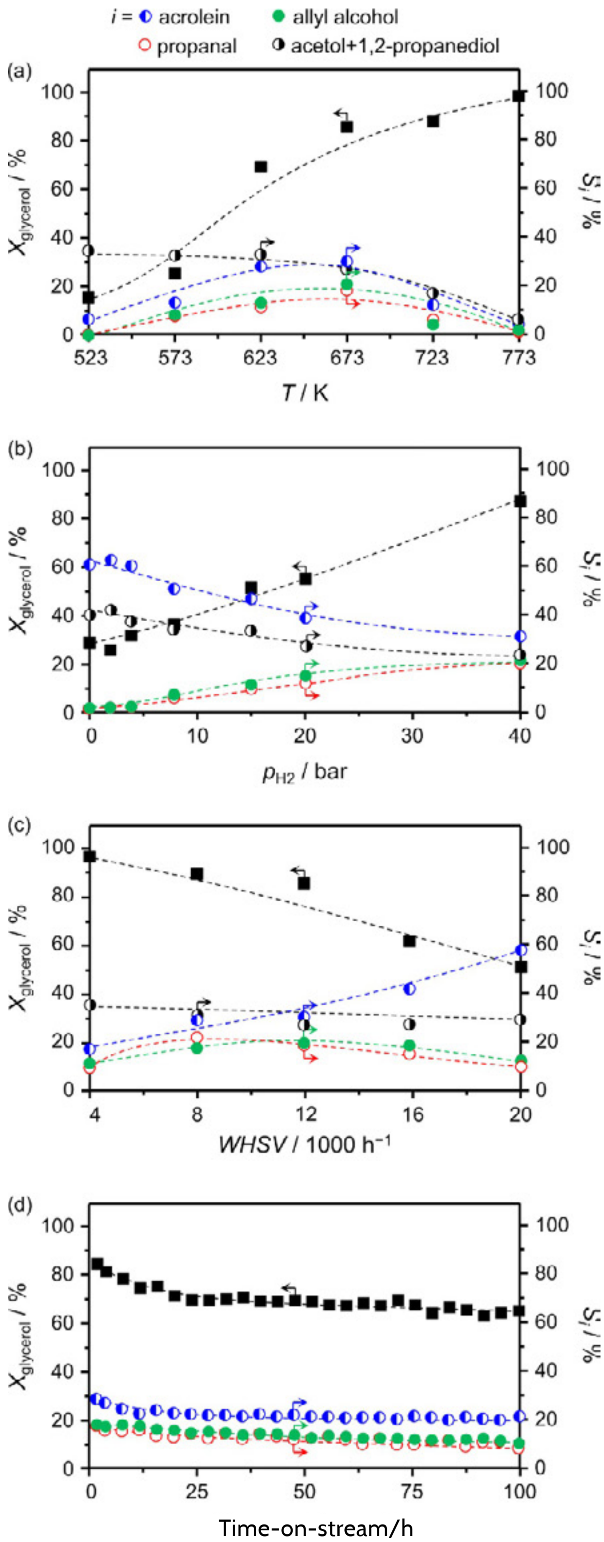


Figure 11: Microreactor trials make it possible to investigate the impact of a) temperature b) hydrogen pressure and c) weight hourly space velocity (WHSV) using minimal catalyst volumes. Catalyst stability can also be assessed (d).

The full paper describing this work provides significant detail as to the rationale for the observed results and shows how microreactor trials dovetail with analyses carried out with other characterization tools already discussed such as physisorption to provide detailed insight into catalyst behavior. However, a key point to note is the wealth of data that testing with the Microactivity Effi system generates to directly support process development, using only minimal quantities of catalyst, and over a relative short timeframe.

In conclusion

Heterogeneous catalysis remains an area of considerable technical challenge but offers the potential for highly selective reaction within a simplified process design. These are essential elements of sustainable, more environmentally benign chemical manufacturing. Nanocatalysis, the development of nanostructured support materials with precisely controlled porosity and surface area, for example, and/or the shift to increasingly small active metallic clusters to promote greater selectivity, is a vital area of focus. Our growing understanding of the factors that influence behavior in the nanoregion and how to control them holds considerable promise for improving heterogeneous catalyst performance. Accurate and precise analytical data provide a foundation for progress, enabling researchers to refine preparation methods, to probe the properties of the resulting materials and to realistically assess catalyst performance, with confidence and cost-efficiency.

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