



Catalysis Applications

INTRODUCTION

Catalysis Applications

Catalysis is the process of increasing the rate of a chemical reaction by the addition of a substance known as a catalyst. The reaction itself does not consume the catalyst but it does allow more preferential products to be produced at a faster rate under more favourable conditions.

The use of catalysts is vitally important to all areas of modern life and the economic impact of catalysis is huge, contributing 30–40% of global GDP. It is estimated that 85% of all manufactured products involve catalysis somewhere in their production chain, and such products have considerable impact in:

- ▶ **Energy** – petrochemicals
- ▶ **Healthcare** – pharmaceuticals
- ▶ **Materials** – polymers, batteries
- ▶ **Transport** – catalytic convertors
- ▶ **Environment** – water, air quality, renewable and bio-produced materials

Hidden Analytical produces a range of gas analysis systems that have been crucial in the study of the catalytic process, from catalyst characterisation and development to reaction monitoring and optimisation.



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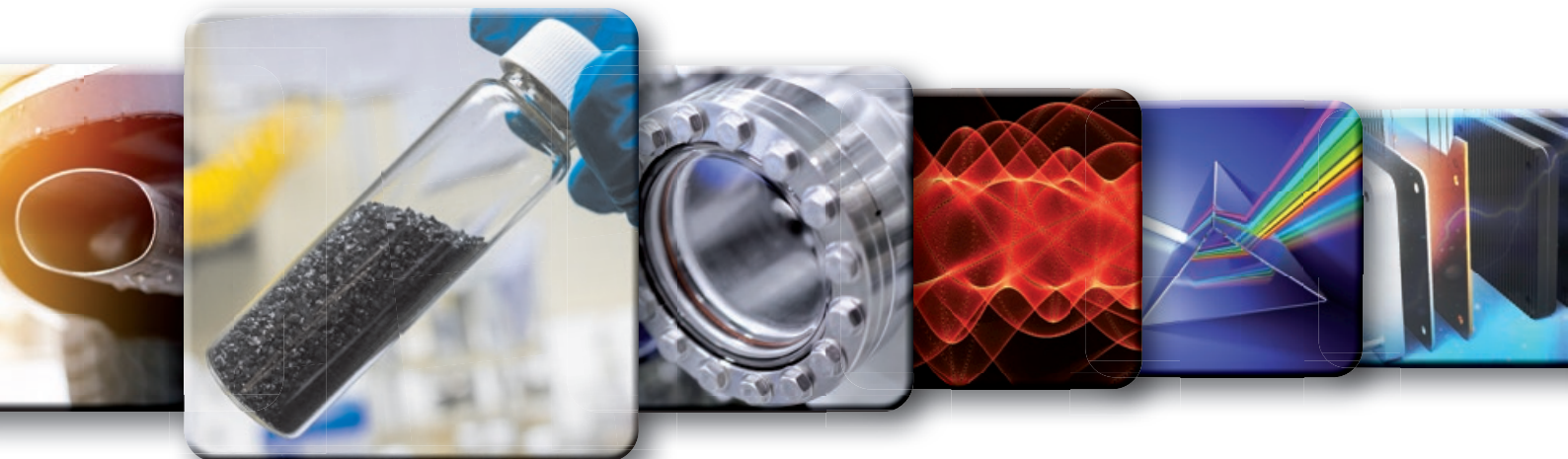
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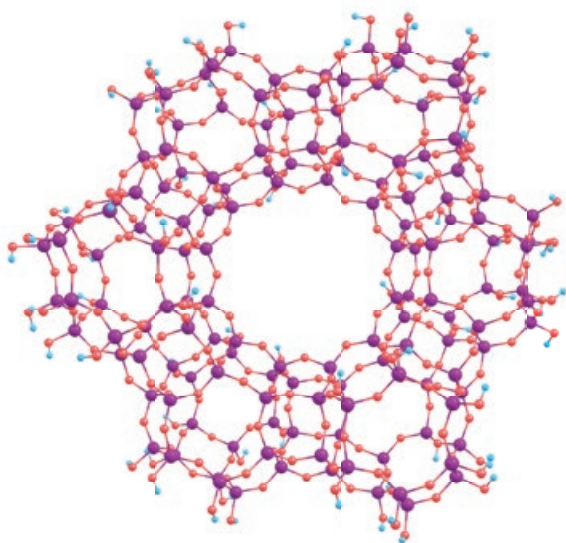
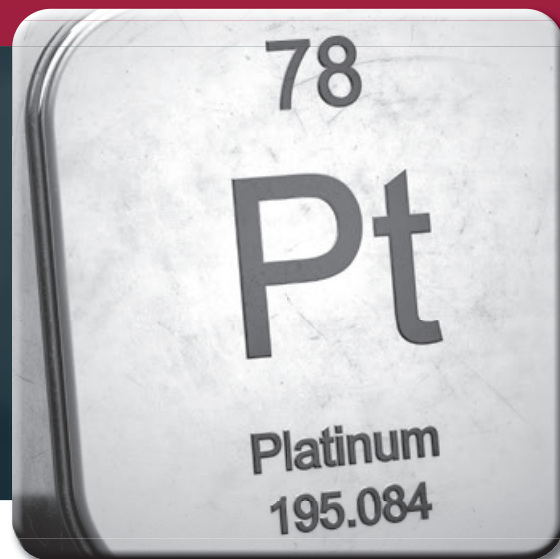
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Heterogeneous Catalysis



Heterogeneous catalysis covers an enormous range of chemical reactions. The defining feature of heterogeneous catalysis is the reaction of gas or liquid phase reactants occurring at the surface of solid catalysts. As the surface is where the reaction occurs the catalyst is generally prepared in ways that produce large surface areas per gram of catalyst. Examples of this are finely divided metals, metal gauzes, metals incorporated into supporting matrices, and metallic films.

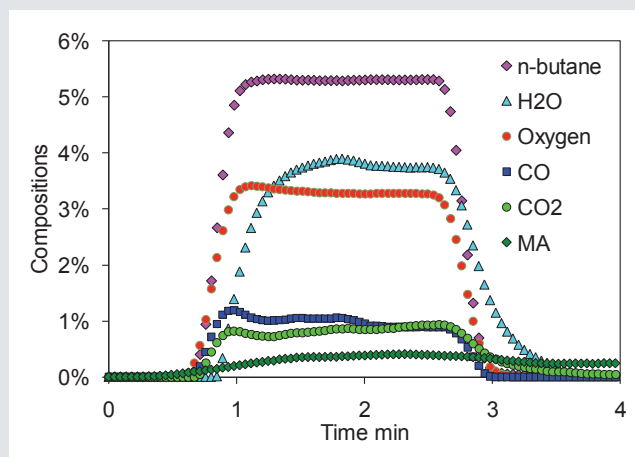
The wide variety of gas or vapour phase reactions are ideal for study with the Hiden gas analysis products.

MALEIC ANHYDRIDE PRODUCTION

Maleic anhydride (MA) is an important intermediate chemical primarily used in the production of resins and polymers. Commercially it is produced from the partial oxidation of n-butane by air over a vanadium pyrophosphate (VPP) catalyst. There has been huge research effort to better understand the different aspects of this industrially attractive reaction including mechanism, dynamic catalyst phase evolutions as well as the effect of redox operating conditions such as gas/solid residence time, temperature, pressure and gas composition on the reaction yield.

The example shown here of the transient analysis of the partial oxidation of n-butane is part of a wider investigation into the effect of a range of redox conditions covering the actual conditions existing in industrial reactors. The transient redox conditions are simulated using the Hiden CATLAB microreactor coupled to a QGA gas analyser. Characterising the transient behaviour of the VPP catalyst

under different operating conditions can then be used in modelling the underlying transient kinetics of this complex reaction over the full range of studied operating conditions.



MS transient response.

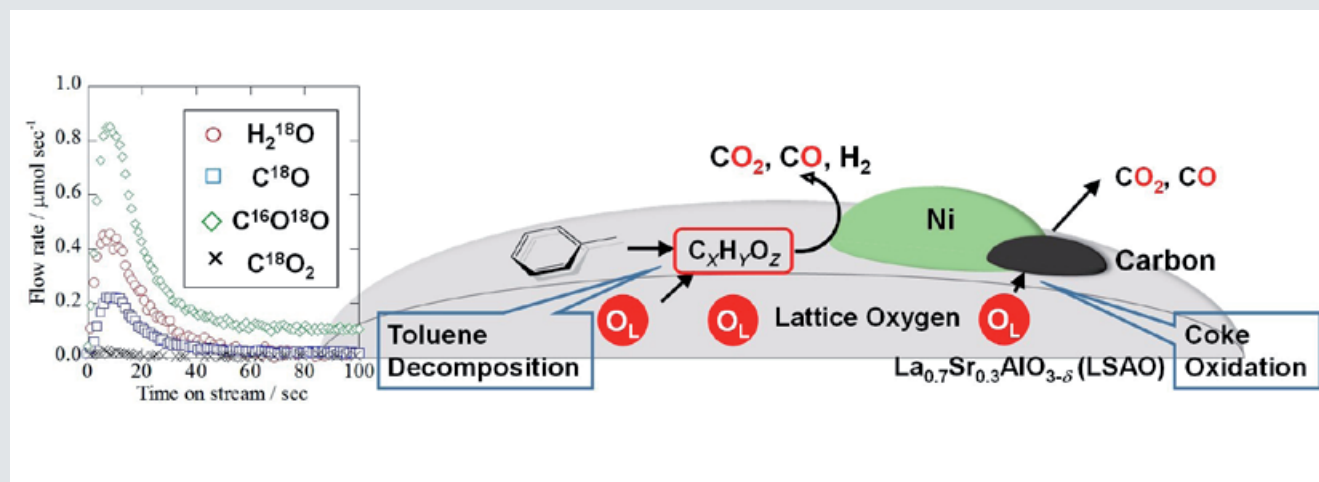
BIOMASS TAR

Climate change and depletion of fossil fuel sources has seen the requirement to find sustainable alternatives become more pressing. Steam reforming of biomass tar offers one such alternative. The data shown here describes a study into this reaction, specifically investigating catalysts that minimise the role that aromatic hydrocarbons can play in the deactivation of the catalyst.

The biomass tar includes toluene-like compounds in its structure. Generally, for Ni supported on metal oxide, aromatic hydrocarbons tend to form carbon covered active sites of catalyst and this deactivates the catalyst.

Nevertheless, it was revealed that $\text{Ni/La}_{0.7}\text{Sr}_{0.3}\text{AlO}_3$ has high activity and low carbon deposition during toluene steam reforming.

In this reaction, lattice oxygen plays an important role for oxidizing surface carbon and decomposing reactant toluene. Therefore, this type of experiment can be used to confirm the relationship between lattice oxygen release rates and reaction rates, while also determining amounts of deposited carbon by detecting the emission behaviour of lattice oxygen in/on the perovskite oxide.



Analysis of lattice oxygen release and proposed reaction mechanism.

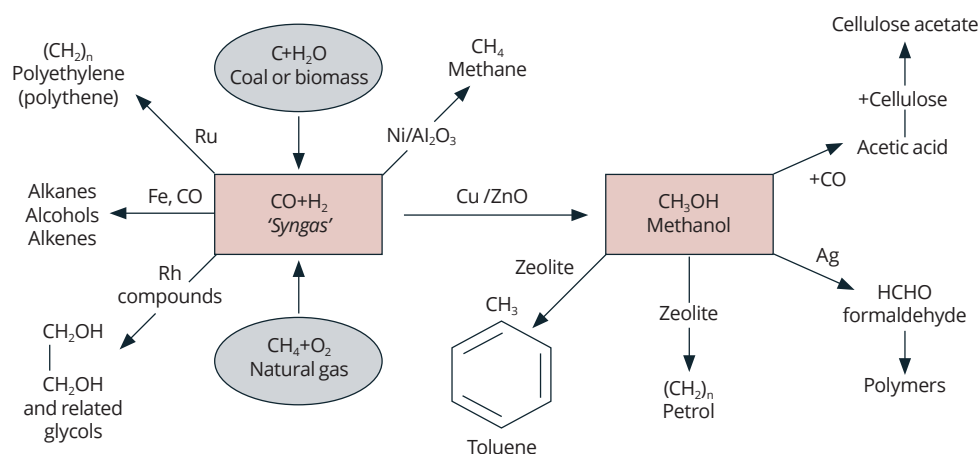
Syngas



One of the most diverse areas of heterogeneous catalysis involves the use of synthesis gas or syngas.

This gas comprises a mixture of carbon monoxide and hydrogen and is typically produced either by oxidising coal with steam or by the partial oxidation of methane. Syngas can be used to produce a wide range of products such as fertilizers, fuels, solvents and synthetic materials.

The scheme below shows some of the range of processes that involve syngas.

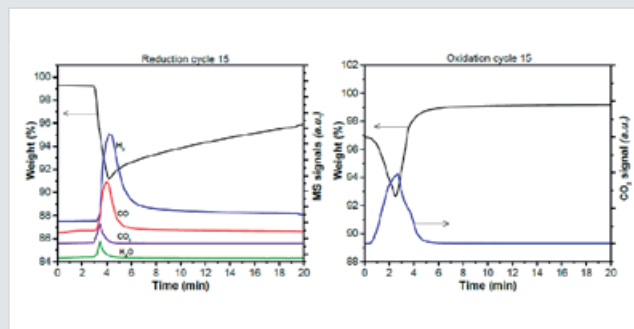


HYDROGEN PRODUCTION

Steam reforming of methane is a method for producing syngas and is the dominant process for industrial hydrogen production today. The complete process involves multiple steps and severe operating conditions. Although a mature process, steam reforming remains very energy intensive and emits a significant amount of CO_2 , aggravating global warming. The study here looks at sorption enhanced chemical looping steam methane reforming (SE-CL-SMR), a novel low-carbon process for hydrogen production.

The redox activity and stability of NiO -based materials was investigated by performing methane reduction/air oxidation cycles in a thermogravimetric analyzer (TGA) unit. By analysing the weight changes and gaseous species

evolution monitored by the HPR-20 gas analyser, it was found that zirconia supported NiO exhibited good redox activity and stability during multiple CH_4 reduction-air oxidation cycles.



Evolution of gaseous products during the methane and air oxidation step as a function of time in a typical redox cycle for 40% NiO/ZrO_2 .

Operando Spectroscopy



Operando spectroscopy is an analytical methodology that combines spectroscopic characterization with simultaneous measurement of catalytic activity and selectivity. The main concern of this methodology is to determine structure-reactivity or selectivity relationships of catalysts and thereby yield information about mechanisms. It also has applications in engineering improvements to existing catalytic materials and processes and in developing new ones.

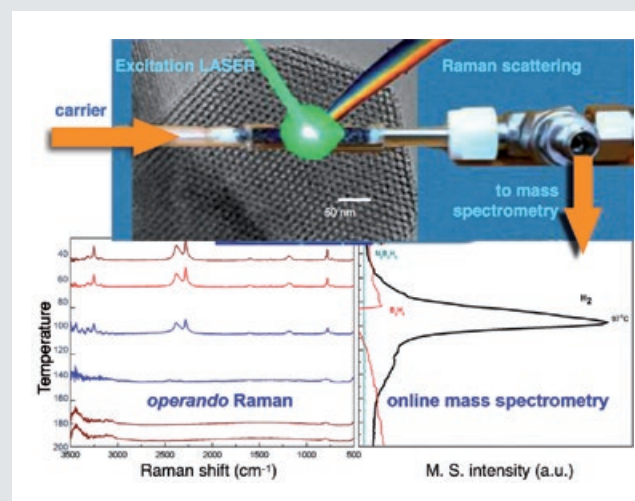
OPERANDO SPECTROSCOPY

Operando Raman-Mass Spectrometry investigation of hydrogen release by thermolysis of ammonia borane confined in mesoporous materials.

Ammonia borane (NH_3BH_3 , AB hereafter) is a white crystalline inorganic solid with 19.6 wt. % mass content of hydrogen whose thermal decomposition releases up to 2 equivalents of hydrogen below 200 °C and therefore constitutes a promising hydrogen storage material. However, the application of AB is hindered by slow hydrogen release kinetics among other factors. Confinement of AB in scaffolding nanoporous materials has shown to improve its performance in terms of lower decomposition temperature, better kinetics and suppression of volatile impurities. However, hydrogen release mechanisms are still unclear.

In this work, hydrogen thermal desorption from AB, which has been incorporated into various mesoporous carriers, has been investigated by means of operando Raman - Mass Spectrometry methodology which consists in using a combination of real-time Raman spectroscopy measurements and simultaneous on-line analysis of the effluents by the HPR-20 gas analyser.

This technique allows the study of the relationship between the structural/compositional changes in AB with hydrogen desorption properties in order to elucidate the mechanisms of decomposition, as well as, to clarify the benefits of dispersion and destabilization of AB by nanoconfinement.



Simultaneous acquisition of Raman spectra and Mass spectrometry profiles for gases evolved during thermal decomposition of AB impregnated in porous SBA-15 materials.

During operando Raman-MS measurements, each sample was linearly heated at $1^\circ\text{C}\cdot\text{min}^{-1}$ up to 200 °C under a $50\text{ mL}\cdot\text{min}^{-1}$ 99.9995 % N_2 flow and Raman spectra were acquired every 600 seconds.

Catalyst Characterisation



For many catalysts it is not only important to understand how a catalysts performs during a chemical reaction, it is also desirable to know about the physical properties of the catalyst. By obtaining knowledge of the physical properties this information can be used to design and adapt new catalyst technology. The important properties to understand include metal surface area of the active catalyst material, the dispersion of metal catalyst on the support structure and the number and type of reaction sites of the catalyst.

Characterisation techniques such as temperature programmed desorption (TPD), reduction (TPR) and oxidation (TPO) and pulse chemisorption can be used to elucidate many of the physical properties of the catalyst. The Hiden gas analysis systems such

as the QGA or HPR-20 R&D are used in many research laboratories with a variety of reactors or can be coupled to the Hiden CATLAB microreactor to utilise these techniques and provide a better overall understanding of the catalyst.

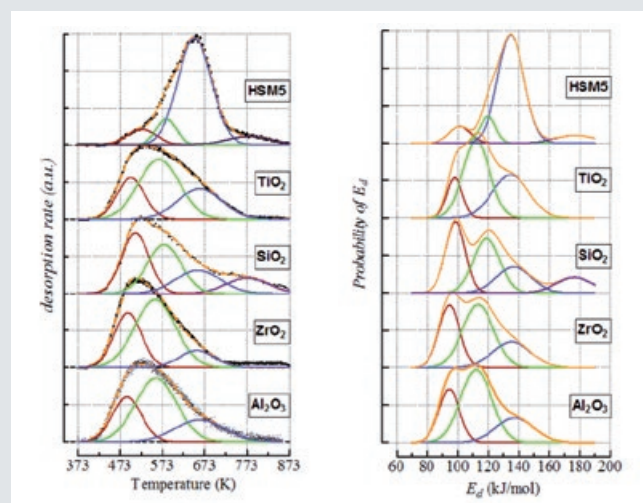
NH₃ TPD

The surface acidic properties of a heterogeneous catalyst can be probed using a combination of a basic molecule such as ammonia and the technique of temperature programmed desorption (TPD).

The study shown here is of the surface acidic properties of oxide catalysts and carriers (Al₂O₃, CeO₂, ZrO₂, SiO₂, TiO₂, HZSM-5 zeolite), comparatively probing their surfaces by NH₃ TPD measurements. This TPD measurement is a simple and reliable technique in which a surface, after saturation with NH₃ at low temperature, is subject to a linear temperature ramp, which causes desorption of the probe molecule along with a temperature profile. By qualitatively and/or quantitatively analysing the desorption pattern, it is possible to obtain information about the adsorption/desorption energy and the quantity of NH₃ that has been adsorbed on the surface (NH₃ uptake). This information can help understand the catalytic behavior of a sample, or even help in fine tuning the synthesis of new systems. Instead of using a traditional TCD Detector for this task, the HPR-20 gas analyser was used and allows for the separate analysis

of desorbed NH₃ and H₂O, thus overcoming a limitation of the TCD detector.

By tuning of the ionization potential in the ion source of the HPR-20 gas analyser, it is possible to avoid H₂O molecule fragmentation and related interferences with the NH₃ m/z signal allowing accurate and reliable measurements and flexibility in the technique employed.



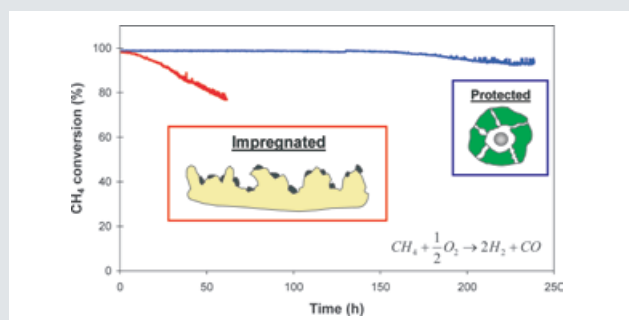
CHARACTERISATION OF H₂ PRODUCTION CATALYSTS

Hydrogen as an energy transport medium in combination with fuel cells is one of the emerging energy solutions in terms of sustainability and low environmental impact. There are a variety of methods for the production of hydrogen such as the partial oxidation of methane, steam reforming of methanol or ethanol and ammonia decomposition.

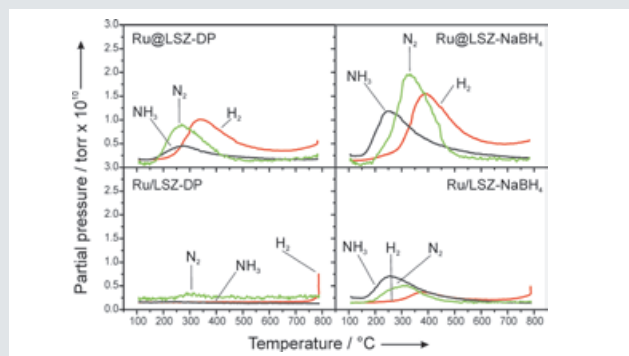
The top data shown here demonstrates the methane conversion reaction, collected using the HPR-20 gas analyser and is used to prove the superior thermal stability, during methane partial oxidation, of an innovative embedded Rh/Al₂O₃ catalyst with respect to conventional impregnated material.

The second data set shown here is the comparison of the characterisation of an embedded and impregnated Ru/ZrO₂ based catalyst during the ammonia decomposition reaction.

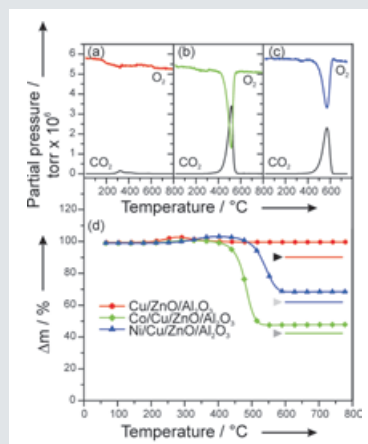
Finally, the amount and nature of coke deposited is evaluated by temperature programmed oxidation (TPO) during ethanol steam reforming on Cu/ZnO/Al₂O₃ based catalyst.



CH₄ conversion at 750 °C vs time. Conventional vs protected Rh(1wt%)/Al₂O₃



NH₃-TPD on embedded Ru/LSZ and impregnated Ru/LSZ catalysts.



Coke characterisation by TPO after ethanol steam reforming on Cu/ZnO/Al₂O₃-C (a), Co/Cu/ZnO/Al₂O₃-C (b) and Ni/Cu/ZnO/Al₂O₃-C (c) and TGA analysis of the same samples (d).

Automotive

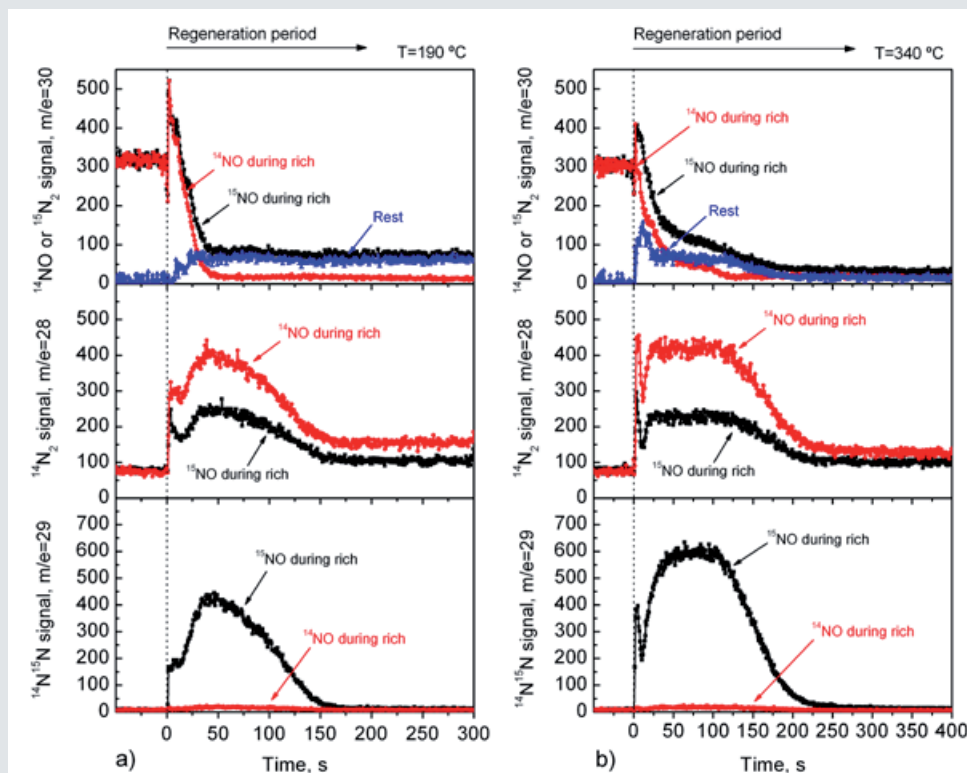


Probably the most familiar use of catalysis in the wider public is the use of catalytic converters in vehicles. This automotive catalyst is used in the exhaust system of vehicles to control the emission of harmful gases, such as hydrocarbons, carbon oxides, nitrogen oxides, and other particulate matter, into the atmosphere. The catalyst helps convert harmful gases into less toxic gases such as nitrogen and carbon dioxide.

NO_x REMOVAL

NO_x storage and reduction (NSR) or lean NO_x trap (LNT) catalysts are considered to be one of the most promising technologies for NO_x removal from lean burn engine exhausts. In the NSR reaction, NO_x is stored under lean conditions and then reduced by H₂ or CO or hydrocarbons to N₂ during a short rich period.

However, the reaction mechanism is not well-understood especially when using typical reaction conditions and the Hidden gas analysis systems can be used to investigate the effects of using different reactants in both lean and rich periods. The figures below show the evolution of different nitrogen containing species during lean and rich periods in LNT regeneration.



Evolution of ¹⁵N₂ or ¹⁴NO (m/e=30), ¹⁴N₂ (m/e=28) and ¹⁵N¹⁴N (m/e=29) during LNT regeneration, in the presence of ¹⁴NO (red points) or ¹⁵NO (black points). (a) 190 °C; (b) 340 °C.

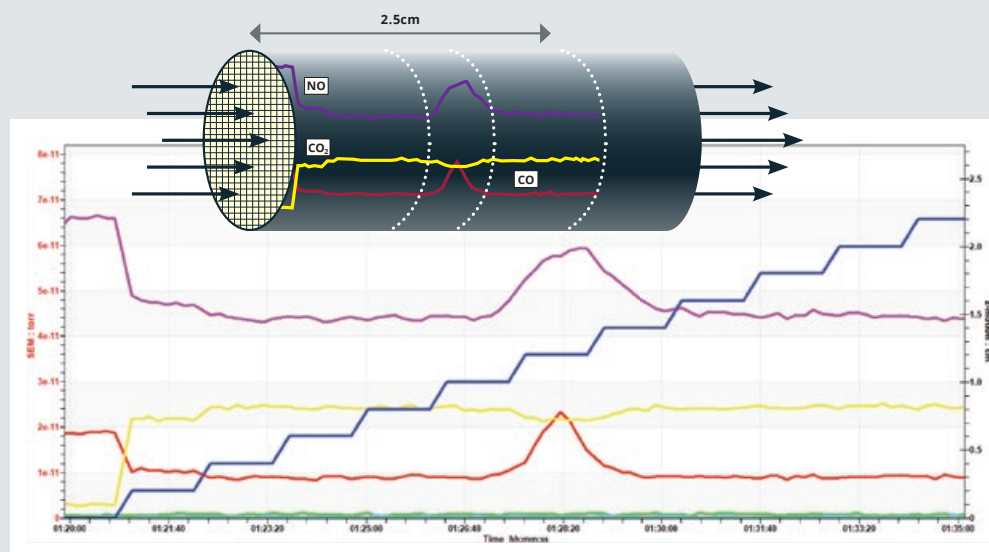
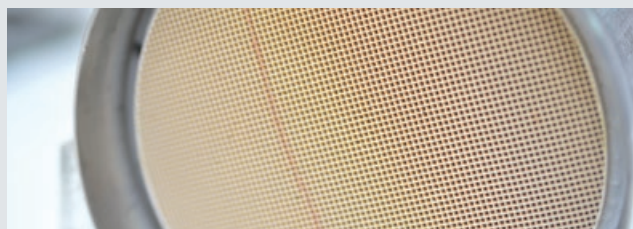
Typically the analysis of automotive catalyst performance is performed by analysing the gas at the exit of the exhaust. However there are often different regions of the catalyst monolith which control different parts of the reaction. It is possible to probe these different reaction zones within the monolith by a capillary inlet system inside the monolith channels – SpaciMS.

SpaciMS

The automotive catalyst used in the exhaust system of vehicles is typically based on a metal or combination of metals being deposited on an inert monolithic material.

The use of a monolith greatly enhances the surface area of the material compared with the same weight of powdered material and therefore enhances the performance of the overall catalyst. However, the effect that the shape of the monolith has on the catalyst efficiency is not well understood. To probe the effect of the monolith spatially resolved capillary inlet mass spectrometry (SpaciMS) has been used.

The SpaciMS consists of a number of capillaries that can be used to determine gaseous species and temperature profiles in both a radial and axial orientation, with high spatial and temporal resolution, allowing mapping of temperature and species distribution. The example here shows how the CO, CO₂ and NO concentration changes along the length of a catalyst monolith.



Surface Chemistry



Catalytic reactions can only occur at the surface of the catalyst. Therefore determining how molecules interact with a surface is important when trying to understand these reactions. The adhesion of gas or liquid molecules to the surface is known as adsorption. This can be due to either chemisorption or physisorption, and the strength of molecular adsorption to a catalyst surface is critically important to the catalyst's performance. However, it is difficult to study these phenomena in real catalyst particles, which have complex structures.

Instead, well-defined single crystal surfaces of catalytically active materials such as platinum are often used as model catalyst and are studied under ultra high vacuum (UHV) conditions allowing much greater control of surface conditions for analysis. In addition to studying single metal

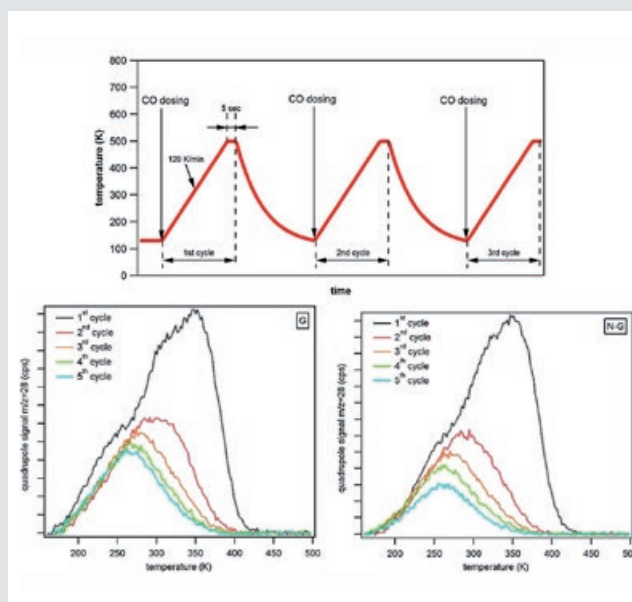
crystals multi-component materials systems can be produced by growing ultra-thin films or particles on single metal crystal surfaces.

Understanding catalysts at a fundamental level can be used to develop the next generation of catalytic materials.

CO TEMPERATURE PROGRAMMED DESORPTION

A commonly used technique to probe surfaces at UHV is temperature programmed desorption (TPD). The data shown here probes the dynamics of Fe intercalation on pure and nitrogen doped graphene grown on Pt(111) by CO adsorption/desorption.

The CO TPD profiles compare the intercalation rate of iron (Fe) nanoparticles supported on pure graphene (G) and nitrogen doped graphene (N-G) grown on platinum Pt(111) single crystal. Carbon monoxide (CO) desorption from Fe sites is used to probe the overall quantity of Fe present on the surface. It is seen that a faster intercalation occurs when the Fe nanoparticles are deposited on N-G with respect to those supported on pure G. This phenomenon can be related to nanoholes created by pyridinic and pyrrolic functionalities and/or to the lower bond enthalpy of C-N with respect to C-C bonds, which allow the formation of transient holes in the graphene layer.



Upper: representation of the temperature vs time for the CO-TPD experiment.

Lower: cycles of CO-TPD (CO on Fe deposited on G/Pt(111) (left) and N-G/Pt(111) (right).

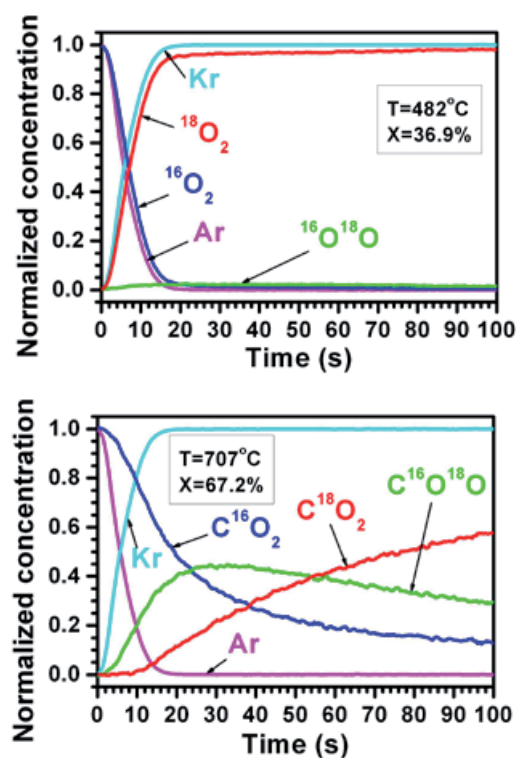
Kinetic parameters of catalyst-surface reaction intermediates, such as concentration, site coverage, reactivity, and rate constants can be obtained and processed to provide valuable information about the reaction mechanism.

METHANE OXIDATION BY SSITKA

The catalytic process of complete methane oxidation is a highly promising alternative to flame combustion, because it makes it possible to reduce the emission of NO_x , CO and non-oxidized hydrocarbons into the Earth's atmosphere. Some of the most active catalytic materials for complete methane oxidation are supported palladium and platinum catalysts.

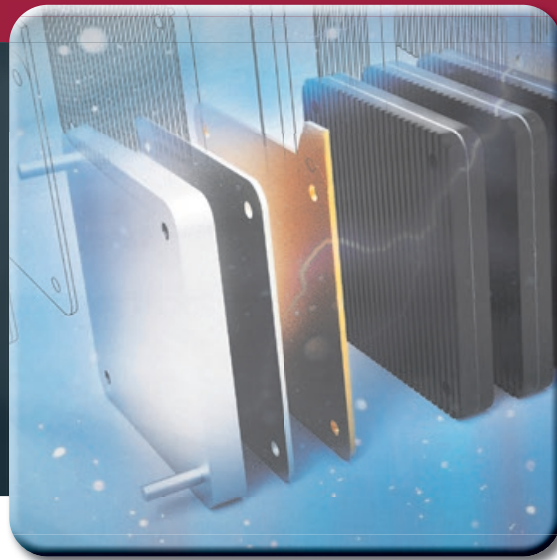
These active metals demonstrate very high activity and selectivity. Additionally their resistance to high temperature and mechanical damage provides further benefits to their use. However, for the wide application of palladium and platinum catalysts in the industry, there is still a need for clear answers to many important questions. One of the most crucial issues is the reaction mechanism of complete methane oxidation over palladium and platinum catalysts. Here the reaction mechanism is probed using fast switching of isotopically labelled reactant and following the products with the Hiden gas analysis system. A typical model recommended for SSITKA measurements is the fast response Hiden HPR-20 TMS featuring the HAL 3F PIC detector.

One of the most useful techniques to obtain this information on catalysed heterogeneous reactions at, or near to, molecular level is the Steady-State Isotopic Transient Kinetic Analysis (SSITKA)



Effect of the switching between reaction streams including $^{16}\text{O}_2/\text{Ar}/\text{CH}_4/\text{He}$ and $^{18}\text{O}_2/\text{Kr}/\text{CH}_4/\text{He}$ (X is the conversion of methane).

Electrocatalysis



Electrocatalysis can be defined as the heterogeneous catalysis of electrochemical reactions, which occur at the electrode–electrolyte interface and where the electrode plays both the role of electron donor/acceptor and of catalyst.

Mass spectrometry (in combination with electrochemical methods) is a powerful technique which allows both evolved off-gas and dissolved species analysis to be performed in real-time.

EFFECTS OF IMPURITIES ON FUEL CELL PERFORMANCE

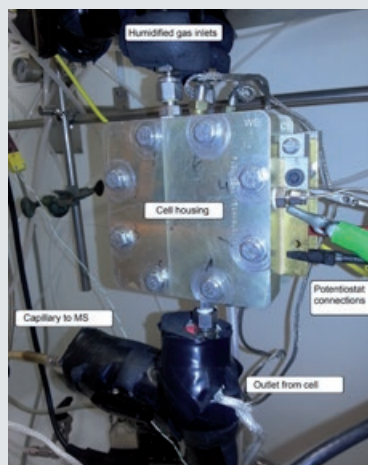
A fuel cell is an electrochemical cell that converts the chemical energy of a fuel (often hydrogen) and an oxidizing agent (often oxygen) into electricity through a pair of redox reactions. The catalyst used in a certain class of fuel cells (that use hydrogen as a fuel) can be severely affected by some of the impurities in the hydrogen while other impurities will have little or a moderate effect.

Knowledge of how and to what extent the presence of different

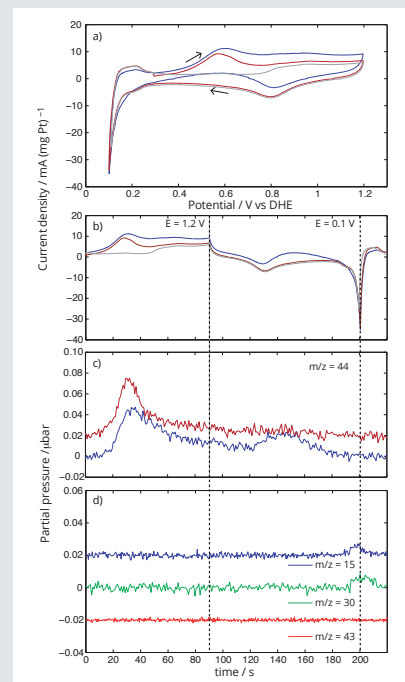
impurities in the hydrogen feed gas affects the performance of the fuel cell is important. Using mass spectrometry combined with electrochemical techniques gives information on not only how the cell performance is affected, but an indication of why.

Using ethene as an example impurity, three different cyclic voltammograms (CVs) were recorded (figure a); a base CV, recorded in pure argon (grey), a CV recorded in a continuous flow of 100 ppm ethene contaminated argon (blue), and a stripping CV, where the electrode has been exposed to ethene contaminated argon for some time followed by purging the system prior to recording the CV (red). The oxidation peaks around 0.6 V (shown at 30 and 145 seconds in the continuous CV scan (figure b)) corresponds nicely with the $m/z = 44$ signal attributed to CO_2 (figure c), indicating that adspecies originating from ethene are oxidised to CO_2 at potentials > 0.35 V vs RHE. The signals at $m/z = 15$ and 30 recorded in 100 ppm ethene/argon

(figure d) appear around the hydrogen evolution peak, indicating the formation of methane and ethane at these low potentials. These results demonstrate that traces of ethene in the hydrogen feed have a minimal effect on the performance of this PEM fuel cell.



Labelled Fuel Cell during operation.



Cyclic Voltammograms recorded in a fuel cell at 80°C and 90%RH, at a scan rate of 10 mV s⁻¹ and selected m/z signals.

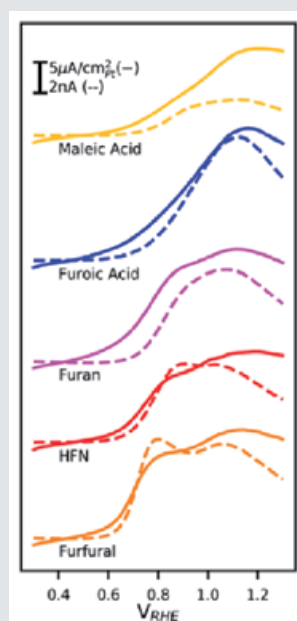
VALORISATION OF BIOMASS-DERIVED FEEDSTOCKS

Electrocatalysis poses several potential advantages for the valorisation of biomass-derived feedstocks, most importantly its ability for direct conversion in acidic aqueous media. Some biomass derivatives can be converted to valuable products and precursors via partial oxidation. Combining such partial oxidations with H_2 evolution or other reduction reactions (e.g. CO_2) in an electrochemical cell presents an opportunity to perform electrolysis at lowered voltages, while coproducing products that are more valuable than O_2 .

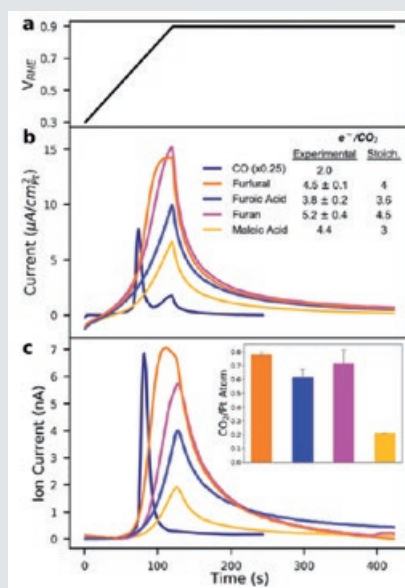
On-Line Electrochemical Mass Spectrometry (OLEMS) using the HPR-40 gas analyser system in combination with a custom-built flow-through electrolysis cell and other characterisation techniques has been used to probe the oxidative reaction pathways of furfural on platinum catalysts in acidic electrolyte.

In order to investigate the performance of the electrocatalyst and the potential reaction pathways in operation, the decomposition of furfural and several of its partially oxidized derivatives to CO_2 was performed using voltammetric stripping experiments with simultaneous OLEMS. Trends in the relative yield of CO_2 to other products provide insight into the relative stability and surface chemistry of each adsorbed species.

This technique is similar in methodology to temperature programmed desorption studies typically performed in heterogeneous catalysis. Based on the results from this research, a reaction pathway and guide for the design of more active and selective electrocatalysts has been proposed.

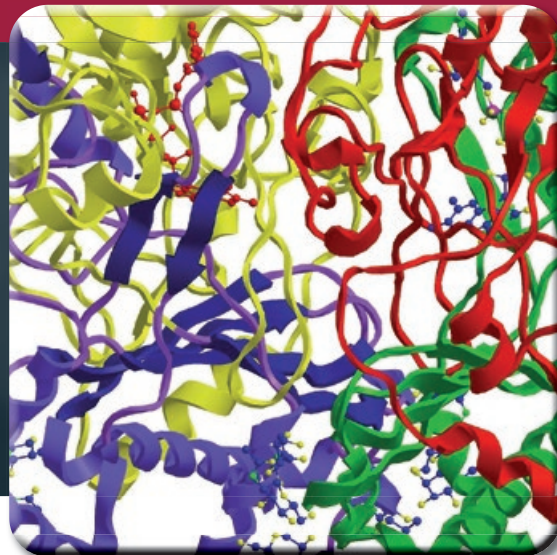


Voltammetric stripping (solid line) paired with CO_2 -OLEMS (dotted line) for furfural (100 mM, orange), HFN (5 mM, red), furan (saturated, magenta), FA (100 mM, blue), and MA (100 mM, yellow) after 300 s adsorption periods at 0.3 VRHE on Pt black in 0.25 M $HClO_4$.



Voltammetric stripping with a 5 mV/s ramp and hold program (a), with Faradaic responses (b) paired with CO_2 -OLEMS (c) after 5 min adsorption periods of CO (saturated), 100 mM furfural, 100 mM FA, furan (saturated), and 100 mM MA in 0.25 M $HClO_4$ on Pt Black.

Biocatalysis

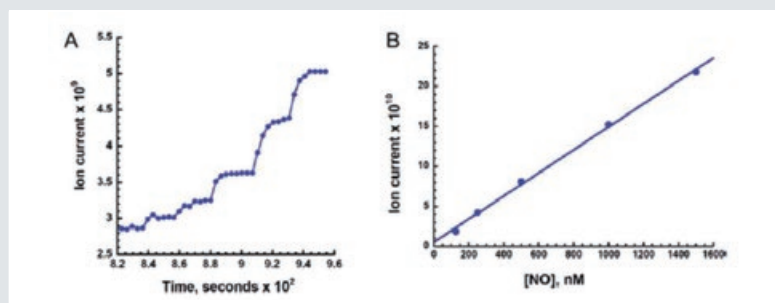


Biocatalysis refers to the use of living systems or their parts to speed up chemical reactions. In biocatalytic processes, natural catalysts such as enzymes perform chemical transformations on organic compounds. Enzymes have pivotal role in the catalysis of hundreds of reactions that include production of alcohols from fermentation and cheese by breakdown of milk proteins. Currently, there are many different biocatalytic processes that have been implemented in various pharma, biochemical, food, and agro-based industries. With further development, enzymes could also catalyse many of the industrial reactions that produce the chemicals and materials that are essential for our modern world.

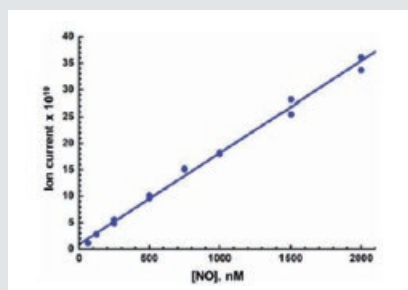
MEASUREMENT OF GENERATED NITRIC OXIDE

Membrane inlet mass spectrometry (MIMS) is a reproducible and reliable method for the measurement of nitric oxide in aqueous solution with a lower limit of detection of 10 nM and a linear response to 50 μ M.

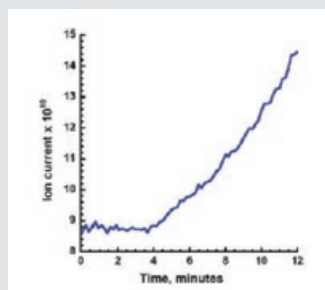
The HPR-40 gas analyser (with the specially designed enzyme compatible inlet) has been used to develop an enzyme assay for nitric oxide synthase. Shown below are the measurement of NO generated chemically from nitrite and MAHMA NONOate as well as enzymatically by nitric oxide synthase (NOS).



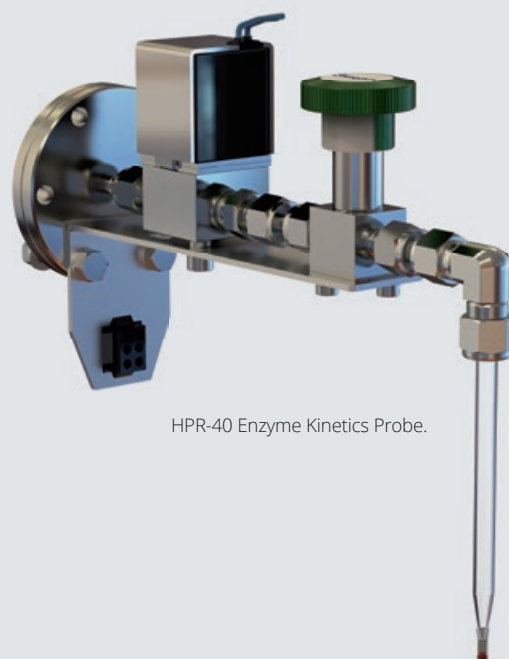
Calibration of the m/z 30 ion current by the (A) stepwise addition of sodium nitrite to the reaction vessel. (B) MIMS calibration curve relating nitrite derived NO to ion current.



MIMS calibration curve relating MAHMA NONOate generated nitric oxide to ion current at m/z 30 showing the linear response to 50 μ M.



Direct, continuous, real-time assay measuring enzymatically generated NO.

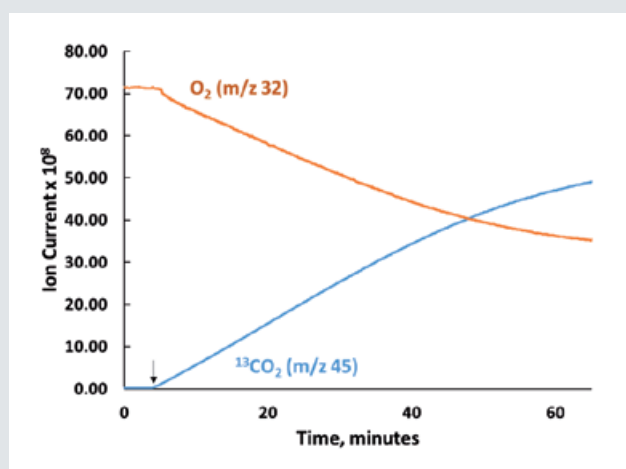


HPR-40 Enzyme Kinetics Probe.

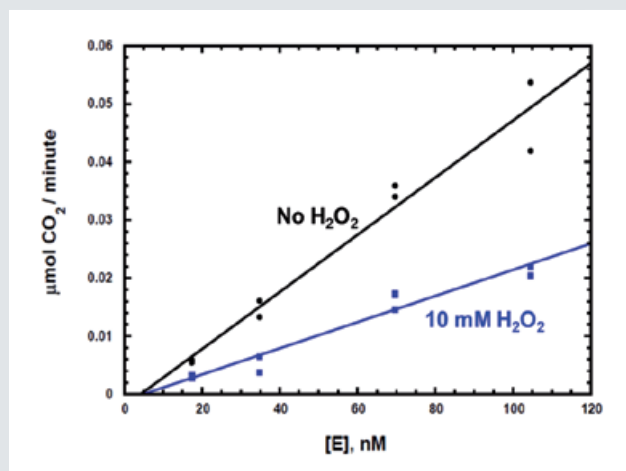
OXALATE OXIDASE ENZYME

Oxalate oxidase is a manganese containing enzyme that catalyzes the oxidation of oxalate to carbon dioxide in a reaction that is coupled with the reduction of oxygen to hydrogen peroxide. Oxalate oxidase from *Ceriporiopsis subvermisporea* (CsOxOx) is the first fungal and bicupin enzyme identified that catalyzes this reaction. Potential applications of oxalate oxidase for use in pancreatic cancer treatment, the prevention of scaling in paper pulping, and in biofuel cells have highlighted the need to understand the extent of the hydrogen peroxide inhibition of the CsOxOx catalyzed oxidation of oxalate.

A membrane inlet mass spectrometry (MIMS) assay (using the HPR-40 gas analyser and a special designed enzyme compatible inlet) was used to directly measure initial rates of carbon dioxide formation and oxygen consumption in the presence and absence of hydrogen peroxide (top figure). In order to distinguish the CO_2 generated by CsOxOx from CO_2 dissolved in the reaction mixtures, ^{13}C labelled oxalate was employed. The bottom data shown (performed with and without hydrogen peroxide present) do not appear to have significant different x-intercepts and they are not significantly different from zero suggesting that CsOxOx is not inactivated upon addition of hydrogen peroxide within the time frame of the kinetic assay. The curve with hydrogen peroxide present has a smaller slope and goes through the approximate origin which is consistent with hydrogen peroxide being a reversible non-competitive inhibitor of the CsOxOx catalyzed oxidation of oxalate and an irreversible inactivator. The build-up of the turnover-generated hydrogen peroxide product leads to the inactivation of the enzyme. The introduction of catalase to reaction mixtures protects the enzyme from inactivation allowing reactions to proceed to completion.

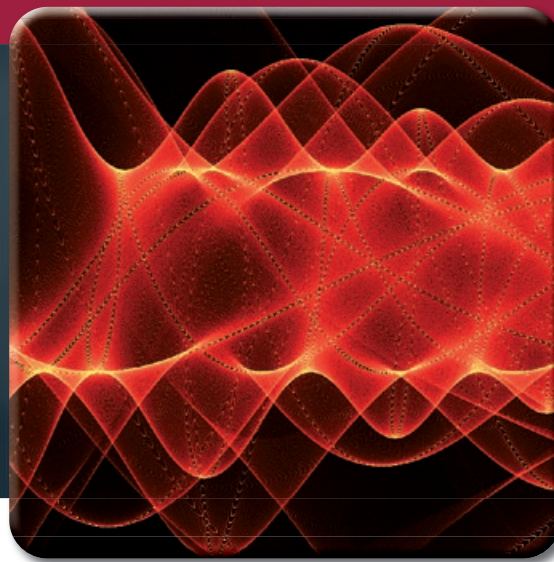


The production of $^{13}\text{CO}_2$ and consumption of O_2 (in arbitrary ion currents) during the CsOxOx catalyzed oxidation of $^{13}\text{C}_2$ -mesoxalate. The ion currents for the dissolved gases at their respective peak heights were recorded: blue, CO_2 at m/z 45; orange, O_2 at m/z 32.



Plot of $V_{\text{max app}}$ versus $[\text{E}]$ of the CsOxOx catalyzed oxidation of oxalate with (blue, 10 mM) and without (black) hydrogen peroxide present. Each point represents a $V_{\text{max app}}$ determination at five concentrations of oxalate (0.2, 0.5, 1.0, 5.0, and 10.0 mM).

Plasma Catalysis



The combination of a plasma discharge with material that has catalytic properties is known as plasma catalysis. Although a range of plasmas could be used, the most common are non-thermal, atmospheric pressure plasmas and solid catalysts with gas phase reactions.

Plasma catalysis is gaining increasing interest for various gas conversion applications, such as CO_2 conversion into value-added chemicals and fuels, synthesis of NH_3 from N_2 fixation or NO_x , and CH_4 conversion into higher hydrocarbons or oxygenates. Additionally, it has been shown to be useful for air pollution control by reducing volatile organic compounds (VOC's) in waste gas treatment.

Plasma allows thermodynamically difficult reactions to proceed at an ambient pressure and temperature because the gas molecules are activated by energetic electrons

created in the plasma. Plasma consist of a mixture of many different types of reactive species such as electrons, ions, radicals and neutral gas molecules, but due to the nature of these species the selectivity of the reactions are difficult to control.

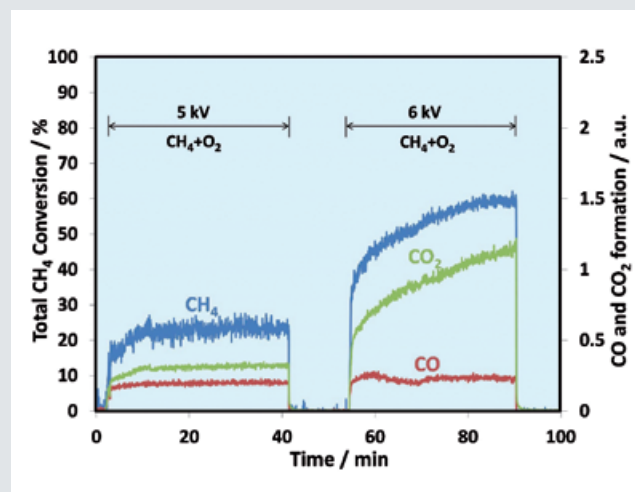
On the other hand a catalyst can offer excellent selectivity but traditionally may need to operate at high temperature and or pressure. By combining the plasma with a traditional heterogeneous catalyst new reaction pathways can be formed under more favourable conditions.

NTP ASSISTED METHANE OXIDATION

The effect of Non Thermal Plasma (NTP) was investigated on the methane oxidation reaction. Methane is difficult to oxidise due to its high C-H bond strength and the reaction has been extensively investigated under standard thermal conditions. Relatively high temperatures are usually required to oxidise methane even over Pt and Pd catalysts especially in the presence of water. The application of NTP offers a low temperature route to methane oxidation. One effective catalytic candidate for this reaction is $\text{Pd}/\text{Al}_2\text{O}_3$.

This figure shows the influence of plasma voltage on CH_4 conversion as well as CO/CO_2 productions over 2% $\text{Pd}/\text{Al}_2\text{O}_3$. A significant change in gas phase species detected by the HPR-20 gas analyser was observed when increasing the peak voltage from 5 to 6 kV. The conversion increased to 60% over 35 minutes on stream, a similar trend was also observed for the production of CO_2 . However, the change in CO formation did not follow the same variation as for the CH_4 conversion and CO_2

formation, suggesting that CO formation occurs via a different reaction pathway than that of CO_2 . This CO formation is likely to predominantly take place through gas phase reaction under plasma conditions.



Changes in CH_4 conversion, CO_2 and CO formation as a function of plasma voltage applied to 2% $\text{Pd}/\text{Al}_2\text{O}_3$ under 0.5% CH_4 + 10% O_2 reaction conditions.

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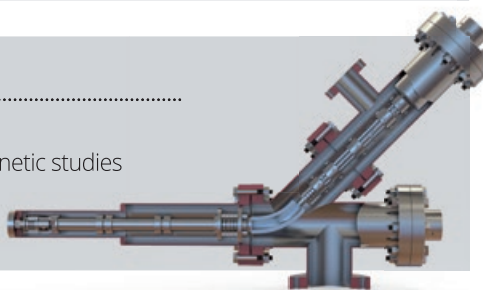


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