HIDEN ANALYTICAL



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:

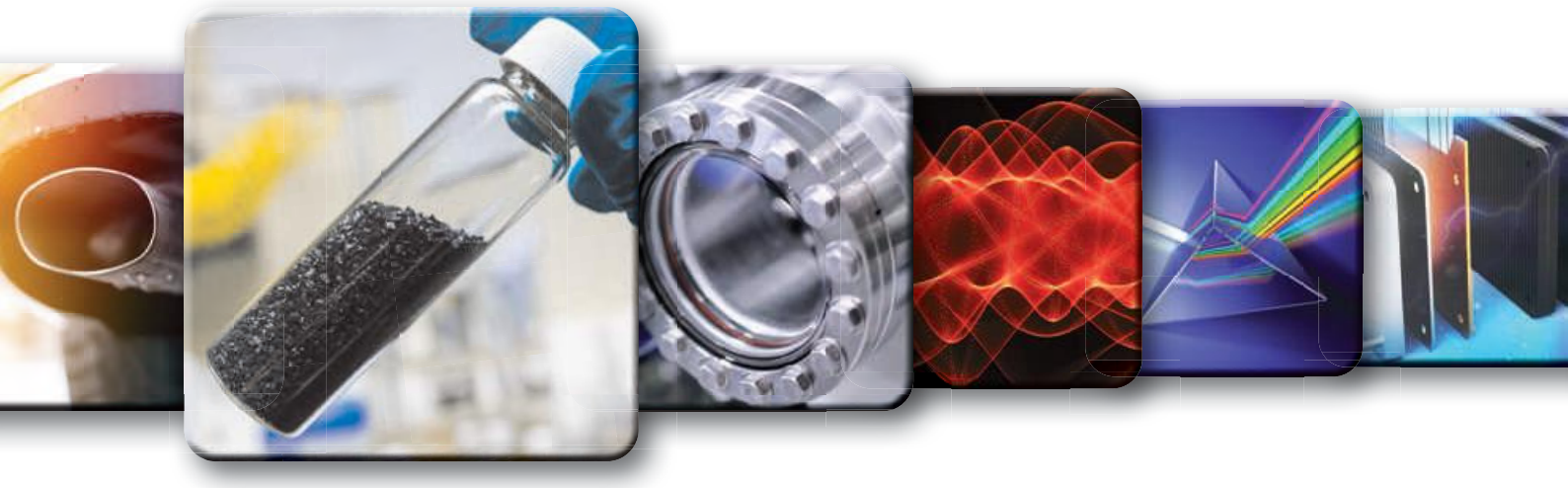
- **Energy –** petrochemicals
- **Healthcare –** pharmaceuticals
- **Materials –** polymers, batteries
- **Transport –** catalytic convertors
- **Environment –** water, air quality, renewable and bio–produced materials

Hiden 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.

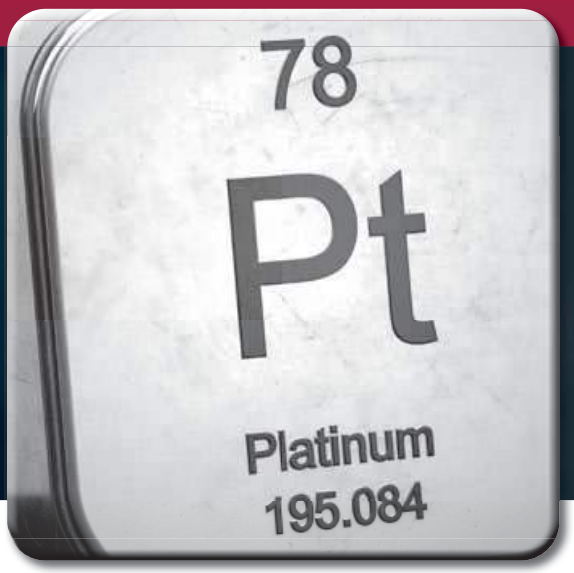


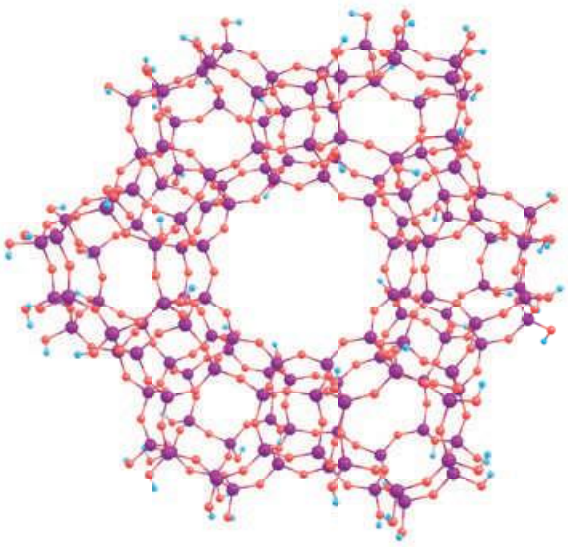
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Heterogeneous Catalysis





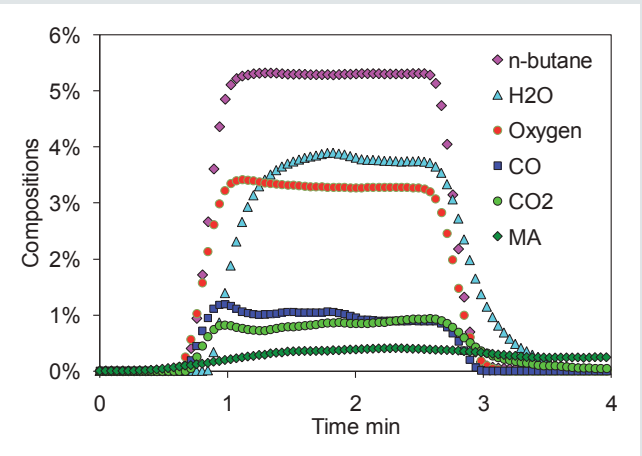
Heterogeneous catalysis covers an enormous range of chemical reactions. The defining feature of heterogeneous catalysis is the reaction of gas or liquid phase reactants occurring at the surface of solid catalysts. As the surface is where the reaction occurs the catalyst is generally prepared in ways 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 ANYDRIDE 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.

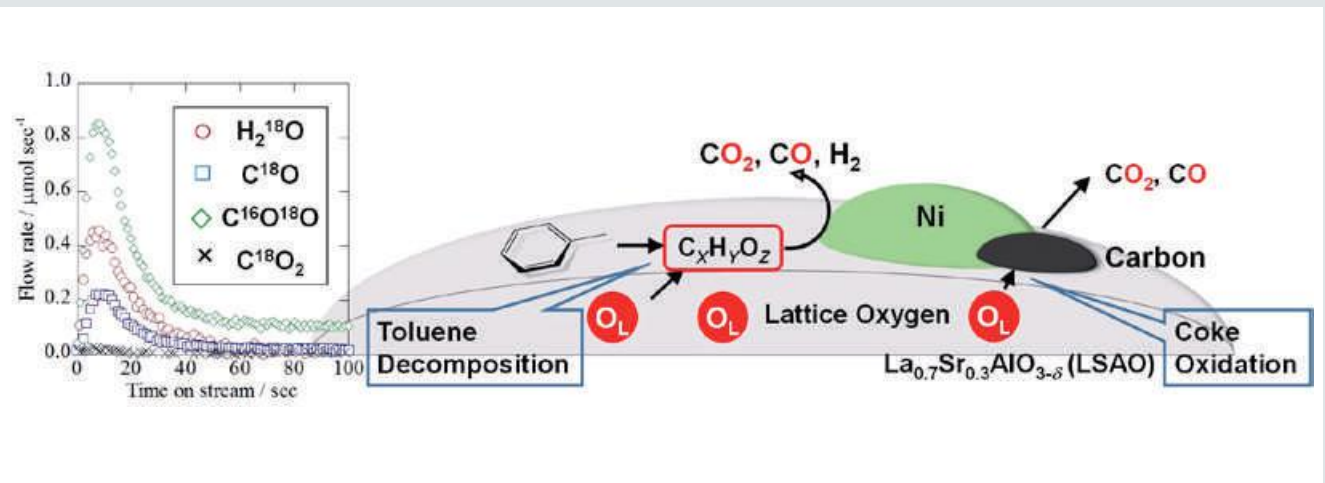
BIOMASS TAR

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 $Ni/La_{0.7}Sr_{0.3}AlO_3$ 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 from the metal oxide 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.

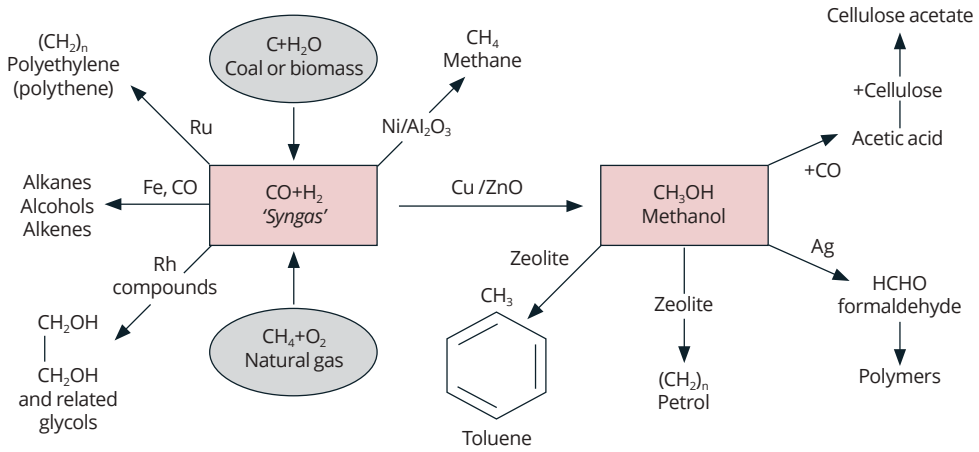
Syngas



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.

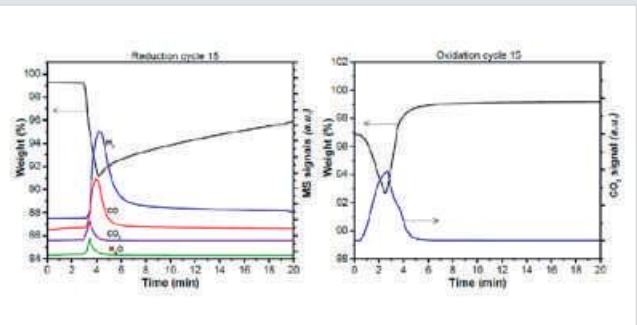
The scheme below shows some of the range of processes that involve syngas.



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.

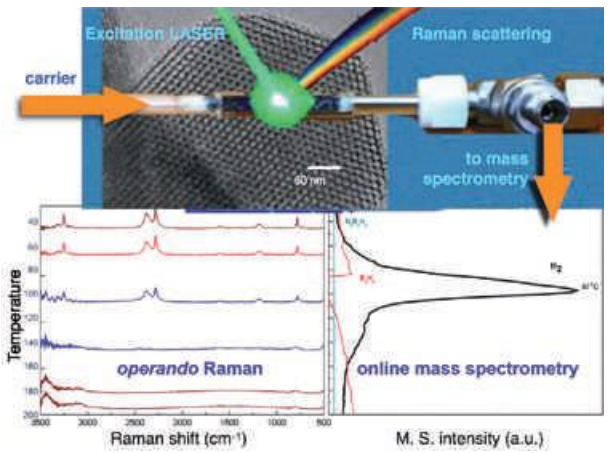
OPERANDO SPECTROSCOPY

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°C·min^{-1} up to 200 °C under a 50 mL·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.

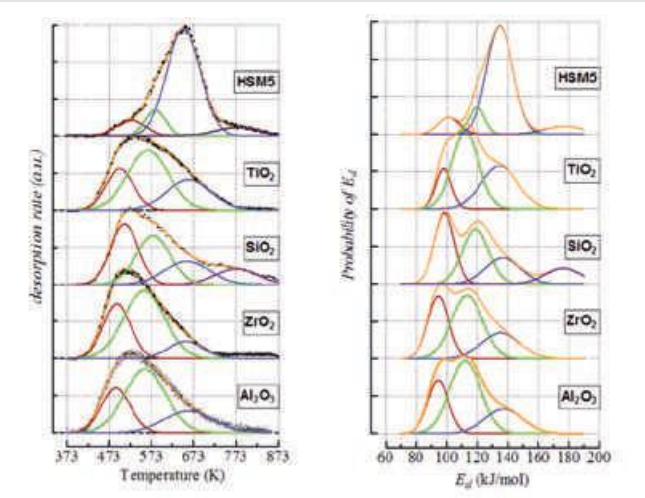
Characterisation techniques such as temperature programmed desorption (TPD), reduction (TPR) and oxidation (TPO) and pulse chemisorption can be used to elucidate many of the physical properties of the catalyst. The Hiden gas analysis systems such as the QGA or HPR-20 R&D are used in many research laboratories 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.

NH_3 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 (Al_2O_3, CeO_2, ZrO_2, SiO_2, TiO_2, HZSM-5 zeolite), comparatively probing their surfaces by NH_3 TPD measurements. This TPD measurement is a simple and reliable technique in which a surface, after saturation with NH_3 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 NH_3 that has been adsorbed on the surface (NH_3 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 NH_3 and H_2O, 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 H_2O molecule fragmentation and related interferences with the NH_3 m/z signal allowing accurate and reliable measurements and flexibility in the technique employed.



CHARACTERISATION OF H_2 PRODUCTION CATALYSTS

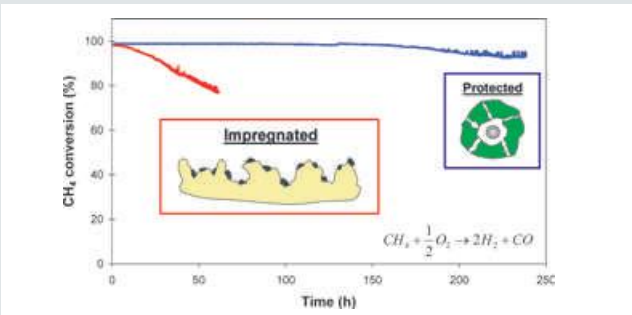
Hydrogen as an energy transport medium in combination with fuel cells is one of the emerging energy solutions in terms of sustainability and low environmental impact. There are a variety of methods for the production of hydrogen such as the partial oxidation of methane, steam reforming of methanol or 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/Al_2O_3 catalyst with respect to conventional impregnated material.

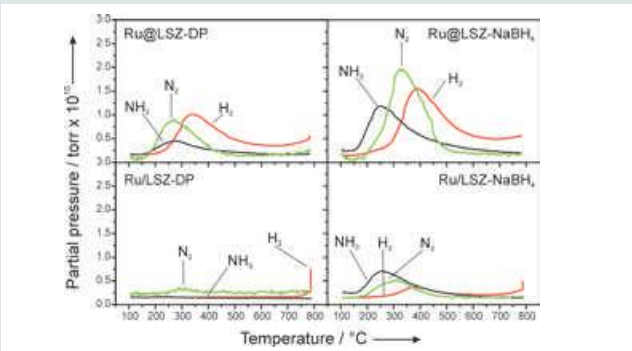
The second data set shown here is the comparison of the characterisation of an embedded and impregnated Ru/ZrO_2 based catalyst during the ammonia decomposition reaction.

Finally, the amount and nature of coke deposited is evaluated by temperature programmed oxidation (TPO) during ethanol steam reforming on $Cu/ZnO/Al_2O_3$ based catalyst.

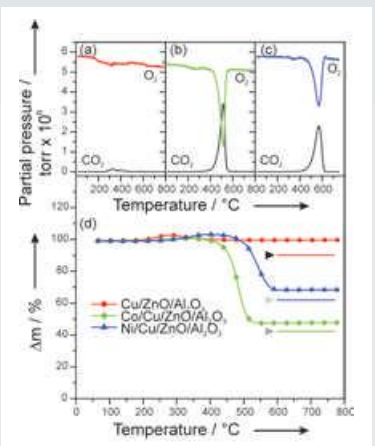




CH_4 conversion at 750 °C vs time. Conventional vs protected $Rh(1wt\%)/Al_2O_3$



NH_3-TPD on embedded Ru/LSZ and impregnated Ru/LSZ catalysts.



Coke characterisation by TPO after ethanol steam reforming on $Cu/ZnO/Al_2O_3$-C (a), $Co/Cu/ZnO/Al_2O_3$-C (b) and $Ni/Cu/ZnO/Al_2O_3$-C (c) and TGA analysis of the same samples (d).

Automotive

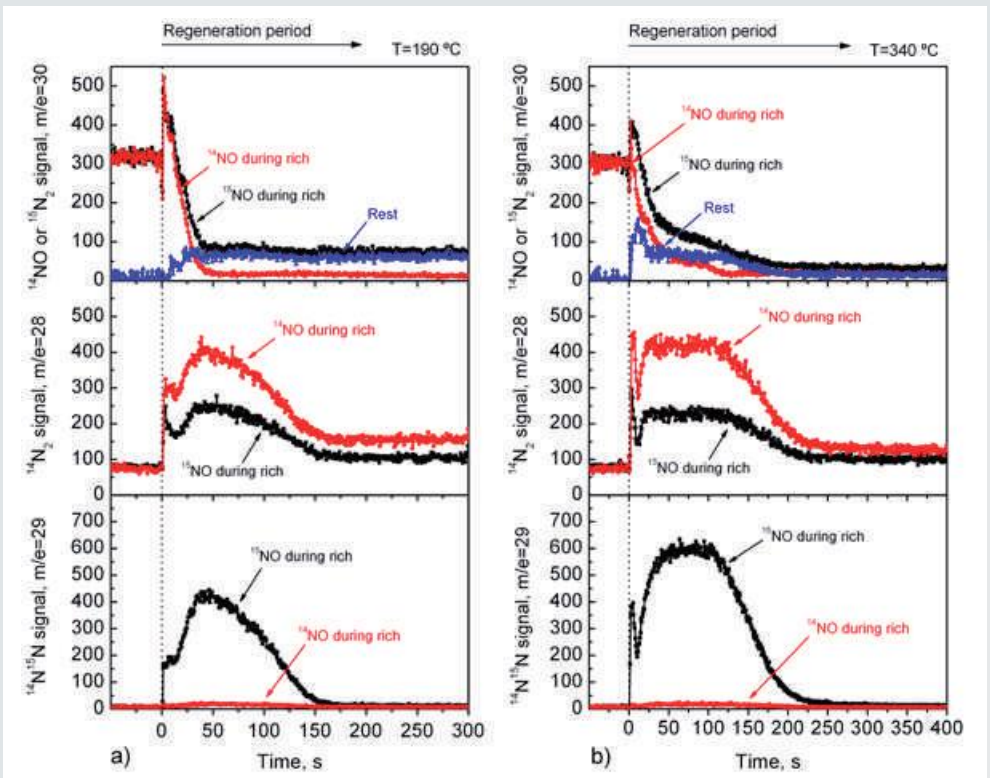


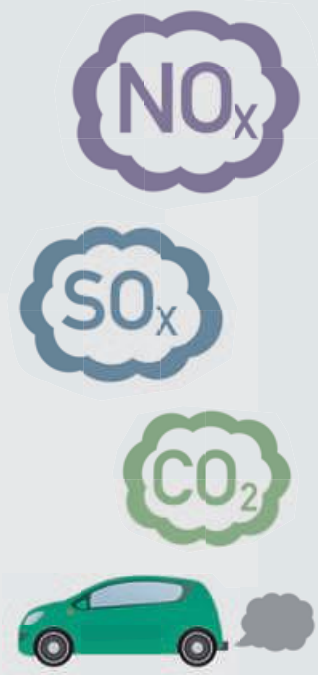
Probably the most familiar use of catalysis in the wider public is the use of catalytic converters in vehicles. This automotive catalyst is used in the exhaust system of vehicles to control the emission of harmful gases, such as hydrocarbons, carbon oxides, nitrogen oxides, and other particulate matter, 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 H_2 or CO or hydrocarbons to N_2 during a short rich period.

However, the reaction mechanism is not well-understood especially when using typical reaction conditions and the Hiden 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 $^{15}N_2$ or ^{14}NO (m/e=30), $^{14}N_2$ (m/e=28) and $^{15}N^{14}N$ (m/e=29) during LNT regeneration, in the presence of ^{14}NO (red points) or ^{15}NO (black points). (a) 190 °C; (b) 340 °C.