



Catalysis & Gas Reactions

Customer Contributions:

Pd catalysts for methane combustion

Zi Xuehong | Beijing University of Technology

Reduction of NO_x from diesel exhausts

Upakul Deka, Bert M. Weckhuysen and Andrew M. Beale | Universiteit Utrecht

Thermal studies with graphite oxide

S. J. Yang, T. Kim, H. Jung and C. R. Park | Seoul National University

H₂S abatement from biogas

V. Palma & D. Barba | University of Salerno

Calorimetric adsorption for catalyst characterisation

E. Andrijanto, E. A. Dawson, D. R. Brown | University of Huddersfield

Related Products:

HPR-20 QIC

- for Real time Gas Analysis

CATLAB-PCS

- for Catalysis Studies

HPR-20 QIC TMS

- for Fast Event Transient Analysis

In the press:

Multicapacity Microreactor
for Catalyst Characterisation

A very big thank you to all who have contributed:



Universiteit Utrecht



University of Salerno
Department of
Industrial Engineering

University of
HUDDERSFIELD

The durability of alumina supported Pd catalysts for the combustion of methane in the presence of SO₂



LEFT: Hiden Analytical HPR-20 QIC in the Laboratory

sulphate formation were mainly responsible for the catalyst deactivation. The PdO species contributed to the formation of sulphates by oxidizing SO₂ to SO₃ species. The sulphates were formed below 600 °C and decomposed above 600-700 °C in the reactions over the catalysts, which led to the inhibition and recovery of the catalytic activity, respectively. The effluent gases (SO₂, SO₃, and O₂) of the SO₂-TPD experiments were monitored on-line by a mass spectrometer (Hiden HPR-20 QIC). The results indicated that the introduction of CeO₂ or Ce_{0.6}Zr_{0.4}O₂ decreased the decomposition temperature of sulphates by 50-100 °C. Sulphur accumulation on the catalyst surface was investigated by sulphur content analysis and TG measurements after pre-treatment with SO₂. The saturated sulphur contents were all about 5 wt% for the three catalysts. In spite of sulphur poisoning, no obvious changes in the particle morphologies or dimensions were observed for the fresh and used catalysts. The introduction of CeO₂ or Ce_{0.6}Zr_{0.4}O₂ decreased the decomposition temperature of sulphates by 50-100 °C, indicating that the durability of the catalysts studied in this work could be satisfied for the catalytic combustion of methane that usually takes place above 800 °C.

Our Reference: AP0242

PROJECT SUMMARY BY:



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PAPER REFERENCE:

X. Zi, L. Liu, B. Xue, H. Dai, H. He (2011)
"The durability of alumina supported Pd
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Catalysis Today **175** (1), 223-230

HIDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

In the present work, the 1 wt% Pd/ γ -Al₂O₃, 1 wt% Pd/10 wt% CeO₂/ γ -Al₂O₃ and 1 wt% Pd/10 wt% Ce_{0.6}Zr_{0.4}O₂/ γ -Al₂O₃ catalysts were prepared and used for the catalytic combustion of methane. The durability of the catalysts were investigated based on the phenomena of SO₂ poisoning in methane catalytic combustion. The presence of SO₂ in the reaction gases resulted in a 70-250 °C increase of light-off temperature for methane conversion for all tested catalysts. Pre-treatment of the catalysts with SO₂ also led to a decrease in catalytic activity to some extent. The sulphur poisoning and

FIGURE 1 [OPPOSITE]: Simplified schematic illustration of the in-house built catalytic rig used to mimic exhaust conditions and perform selective catalytic reduction of NO in the presence of NH₃. All gas lines used were stainless steel grade. All (red colored) lines between the MFC's and analysis instruments (via the reactor) were heated using electrical heat tracing and insulated using quartz wool bands. The electronics, including controls for the MFC units, heating for the gas lines and oven are excluded for clarity. The whole setup can be interfaced into one computer using commercially available lab-view software for automation of the running process. The analytical instruments can work as stand-alone (as in this case) for ease of individual software use, or can be interfaced together with the rest of the setup. Towards the right bottom is an extended illustration of the use of a similar setup at synchrotron beamlines for performing in situ/operando type experiments. Samples can be placed in a capillary (to mimic plug-flow conditions), and connected to a MS at the end for online product analysis. X-ray absorption/X-ray diffraction data can be collected in sequence as a function of reaction conditions.

Structure-performance relationships of Cu based porous catalysts for selective catalytic reduction (SCR) of NO_x gases from diesel exhausts

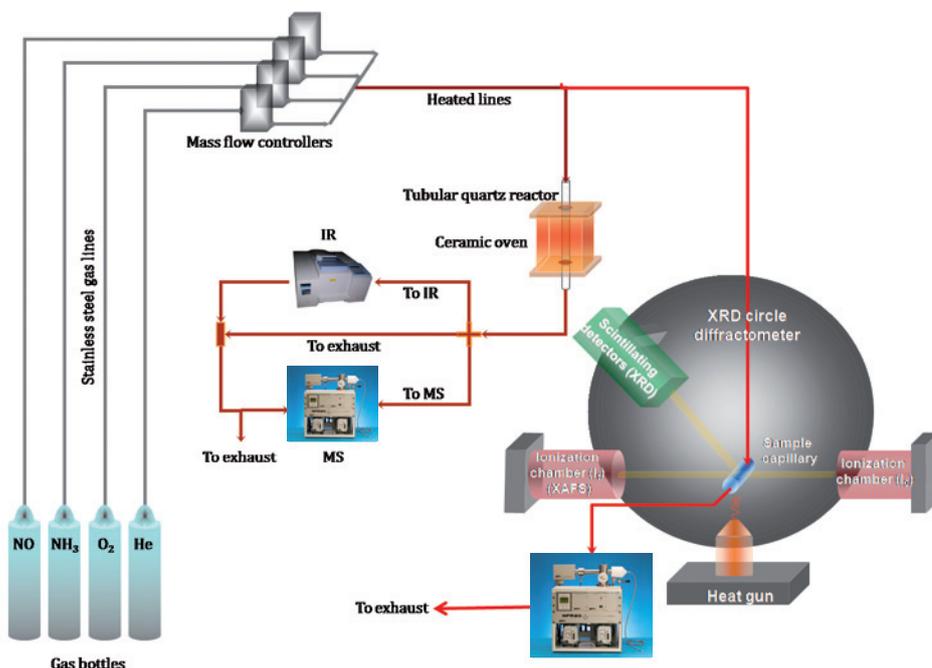
The aim of this project is to obtain a fundamental understanding of Ammonia-Selective Catalytic Reduction (NH₃-SCR) systems commonly used for emission abatement in heavy duty diesel vehicles. An important aspect of the work involves synthesis of various copper exchanged zeolites using different preparation techniques. The catalysts are pre-characterized using conventional laboratory techniques such as UV-Vis spectroscopy and X-ray diffraction. The materials are further tested for their catalytic activity using an in-house built catalytic rig under plug-flow conditions. The output gasses are analysed online using infra-red spectroscopy and a Hiden Analytical, HPR-20 QIC bench top gas analysis system. Fast and continuous monitoring of the output gasses allows for the determination of activity/selectivity profiles of catalysts in question.

The catalysts are further analysed using synchrotron light sources under in situ NH₃-SCR reaction conditions. Catalysts are loaded into quartz capillaries connected to a pre-set gas rig. The output gasses are continuously monitored using mass spectrometry to obtain accurate information on the conversion profiles. The pre-determined positions of cations within zeolites make it possible to combine both long and short range probing techniques to yield information on the structure and co-ordination of the active sites. To that end, combined X-ray absorption and X-ray

diffraction data are collected at different temperatures under SCR conditions which help elucidate the local Cu environment in these catalysts.

In this particular case-study, an attempt was made at tailoring the active sites in Cu-CHA based catalysts. Three different synthetic routes were adapted to achieve this goal: two methods are based on post-synthetic treatment of the zeolite material (via aqueous or vapour phase) and a third one involving the direct synthesis of a Cu-loaded SAPO-34. Product analysis under SCR

conditions revealed that whilst the catalyst materials prepared via wet chemical routes show excellent deNO_x activity and high selectivity to N₂, the one prepared via chemical vapour deposition gave the undesired product N₂O in significant quantities. Isolated mononuclear Cu²⁺ ions in the vicinity of six-membered rings (*6mrs*, part of the *d6r* sub-units of CHA) were found to be active sites in both catalyst materials prepared via the wet chemical approaches. In contrast, the catalyst prepared via chemical vapour deposition possesses Cu in two different environments: isolated Cu²⁺ cations and CuAlO₂-type species. Catalytic experiments revealed a strong correlation between the number of isolated mononuclear Cu²⁺ in or near the plane of the *6m* rings and N₂ production, whereas the presence of CuAlO₂ species appears to promote the formation of undesired N₂O.



Our Reference: AP0368

PROJECT SUMMARY BY:



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PAPER REFERENCE:

U. Deka, I. Lezcano-Gonzalez, S. J. Warrender, A. L. Picone, P. A. Wright, B. M. Weckhuysen, A. M. Beale (2013) "Changing active sites in Cu-CHA catalysts: deNO_x selectivity as a function of the preparation method" *Microporous and Mesoporous Materials* **166**, 144-152

HIDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

The effect of heating rate on porosity production during the low temperature reduction of graphite oxide

Our Reference: AP0449

PROJECT SUMMARY BY:



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PAPER REFERENCE:

S. J. Yang, T. Kim, H. Jung, and C. R. Park
(2013) "The effect of heating rate on
porosity production during the low
temperature reduction of graphite oxide"
Carbon **53**, 73-80

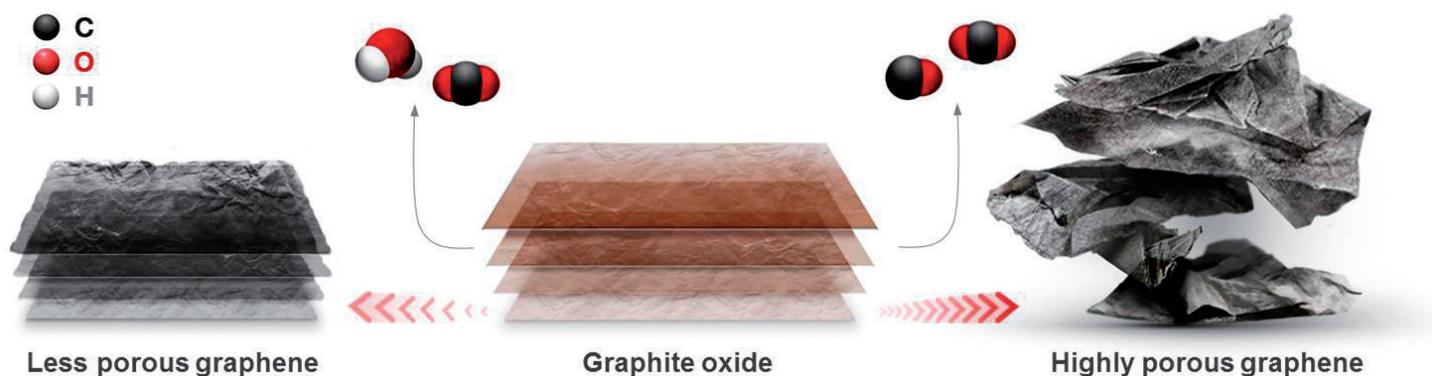
HIDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

Thermally reduced porous graphite oxide (TH-rGO), prepared by thermal reduction, is an emerging promising candidate material for use in energy and environmental applications. The effects of thermal reduction conditions on the evolution of pore characteristics in TH-rGO and the kinetics of thermal reduction are not well understood. Therefore a study was undertaken of the correlation of the thermal conditions with the evolution of the porosity in TH-rGO and the kinetics of thermal reduction.

The heating rate, rather than thermal conditions, plays a crucial role in the evolution of porosity during the thermal reduction of graphite oxide at low temperatures. Higher heating rates increase the porosity of the TH-rGO. A slow heating rate facilitates the evolution of H₂O and CO₂ whereas a higher heating rate releases CO₂ and CO gases with the concurrent development of a folded and crumpled morphology, investigated by using mass spectroscopy (HPR-20; Hiden Analytical). More importantly, the reduction time and temperature are found to be dependent on the heating rate. High heating rates shortened the reduction time (less than 5 min in $\geq 10\text{ }^{\circ}\text{Cmin}^{-1}$) with lower reduction

temperature (below 140 °C), whereas higher temperatures and longer times were required to complete the reduction reaction at low heating rates. With the results it may be possible to rationally design the pore textures and chemical structure of the chemically-reduced graphite oxide to fit a variety of end-uses, particularly in electrochemical energy storage, adsorbents, and conductive/reinforced carbon nanocomposites.



REPRESENTATIVE FIGURE. Schematic representations of the creation of a porous structure as a function of the heating rate during the low-temperature reduction of GO.

Screening of catalysts for H₂S abatement from biogas to feed molten carbonate fuel cells

Our research project concerns the H₂S abatement from a biogas stream to feed to molten carbonate cells (MCFC) for energy production.

Biogas is a renewable energy source that can be produced from biomass, agricultural and industrial waste and sewage sludge. Its main constituents are CH₄, CO₂ but unfortunately sulphur based compounds are present as H₂S, COS.

The main limitation to the use of biogas as fuel in these systems is linked to the presence of sulphur compounds such as H₂S that can poison the fuel cells components, anode and electrolyte.

For the small scale plant, a very interesting solution can be represented by the direct and selective H₂S oxidation to sulphur at low temperature by using a suitable catalyst.

The aim of the work is the study of the catalytic behavior of V₂O₅/CeO₂ samples at various vanadium loading (2.55 - 20 wt % as V₂O₅) to determine the optimal catalyst

formulation and operating conditions to obtain a very high H₂S conversion and the SO₂ selectivity minimisation.

The catalytic tests were carried out in a fixed bed flow reactor, made of a steel tube 21cm long and a 14 mm of internal diameter. The reactor is inserted in an electrical furnace equipped with a PID electronic temperature controller. A thermocouple is inserted in a steel sheath of the inner diameter of 6 mm concentric to the reactor.

Catalytic activity tests were carried out at atmospheric pressure and GHSV=9.5·10⁴ h⁻¹ (40 ms), in the temperature range 150 – 250 °C, by feeding a mixture of 200 ppm of H₂S, 100 ppm of O₂ and N₂ to balance (see Fig. 1)

The exhaust system was equipped with a sulphur trap and analysed by a quadrupole mass spectrometer (Hidden Analytical, HPR-20 QIC). Figure 2 shows typical behaviour of a catalytic activity test carried out by using a catalyst using the highest

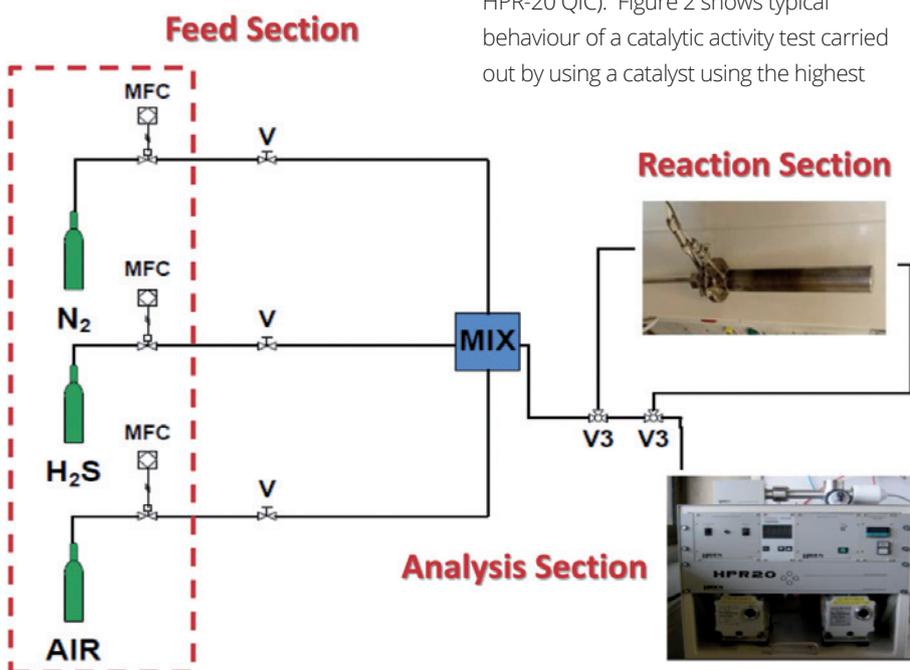


FIG. 1: Experimental apparatus for the catalytic tests

Our Reference: AP0491

PROJECT SUMMARY BY:



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PAPER REFERENCE:

V. Palma, D. Barba, P. Ciambelli (2013) "Screening of catalysts for H₂S abatement from biogas to feed molten carbonate fuel cells" *International Journal of Hydrogen Energy* **38** (1) 328-335

HIDDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

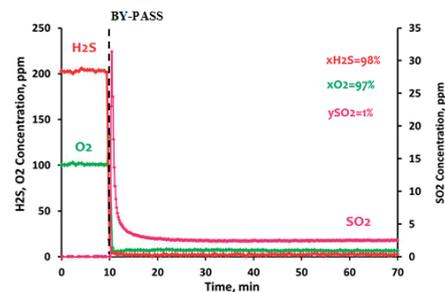


FIG. 2: Catalytic activity test of 20% V₂O₅/CeO₂ catalyst at 150°C

vanadium loading (20%). With this condition being the optimal catalytic performance and more selective to sulphur (99%) at lower temperature.

It can be seen from the data above, in the first 10 minutes of the experiment, that the feed stream was added in the by-pass position to stabilise the initial concentrations of H₂S and O₂. After this time, the feed stream was sent to the reactor, and large increases in the concentrations of H₂S, SO₂ and O₂ were observed. After a further 10 minutes the concentrations stabilised, showing high activity and stability of the catalyst.

The H₂S and O₂ conversions were 97 and 98% respectively, while the SO₂ concentration remained very low (~1%).

Calorimetric Adsorption for Catalyst Characterisation

The development of new solid acid and base catalysts depends on the availability of suitable catalyst characterisation techniques. One of the accepted methods for characterising surface acidity and surface basicity is adsorption calorimetry, using probe compounds to study the concentration and strength of active sites. For solid acids a basic probe such as NH_3 is used, and for solid bases acidic probes such as SO_2 or CO_2 are used.



FIGURE 1: Flow adsorption calorimetry instrumentation. The flow-through Setaram DSC111 differential calorimeter is visible on the extreme left. The sample tube is held vertically in the stainless steel furnace. The automated gas sampling valve is held on the platform. The low-flow capillary interface to the Hiden HPR-20 Mass Spectrometer can be seen under the valve platform. The tube furnace alongside the calorimeter is for catalyst activation.

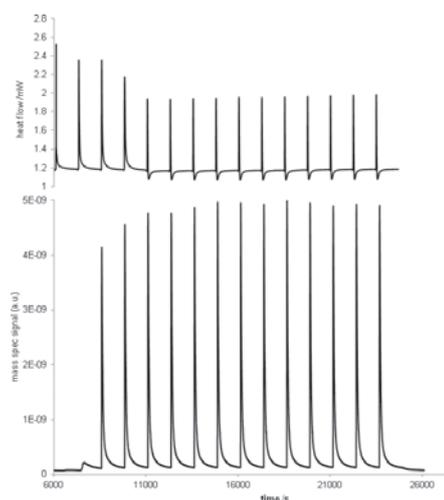


FIGURE 2: Differential calorimeter output (top trace), and downstream Hiden HPR-20 output for $m/z = 15$ (lower trace) for NH_3 adsorption on an acid catalyst (50 mg), held at 120°C , under flowing N_2 (5 ml min^{-1}) into which 1 ml pulses of 1% NH_3 in N_2 are introduced. In this experiment, the first two pulses are completely adsorbed by the sample. Pulses three to eight are partially adsorbed.

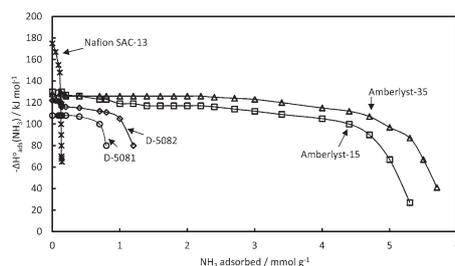


FIGURE 3: $-\Delta H_{\text{ads}}^0(\text{NH}_3)$ vs. amount adsorbed for catalysts studied, at 120°C .

In our system, a catalyst sample is held in a flow-through differential calorimeter and the probe gas is introduced as a series of pulses injected into a steady flow of carrier gas, normally nitrogen. The outflow from the calorimeter cell is sampled by a low-flow capillary interface linked to a Hiden HPR-20 Quadrupole Mass Spectrometer.

Once calibrated with the probe gas, the mass spectrometer signal (using an m/z unique to the probe gas) provides a measure of the amount breaking through the sample from each pulse and therefore allows the amount adsorbed from each pulse by the sample to be calculated. The output from the differential calorimeter, combined with that from the mass spectrometer, is presented as a profile of $\Delta H_{\text{ads}}^0(\text{probe})$ against the amount adsorbed, which can be broadly interpreted as an active site strength distribution profile for the catalyst.

Our Reference: AP0326

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PAPER REFERENCE:

E. Andrijanto, E. A. Dawson, D. R. Brown (2012) "Hypercrosslinked polystyrene sulphonate acid catalysts for the esterification of free fatty acids in biodiesel synthesis" *Applied Catalysis B: Environmental* **115-116**, Pages 261-268

HIDDEN PRODUCT:

HPR-20 QIC Real time Gas Analyser

The system is shown in Figure 1 and example data from an experiment in which NH_3 is introduced to a solid acid catalyst is shown in Figure 2.

The usefulness of this data in characterising solid acid catalysts is illustrated in Figure 3, where profiles of $-\Delta H_{\text{ads}}^0(\text{NH}_3)$ vs amount of NH_3 adsorbed are shown for a series of polymer-supported sulfonic acid catalysts. The objective of this study was to investigate the relationship between catalyst structure and the concentration and strength of the surface acid sites. The catalysts range from Nafion SAC-13 with 0.1–0.2 mmol g^{-1} of acid sites of high strength, to Amberlyst 35 with over 5 mmol g^{-1} of medium strength sites, to D-5081/2 with approximately 1 mmol g^{-1} of lower strength sites. This information can be related to the catalytic activities of these materials and can be used in a synthetic programme of catalyst optimisation.

Related Products:

Hidden CATLAB-PCS for Catalysis Studies

A catalyst characterisation and microreactor system designed to make the analysis of catalysts rapid and simple:

- ▶ Pulse Chemisorption
- ▶ TPD, TPO, TPR, TP-Reaction
- ▶ Catalyst Screening
- ▶ On-Line Continuous Product Analysis
- ▶ Metal Surface Area
- ▶ Active Surface Area
- ▶ Reaction Kinetics
- ▶ Mechanisms of Surface Reactions
- ▶ Heats of Adsorption



Hidden HPR-20 QIC Real time Gas Analyser

Real time gas analyser for multiple species gas and vapour analysis. Compact bench top analysis system for production and research applications:

- ▶ Process Monitoring
- ▶ In-Situ Analysis
- ▶ Contamination Studies
- ▶ CVD / MOCVD
- ▶ Environmental Gas Analysis
- ▶ Thermal Analysis Mass Spectrometry
- ▶ Catalysis Studies / Reaction Kinetics



HPR-20 QIC TMS for Fast Event Transient Analysis

The HPR-20 QIC TMS system is a compact bench-top gas analysis system for fast event gas studies:

- ▶ Transient Kinetic Analysis
- ▶ In-Situ Analysis
- ▶ Contamination Studies
- ▶ Environmental Gas Analysis
- ▶ Thermal Analysis Mass Spectrometry
- ▶ Catalysis Studies / Reaction Kinetics



OUR REFERENCE: HAPR0088

Multicapacity Microreactor for Catalyst Characterisation

The Hidden Catlab integrated microreactor/mass spectrometer (MS) system now addresses an extended applications range with the introduction of enlarged sample capacity options to accommodate sample volumes up to 2 mL. The system, developed for quantification of catalytic activity and thermal reaction processes in both R&D and QC laboratories, monitors gas and vapour reaction products directly from the sample position via the primary sampling interface embedded within the 1000 °C fast-response furnace. The interface concept maintains optimum system performance throughout the full sample capacity range down to 0.1 mL, with the cartridge-style sample holders enabling fast and accurate sample placement.



LabVIEW-based software is fully user-programmable to define the furnace temperature profile and ramp rate, establish MS data acquisition parameters, input gas/vapour flow through up to 8 mass flow controllers (MFC's), and select valve switching functions including pulse gas injection for chemisorption measurement. The temperature profile determines the trigger-points to change gas composition, to inject gas pulses and to stop/start data acquisition. Additionally MS analysis files can be selected and matched to specific sections of the experiment to ensure optimum data at each stage.

The CATLAB system is engineered for combined reactor/MS system operation yet is readily decoupled to enable operation of the mass spectrometer as a standalone laboratory and process gas analyser, a secondary interface providing a decoupling point for off-line MS operation.

For further information on these or any other Hidden Analytical products please contact Hidden Analytical at info@hiden.co.uk or visit the main website at www.HidenAnalytical.com

If you would like to submit a project summary for consideration in our next Newsletter, please email a brief summary (*approx. 500 words*) and corresponding images to marketing@hiden.co.uk

Hidden **APPLICATIONS**

Hidden's quadrupole mass spectrometer systems address a broad application range in:

GAS ANALYSIS

- ▶ dynamic measurement of reaction gas streams
- ▶ catalysis and thermal analysis
- ▶ molecular beam studies
- ▶ dissolved species probes
- ▶ fermentation, environmental and ecological studies



SURFACE ANALYSIS

- ▶ UHV TPD
- ▶ SIMS
- ▶ end point detection in ion beam etch
- ▶ elemental imaging - surface mapping

HIDDEN

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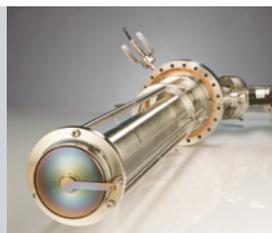
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PLASMA DIAGNOSTICS

- ▶ plasma source characterisation
- ▶ etch and deposition process reaction kinetic studies
- ▶ analysis of neutral and radical species



VACUUM ANALYSIS

- ▶ partial pressure measurement and control of process gases
- ▶ reactive sputter process control
- ▶ vacuum diagnostics
- ▶ vacuum coating process monitoring

