Issue Number: 1120/01

HidenLife

A world of products connected by science & imagination

Hiden Quadrupole Mass Spectrometers *in action*:

Gas reaction studies and catalysis research

Hiden Quadrupole mass spectrometers are used for process, environmental and research applications throughout the world.

This newsletter includes a selection of the most recent application stories from referenced published sources.

Our contributors to this newsletter caught our eye with published articles of the highest quality.

Key data from Hiden QIC series gas analysers, and the Catlab microreactor systems are included.

We are delighted that they have shared a brief synopsis of their research for our newsletter.

A very big thank you to all who have contributed.

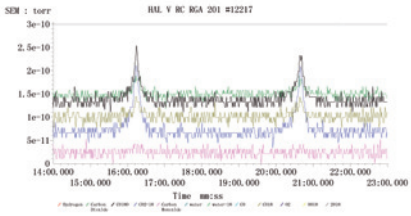
In this issue:

HIDEN ANALYTICAL

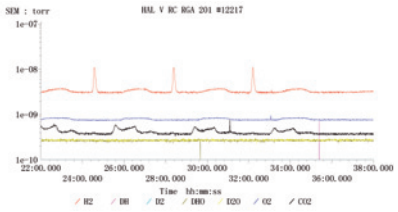
Customer Stories:

In-situ investigation of the cathode catalysts for PEM fuel cells using differential electrochemical mass spectrometry

Differential electrochemical mass spectrometry (DEMS) involves applying a potential across an electrochemical cell and measuring the resulting current while concurrently analyzing gas products with a mass spectrometer. We used DEMS to investigate the mechanism of carbon support corrosion (CSC) in-situ at the cathode of proton exchange membrane fuel cell (PEMFC). The cathode exhaust gases were sampled with a Hiden Analytical QIC-20 mass spectrometer. The spectra of gases were correlated in our laboratory for the first time to characterize most reactions that happen at the cathode in a real PEMFC. Moreover, the sensitivity and resolution of DEMS were improved significantly to enable study of a 5 cm2 membrane electrode assembly (MEA), which makes it very convenient for researchers to compare different catalysts in PEMFC. To further understand the mechanism of CSC, oxygen was isotopically labeled by replacing regular water with oxygen-18 (18O) enriched water (H218O, 98%) in DEMS. Among many surprising results, we showed that water – not oxygen – was the main reaction intermediate in CSC. Knowledge of the CSC mechanism disclosed in our study will boost the design of new carbon supported catalysts for PEMFC with longer lifetime.

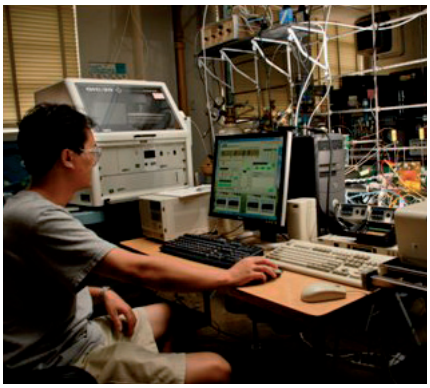


▲ A screen shot of the MS spectra from an oxygen-18 labeled CSC experiment.



▲ A screen shot of the MS spectra from an experiment for resolving H_{UPD} and H_{OPD}.

Hydrogen adsorption/desorption from solution is a common method to determine the electrochemically active surface area (ECSA) of a few transition metals. However, it is not straightforward because of the overlap between overpotential (HOPD) and underpotential deposited hydrogen (HUPD). We demonstrated for the first time how to resolve HOPD and HUPD by DEMS to determine the ECSA of the Pt electrode in a PEMFC. This method has the potential to be extended to other transition metals in acidic or basic media.



Our Reference: AP0007

Project Summary by:

Wei Li and Alan M. Lane, The University of Alabama Department of Chemical and Biological Engineering, Alabama USA

Paper Reference:

"*Analysis of oxygen sources and reaction pathways of carbon support corrosion at the cathode in PEMFC using oxygen-18 DEMS*" Electrochimica Acta, Volume 55, Issue 22, 1 September 2010, Pages 6926-6931

Hiden Product:

QIC-20 Gas Analysis System

(QIC-20 System now updated with the New QGA Atmospheric Gas Analysis System. This latest version was released in 2010. Refer to "Hiden Products" and "In the Press" sections for further information.)

Preparation and Characterisation of Nickel based Catalysts for Partial Oxidation of Methane

Hydrogen, which can be used in many fields without polluting the environment, is thought to be the cleanest fuel source of 21th century. Therefore, low cost production, facile storage and transportation of hydrogen are important research subjects that are investigated by many universities and related commercial facilities.

Steam-hydrocarbon reforming is the major hydrogen production process today. However, this process has many disadvantages like high energy demand and complicated equipment design etc. For this reason, there have been many researches to develop alternative processes for several decades and catalytic partial oxidation and autothermal reforming have come forth as good alternatives. Partial oxidation process doesn't require external heat because of being slightly exotermic and occurs faster 10 or 100 times than the steam reforming, therefore small reactors could be used. Thus, by lowering the total investment and production costs, hydrogen production cost could be lowered. Furthermore, by the help of this process hydrogen, which is needed for the fuel cell, could be produced with a simple on-board fuel conversion device and the problems for hydrogen storage and transportation could be handled. Alike, introducing steam to the reaction area by using autothermal reforming hydrogen production yield can be increased and cost can be lowered.

Methane has seemed to be the best hydrocarbon source for partial oxidation and autothermal reforming process because methane is the main component in natural gas and natural gas is abundant on earth. Additionally, methane has the property of having the highest H/C (H/C=4) ratio in hydrocarbons.

Researchers have tested many catalysts for partial oxidation of methane and have seen that noble based metals catalysts (Rh, Pt, Ru, Ir) with nickel (Ni) based catalysts are active and selective for this reaction. Although, noble metal based catalysts are stable and active, because of their high cost and low availability, the best alternative have thought to be nickel based catalysts. But these catalysts have disadvantages like sintering, coking and phase transformation. There have been many attemps to solve these problems so far but couldn't be solved totally.

With the aim of solving these problems Ni and Ni-Co based catalysts which are loaded on appropriate support will be prepared by impregnation and polyol methods, metallic ratios and methods effect will be investigated. According to literature by using polyol method it is possible to obtain uniformly dispersed and <10 nm active metal size. By uniform dispersion sintering, by <10 nm metallic particle obtaining carbon deposition suppression is thought to be prevented. Additionally, by Ni-Co alloying carbon deposition suppression is sighted. Therefore, low costly, easily producible, highly active, selective and stable catalyst preparing has been planned which can be used commercially.

The catalysts that prepared will be characterized and tested by using TG-DTA, BET, MICROREACTOR-MS, GC which is found in our lab, XRD and AAS which is found in our university research laboratory with SEM which is found in TUBITAK MAM.

Our Reference: AP0027

Project Summary by:

Asistant Prof.Faruk Öksüzömer, Istanbul University Chemical Engineering Department, Istanbul Turkey

Paper Reference:

"*Preparation and characterization of Ni based catalysts for the catalytic partial oxidation of methane: Effect of support basicity on H2/CO ratio and carbon deposition*", International Journal of Hydrogen Energy, Volume 35, Issue 22, November 2010, Pages 12147-12160

Hiden Product:

Integrated Microreactor-MS, with CATLAB-PCS Module & QIC-20 MS Module

(QIC-20 System now updated with the New QGA Atmospheric Gas Analysis System. This latest version was released in 2010. Refer to "Hiden Products" and "In the Press" sections for further information.)

n-butane partial oxidation to maleic anhydride under transient regimes

Maleic anhydride (MA) is commercially produced from partial oxidation of n-butane by air over vanadium pyrophosphate (VPP) catalyst. There has been a huge research interest 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.

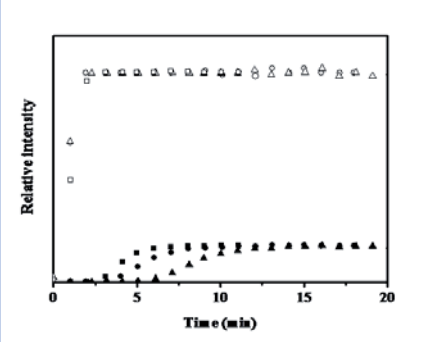
In this research program we have focused on investigating the effect of a wide range of redox conditions covering the actual conditions existing in industrial fixed bed, fluidized bed and circulating fluidized bed reactors. We have simulated the transient redox conditions by conducting experiments in Hiden's Catlab micro-reactor coupled to online MS. We could

CO2 adsorption over ion-exchanged zeolite beta with alkali and alkaline earth metal ions

The need to reduce anthropogenic CO2 emissions has been the driving force to consider new approaches and novel ideas for CO2 management, and carbon capture and storage (CCS) are considered to potentially be the most effective means to alleviate the problem. The most common method for CO2 capture is via gas absorption, with monoethanol amine (MEA) being the most widely used solvent. The current amine based systems for CO2 removal, however, suffer from a high energy requirement for solvent regeneration and corrosion. Thus, alternative processes for CO2 removal via selective adsorption on solid media such as zeolites, activated carbons, alumina, hydrotalcite-like compounds, metal oxides, and metal organic frameworks (MOFs) are being investigated in this laboratory. Solid adsorbents typically employ cyclic and multi module processes of adsorption and desorption, with desorption induced by either a pressure or temperature swing.

▲ Breakthrough instrument

The gas-separation properties of zeolite beta after ion-exchange were recently tested by breakthrough experiments using a CO2/N2 (about 15:85 v/v) gas mixture. 0.5 g of pretreated adsorbent was placed inside a U-type stainless-steel column (1.27 cm inner-diameter and 45 cm total length), and the gas mixture was fed into the column at a flow rate of 30 mL/min. All the experiments were carried out at room temperature. The relative amounts of the gases passing through the column were monitored on a Hiden Analytical HPR20 gas analysis system. The relative intensity of each gas component was normalized to the same level by purging gas mixtures through the bypass before they passed through the column. Similar experimrntal work was also conducted over mesoporous alumina prepared by sol-gel process.



▲ Breakthrough curves for CO2 (15 vol%, N2 balance) adsorption over M-BEA; (○) N2 Na-BEA, (●) CO2 Na-BEA, (□) N2 K-BEA, (▲) CO2 K-BEA, (□) N2 Cs-BEA, and (■) CO2 Cs-BEA.

Our Reference: AP0025

Project Summary by:

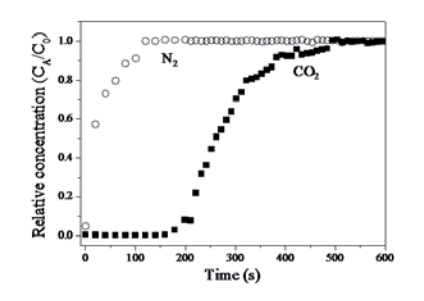
Professor Wha-Seung Ahn, Inha University Department of Chemical Engineering, Catalysis & Nanomaterials Lab. Incheon Korea

Paper Reference:

"*CO2 adsorption over ion-exchanged zeolite beta with alkali and alkaline earth metal ions*", Mesoporous Materials, Volume 135, Issues 1-3, November 2010, Pages 90-94

Hiden Product:

HPR-20 QIC Realtime Gas Analyser

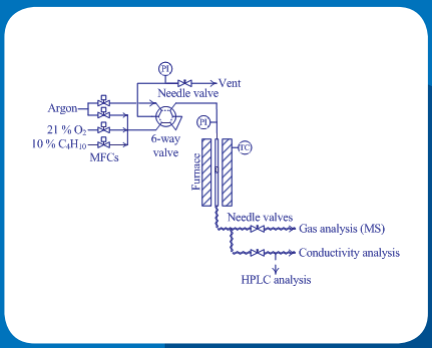


▲ Breakthrough curve of CO2 (15% CO2, 85% balance N2) on mesoporous alumina.

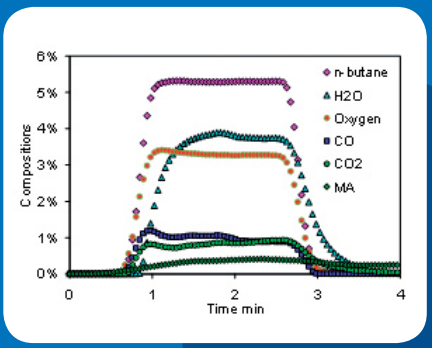
For further information on these or any other Hiden Analytical products please contact Hiden Analytical at **info@hiden.co.uk** or visit the main website at **www.HidenAnalytical.com**

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**

characterize the transient behaviour of the VPP catalyst under different operating conditions and also we have modeled the underlying transient kinetics of this complex reaction over the full range of studied operating conditions.



▲ Redox micro-reactor setup



▲ MS transient response

Our Reference: AP0033

Project Summary by:

Ali Shekari, École Polytechnique de Montréal, Québec Canada

Paper Reference:

"*Maleic anhydride yield during cyclic n-butane/oxygen operation*", Catalysis Today, Volume 157, Issues 1-4, 17 November 2010, Pages 334-338

Hiden Product:

CATLAB-PCS Microreactor

In the Press:

Hiden Products referenced in our Customer Stories in this issue:

Hiden CATLAB-PCS

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

The Hiden HPR-20 QIC

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

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

QGA Atmospheric Gas Analysis System

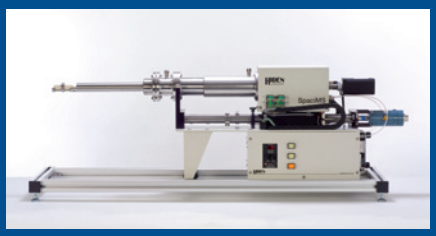
(Hiden's QIC-20 Gas Analysis System has now been updated with the QGA System. This latest version was released at the end of 2010). Compact bench top analysis system for realtime gas and vapour analysis:

- Gas Reaction Studies
- Fuel Cell Reactions Studies
- Contamination Studies
- Fermentation Analysis
- Environmental Gas Analysis
- Thermal Analysis Mass Spectrometry
- Catalysis Studies / Reaction Kinetics

Hiden TMS System for Fast Event Gas Analysis Studies

(Our Reference: PR0046)

The Transient Mass Spectrometer System has been specifically designed for the analysis of fast transient gas events at process pressures near atmosphere. Typical applications include respiratory analysis, process control, pulsed gas experiments for surface reaction/ reduction studies in catalyst characterisation and, with high-speed rotating multiport valve, spacial gas distribution measurement as demonstrated in the award-winning Hiden Spaci-MS system.



QGA Atmospheric Gas Analysis System

(Our Reference: PR0040)

The new QGA compact benchtop mass spectrometer has been configured for continuous real-time multi-species analysis of both gases and vapours in the pressure range from 2 bar to 100mbar absolute. Applications include thermal analysis, fermentation processes, catalysis and general gas reaction studies.

Hiden Applications

Hiden'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 Science

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

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

Sales Offices:

We have sales offices situated around the globe.
Visit our website for further information.

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