

Gas Analysis for Hydrogen Applications



Customer Contributions:

Synthesis and hydrogen storage properties of $Mg(AlH_4)_2$

Y. Liu, Y. Pang, M. Gao & H. Pan † Zhejiang University

Symbiotic $CeH_{2.73}/CeO_2$ Catalyst: a Novel Hydrogen Pump

Huai-Jun Lin, et al. † South China University of Technology

Hydrogen Production by Variable Volume Membrane Batch Reactors with Modulated Liquid Fuel Introduction

Andrei G. Fedorov † Georgia Institute of Technology

Study of the catalyst load for a microwave susceptible catalytic Diesel Particulate Filter (DPF)

V. Palma & E. Meloni † University of Salerno

In the Spotlight:

Gas Analysis for Hydrogen Applications

Related Products:

HPR-20 QIC R&D - for Advanced Research

QGA - for Real-time Gas & Vapour Analysis

CATLAB-PCS - for Catalysis Studies

A very big thank you to all who have contributed:

South China University of Technology



Georgia Institute of Technology

Synthesis and hydrogen storage properties of $\text{Mg}(\text{AlH}_4)_2$

Metal alanates are regarded as a very promising group of materials for high-density solid-state hydrogen storage. Therefore, the search for new alanates with high hydrogen content and sufficiently fast reaction kinetics of absorption and desorption at moderate temperatures is still a very active field.

In this work, we developed a modified synthesis method for $\text{Mg}(\text{AlH}_4)_2$ with high purity. By ball milling the mixture NaAlH_4 and MgCl_2 (molar ratio: 2:1) in Et_2O followed by Soxhlet extraction, $\text{Mg}(\text{AlH}_4)_2$ submicron rods were successfully obtained as the resultant product, and its purity was determined to be as high as 96.1%. Upon heating, ~9.0 wt% of hydrogen was released from the as-prepared $\text{Mg}(\text{AlH}_4)_2$ with a three-step reaction. This was measured by a combination of MS (m/z 2, **Hidden QIC-20**) and volumetric analyses. At 125–200°C, $\text{Mg}(\text{AlH}_4)_2$ decomposed first to liberate hydrogen and generate MgH_2 and Al (Figure 1 (a)). With increasing temperature to 320°C, the newly produced MgH_2 reacted with Al to form the $\text{Al}_{0.9}\text{Mg}_{0.1}$ solid solution along with hydrogen release. As the temperature was further elevated to 440°C, the reaction

between the $\text{Al}_{0.9}\text{Mg}_{0.1}$ solid solution and the remaining MgH_2 occurred to evolve additional hydrogen and form Al_3Mg_2 . DSC measurement showed that the first step dehydrogenation is exothermic while the last two steps are endothermic (Figure 1 (b)).

Analysis of the isothermal and non-isothermal behaviours revealed a diffusion-controlled kinetic mechanism for the first step dehydrogenation, and its apparent activation energy was calculated to be about 123.0 kJ/mol. However, only ~2.3 wt% of hydrogen could be recharged at 140–210°C and 100 bar of hydrogen pressure. Therefore, further improvement on hydrogen storage reversibility of $\text{Mg}(\text{AlH}_4)_2$ should be performed to make it useable as a potential hydrogen storage material.

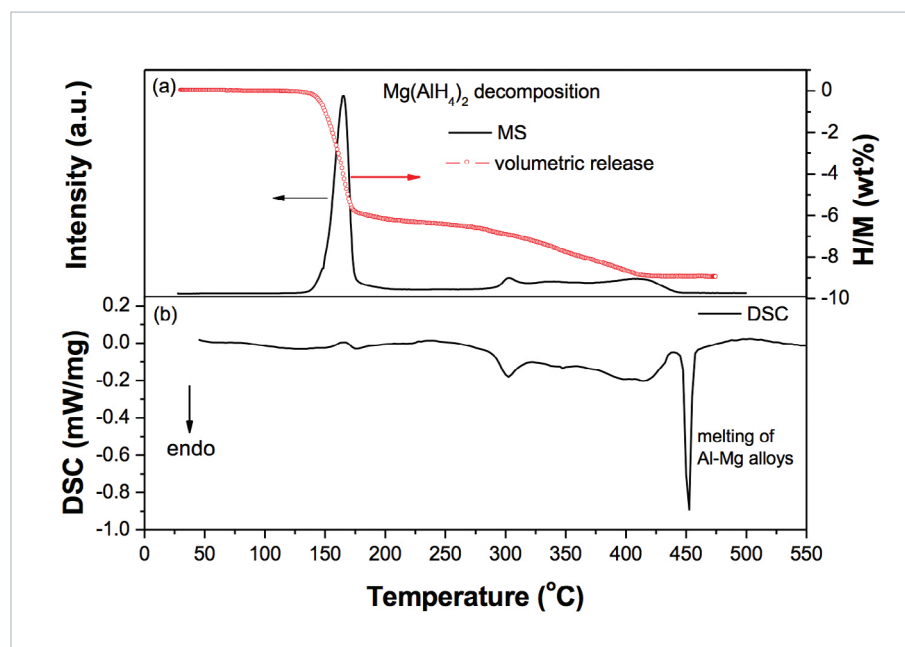


FIGURE 1: H_2 -TPD, volumetric release (a) and DSC (b) curves of the as-prepared $\text{Mg}(\text{AlH}_4)_2$.

Our Reference: AP0466

PROJECT SUMMARY BY:



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PAPER REFERENCE:

Y. Liu et al. (2012) "Synthesis and hydrogen
storage thermodynamics and kinetics of
 $\text{Mg}(\text{AlH}_4)_2$ submicron rods" *International
Journal of Hydrogen Energy*, **37**, (23),
18148-18154

HIDEN PRODUCT:

QGA Atmospheric Gas Analysis System
(was QIC-20)

Symbiotic CeH_{2.73}/CeO₂ Catalyst: a Novel Hydrogen Pump

A novel symbiotic CeH_{2.73}/CeO₂ catalyst was *in situ* induced in Mg-based hydrides, leading to remarkably reduced hydrogen desorption temperatures. More importantly, we reveal a spontaneous hydrogen release effect at the CeH_{2.73}/CeO₂ interface using *in situ* High-Resolution Transmission Electron Microscope (HRTEM) and *ab-initio* calculations.

Using additives/catalysts to destabilize hydrides of high hydrogen storage density, e.g. MgH₂ with 7.6 wt.%-H and desorption temperature as high as 300-400°C, is one of the most important strategies to overcome the hurdle of applying hydrogen storage materials in technologies related to hydrogen energy. Despite tremendous efforts, the development of additives/catalysts with high catalytic activity and easy doping remains a great challenge. In this work, we report a simple method to induce a novel symbiotic CeH_{2.73}/CeO₂ catalyst in Mg-based hydrides, which is capable of being mass produced. The first step is to hydrogenate the amorphous Mg-Ce-Ni alloy to get a multiphase composite of MgH₂, Mg₂NiH₄ and CeH_{2.73}, and the second step is to oxidize the hydrogenated sample to generate CeO₂ from CeH_{2.73}. Moreover, we reveal a spontaneous hydrogen release effect at the CeH_{2.73}/CeO₂ interface, which leads to a dramatic increase of catalytic activity compared with the CeH_{2.73} or CeO₂ catalyst alone. TPD-MS analysis was performed on a **Hidden QIC-20** mass spectrometer (Figure 1 (a)). With the increase

of the CeH_{2.73} to CeO₂ ratio, the hydrogen desorption temperature decreases at first and then increases after reaching the trough at the molar ratio of 1:1. The catalytic activity of the symbiotic CeH_{2.73}/CeO₂ might have a close relationship with their interface density, which reaches the maximum when molar ratio of CeH_{2.73} to CeO₂ is 1:1, however, the mechanism is not well understood. The lowest dehydrogenation onset temperature is only ~210 °C in the presence of the symbiotic CeH_{2.73}/CeO₂, which is ~210°C lower than that of conventional MgH₂. The dynamic boundary evolution during hydrogen desorption was observed in the symbiotic CeH_{2.73}/CeO₂ at atomic resolution using *in situ* High-Resolution Transmission Electron Microscope (HRTEM) (Figure 1 (b)).

The boundary region suffers severe distortions and the distorted areas fluctuates wave-like during hydrogen desorption, suggesting that the interface region of the symbiotic nanocrystals undergo structural evolution at the atomic scale, which presumably plays a prominent role for the release of hydrogen in dehydrogenation.

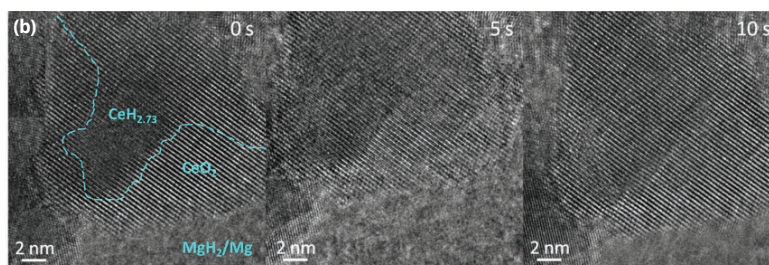
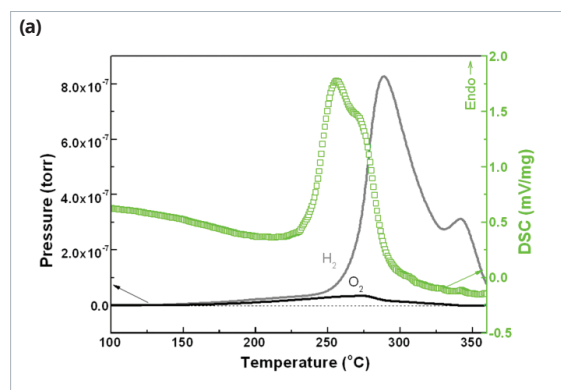


FIGURE 1: (a) DSC and TPD-MS curves of the symbiotic CeH_{2.73}/CeO₂ doped MgH₂, heating rate of 2 K/min. (b) *In situ* HRTEM images of the dehydrogenation process, boundary between CeH_{2.73} and CeO₂ is roughly drawn with a dash line at the beginning of hydrogen desorption

Our Reference: AP0918

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PAPER REFERENCE:

Huai-Jun Lin, et al.(2014) "Symbiotic
CeH_{2.73}/CeO₂ catalyst: A novel hydrogen
pump" *Nano Energy* **9**, 80-87

HIDDEN PRODUCT:

QGA Atmospheric Gas Analysis System
(was QIC-20)

Combining the *ab-initio* calculations, which show significant reduction of the formation energy of hydrogen vacancy in the CeH_{2.73}/CeO₂ boundary region in comparison to those in the bulk MgH₂ and CeH_{2.73}, we demonstrate that the outstanding catalytic activity can be attributed to the spontaneous hydrogen release effect at the CeH_{2.73}/CeO₂ interface.

Hydrogen Production by Variable Volume Membrane Batch Reactors with Modulated Liquid Fuel Introduction

A novel dynamically-controlled membrane batch reactor, which combines the variable volume operation of CHAMP (CO₂/H₂ Active Membrane Piston) with the direct injection of liquid fuel of DDIR (Direct Droplet Impingement Reactor) for enhanced power density, is demonstrated and experimentally characterized in this study.

A laboratory-scale CHAMP-DDIR, consisting of a variable volume piston-cylinder reactor chamber and an actively-controlled micro injector for liquid fuel atomization, is used with a Pd-Ag foil membrane and Cu/ZnO/Al₂O₃ catalyst to steam reform methanol for hydrogen generation (Figures 1 & 2). Two modes of CHAMP-DDIR operation, pulse-modulated fuel injection and batch reaction with dynamically-adjusted reactor volume, were investigated, and their performance was quantified using metrics such as hydrogen yield measured using a mass spectrometer (**Hidden Analytical Quadrupole HPR-20 QIC**) and volumetric power density, and compared with those for a baseline operation (single fuel injection with fixed reactor volume).

The experimental results showed that the residence time for the same hydrogen yield can be reduced by compressing the reactor volume during the conversion cycle. The residence time reduction was primarily as a result of higher hydrogen partial pressure in the reactor chamber and thus higher rates of hydrogen permeation. In addition, pulse-modulated fuel injection experiments revealed that a significant reduction in required reactor volume can be achieved with multi-shot split fuel introduction (Figures 3 (a) & (b)). Both the reduction in required cycle time and the reduction in required reactor volume increase the volumetric power density of CHAMP-DDIR.

Our Reference: AP0937

PROJECT SUMMARY BY:



Andrei G. Fedorov

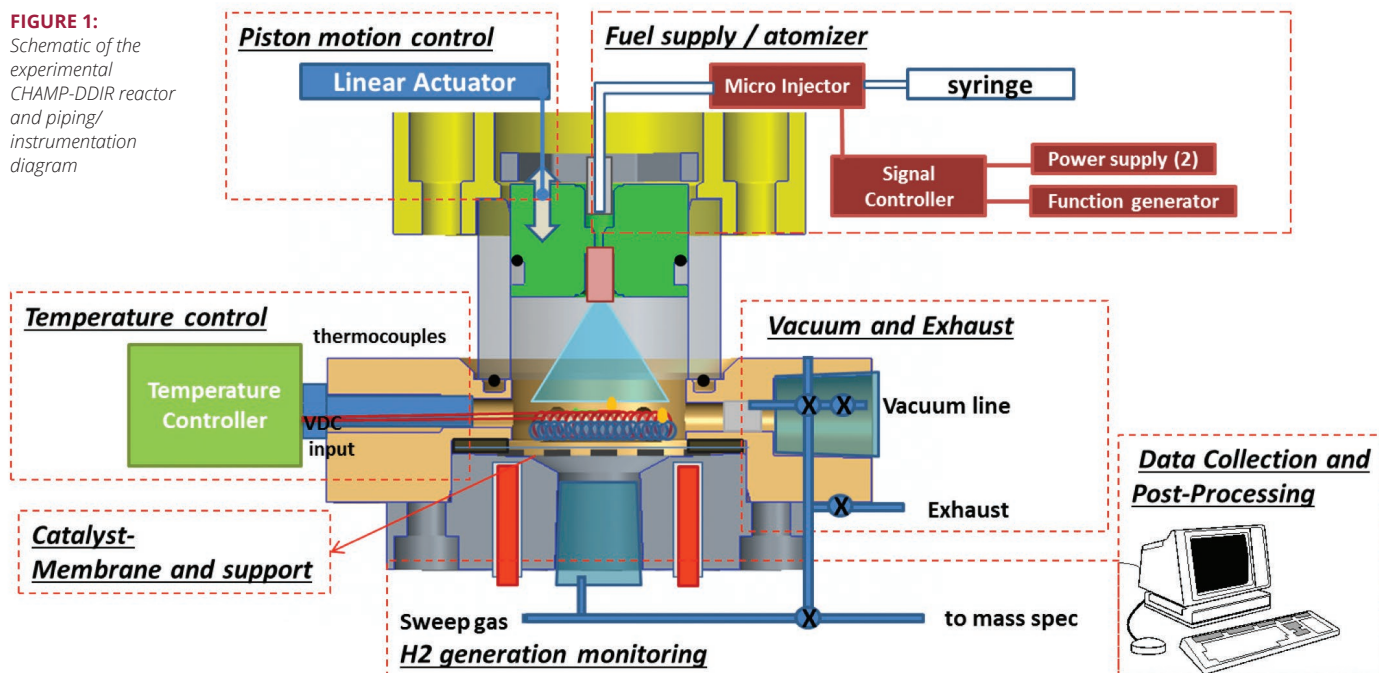
George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332-0405 USA

PAPER REFERENCE:

Yun, T. M., Kottke, P. A., Anderson, D. A., and Fedorov, A. G. (2015) "Experimental investigation of hydrogen production by variable volume membrane batch reactors with modulated liquid fuel introduction" *International Journal of Hydrogen Energy* **40** (6) 2601-2612

HIDEN PRODUCT:

HPR-20 QIC



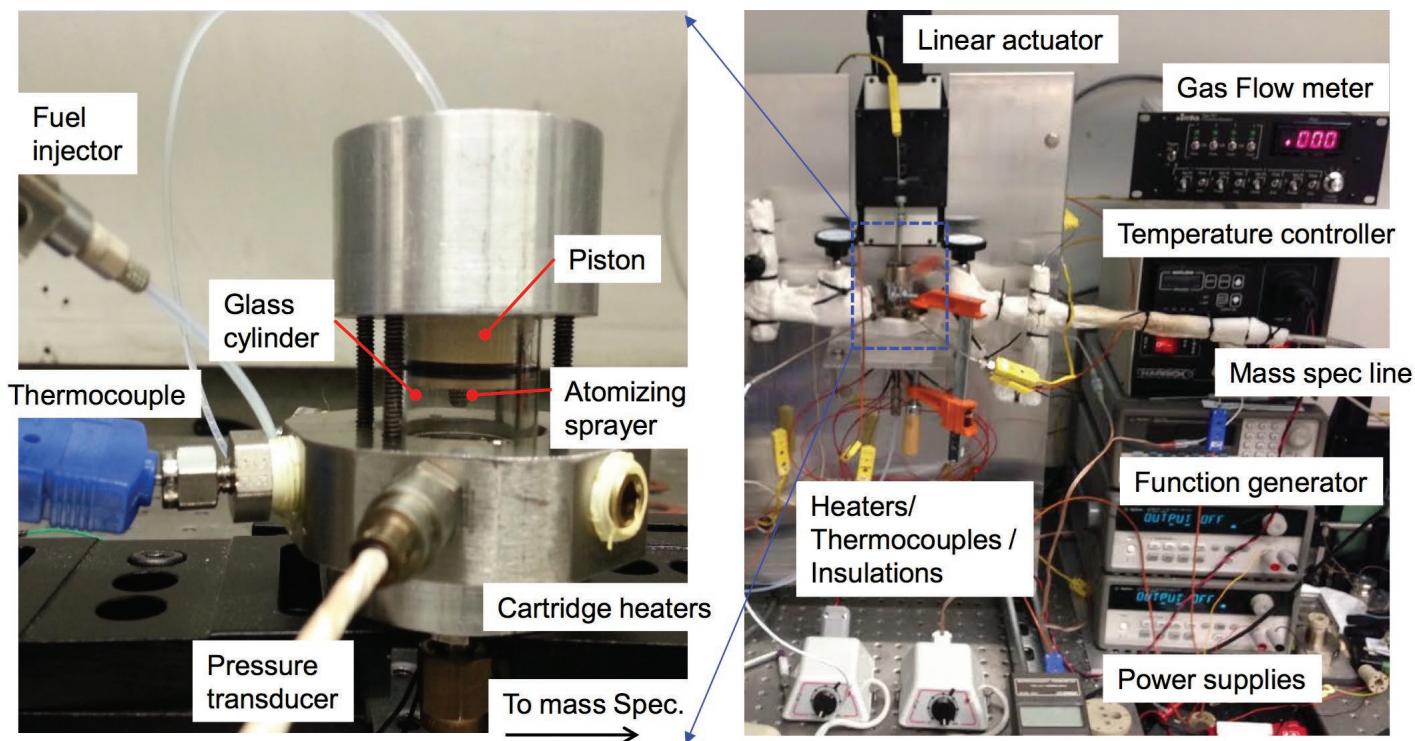


FIGURE 2: Photograph of the experimental testbed used in CHAMP-DDIR performance characterization

Importantly, a significant improvement in volumetric power density is revealed as a result of combining time-modulated fuel introduction with reduced reactor volume. The demonstrated power density enhancement achieved through the dynamic

compression of reactor volume was 17%, and the enhancement achieved through time-modulated fuel introduction was 38% (for 85% hydrogen yield efficiency under the constraints of the same maximum operating pressure and total amount of fuel) (Figure

3(c)). The enhanced power density and potential for hydrogen throughput control demonstrates the value of CHAMP-DDIR for applications such as transportation, where high power density and the ability to meet time varying power demands are important.

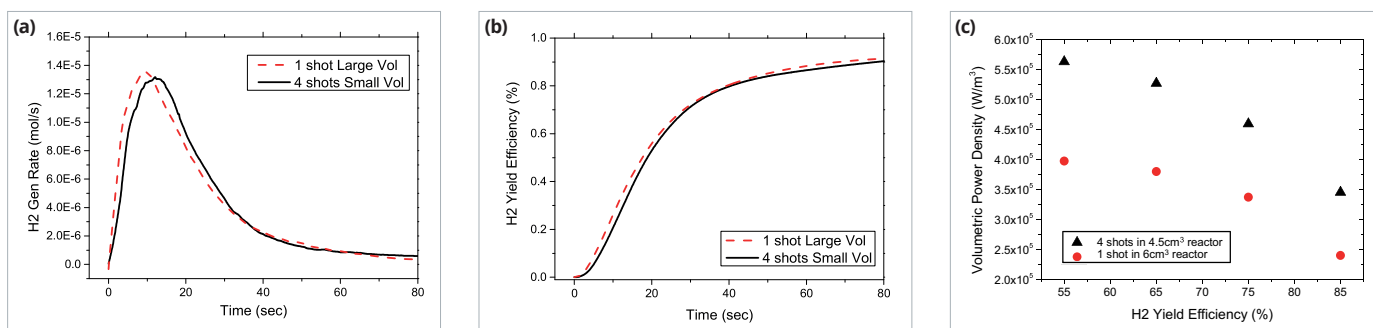


FIGURE 3: Results for time-modulated fuel injection experiments with constant, but different reactor volumes (6cm^3 and 4.5cm^3) under constrained pressure: (a) H_2 permeation rate, (b) H_2 yield efficiency, and (c) volumetric power density for 4 shot injection (4.5cm^3) and single injection (6cm^3) fixed volume operations for the reactors operated under a constraint of the maximum peak pressure. Initially, the hydrogen generation rate is higher with the single shot/large volume operation as compared to the multi-shot/small volume operation. However, because the smaller volume reactor maintains a higher pressure over most of the cycle, total H_2 yield becomes similar around 70% yield efficiency. For 85% hydrogen yield efficiency, volumetric power densities were improved by 38% by splitting fuel injection into 4 shots and using a 25% smaller volume.

Study of the catalyst load for a microwave susceptible catalytic DPF

Motivated by increasingly stringent emissions regulations, Diesel Particulate Filters (DPFs) have seen widespread use as the only technically and economically feasible means for meeting current and future Particulate Matter (PM) emissions limits.

The development of a fast, safe and cost effective Diesel Particulate Filter (DPF) regeneration procedure is the major remaining technological challenge in the use of this device. In our previous works we showed that the simultaneous use of a microwave applicator and a specific catalyst loaded DPF, with 15%wt of CuFe_2O_4 , allows the reduction of the temperature, the energy and the time required for the DPF regeneration. Starting from these very promising results, our research activity is focused on the further improvement of the performances of the catalyzed DPF in terms of catalytic activity, with the aim to reduce the temperature and the microwave energy required for the regeneration. So the objectives of our work are to optimize the preparation procedure of the catalytic DPF, to study the effect of the active species load, and to verify the feasibility of the microwave technology by assessing the energy balance of the regeneration phase, comparing it to the actual employed regeneration technologies. In this assessment, one of the important characterization tests on the prepared catalysts is the Hydrogen – Temperature Programmed Reduction (H_2 -TPR): these measurements are carried out using a SiC catalytic monolith from room temperature to 900°C at a heating rate of



FIGURE 1: *The Hiden Analytical System in the Lab.*

5°C/min in 5% H_2/N_2 flow. The reaction parameters (temperature and concentrations) are monitored by means of a customized HIDEN Analytical system based on **HPR-20 QIC R&D & Proteus Multi-stream Sampling Valve** configuration, able to periodically sample up to 20 discrete gas streams, which were then subsequently analysed by a mass spectrometer (Figure 1).

As an example, Figure 2 shows the result of a H_2 -TPR performed using a SiC monolith loaded with 15%wt of CuFe_2O_4 .

The H_2 -TPR profile shows two pronounced reduction peaks at about 300°C and 610°C; these peaks are attributed to the reduction

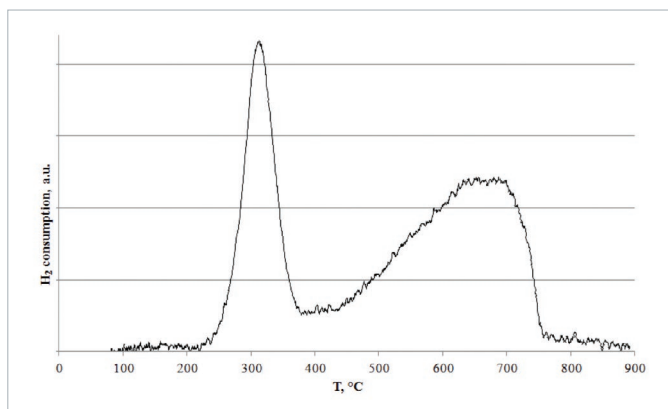


FIGURE 2: *H_2 -TPR profile of a SiC monolith loaded with 15%wt of CuFe_2O_4*

Our Reference: AP0729

PROJECT SUMMARY BY:



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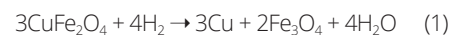
PAPER REFERENCE:

V. Palma, P. Ciambelli, E. Meloni & A. Sin (2013) "Study of the catalyst load for a microwave susceptible catalytic DPF" *Catalysis Today* **216**, 185-193

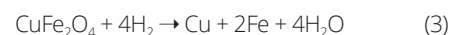
HIDEN PRODUCT:

HPR-20 QIC R&D (with Proteus)

of CuFe_2O_4 to Cu and Fe_3O_4 , and subsequently of Fe_3O_4 to Fe. The two reactions are:



The total amount of H_2 consumed per mole of Cu (H_2/Cu ratio) was 4.4, which is consistent with that for the complete reduction of CuFe_2O_4 to Cu and Fe according to the following reaction:



The value of 4.4 corresponds to about 17%wt of CuFe_2O_4 which is in good agreement with the estimated 15%wt of CuFe_2O_4 on the monolith. Furthermore, as reported in the literature, after the reduction, the mixture of Cu and Fe is favorable for the formation of CuFe_2O_4 at high temperature (about 800 °C in air). The TPR profile shows that the catalyst loaded monolith is able to act as a redox oxidation catalyst active in the temperature range 300 – 800°C due to the presence of a very good and homogeneous copper ferrite dispersion.

Related Products:

HPR-20 QIC R&D - for Advanced Research

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
- ▶ Catalysis Studies/Reaction Kinetics
- ▶ Environmental Gas Analysis
- ▶ CVD / MOCVD / ALCVD
- ▶ Contamination Studies
- ▶ Thermal Analysis Mass Spectrometry



QGA – for Real time Gas & Vapour Analysis

A compact bench top analysis system for real time gas and vapour analysis:

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



CATLAB - for Catalyst Characterisation, Kinetic and Thermodynamic Measurements

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



Gas Analysis for Hydrogen Applications



Hydrogen is being evaluated and promoted worldwide as an environmentally benign replacement for gasoline, natural gas and other fuels in both transportation and non-transportation applications. An extensive amount of research and development is currently being conducted worldwide investigating hydrogen production (reforming of natural gas; gasification of coal and biomass; and the splitting of water by a variety of different techniques) and hydrogen storage (in its three principal forms – gas, liquid and solid). Hydrogen is also a very important molecule in terms of the characterisation of catalysts and materials and the understanding of their properties.

This customer research review provides a selection of applications where the measurements of hydrogen is a significant component of the research.

The Hiden gas analysis systems have key benefits for applications in which light gases such as hydrogen (H_2) are used and/or measured.

Hiden systems demonstrate excellent H_2 sensitivity – more than x2 sensitivity for H_2 compared with published standard RS factors and can include independent foreline and bypass pumps to provide optimum pumping performance.

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

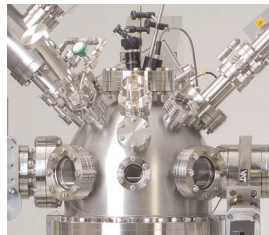
If you would like to submit a project summary for consideration in our next Newsletter, please email a brief summary (approx. 500 words) and corresponding images to marketing@hiden.co.uk

HiddenAPPLICATIONS

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

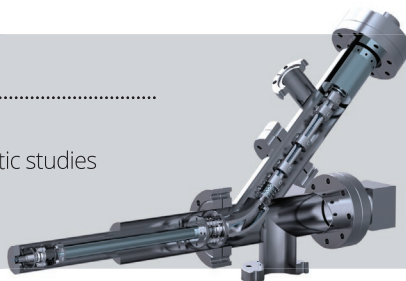


SURFACE ANALYSIS

- ▶ UHV TPD
- ▶ SIMS
- ▶ end point detection in ion beam etch
- ▶ elemental imaging – 3D 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

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