

“Combinatorial and High-Throughput Discovery and Optimization of Catalysts and Materials”

CRITICAL REVIEWS IN COMBINATORIAL CHEMISTRY, VOLUME 1

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A Selective Review by Kim Chandler* and Ann Keep**

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Introduction

This volume is the first in a series which covers molecular diversity and combinatorial chemistry, high-throughput discovery and associated technologies including characterisation techniques. Particular areas of interest having relevance to the platinum group metals (pgms) have been selected for a series of reviews in this Journal. The first of these appeared in the April 2007 issue (1). Here, Kim Chandler reviews Chapter 5: ‘A Combinatorial Method for Optimization of Materials for Gas-Sensitive Field-Effect Devices’, by M. Eriksson, R. Klingvall and I. Lundström (Linköping University, Sweden). Sue Ellis reviews Chapter 7: ‘Infrared Thermography and High-Throughput Activity Techniques for Catalyst Evaluation for Hydrogen Generation from Methanol’, by Eduardo E. Wolf, Stephen Schuyten and Dong Jin Suh (University of Notre Dame, Indiana, U.S.A.). Ann Keep reviews Chapter 8: ‘New Catalysts for the Carbonylation of Phenol: Discovery Using High-Throughput Screening and Leads Scale-Up’, by Donald W. Whisenhunt and Grigori Soloveichik (General Electric Global Research, U.S.A.); and Sarah Ball reviews Chapter 14: ‘High-Throughput Screening for Fuel Cell Technology’, by Jing Hua Liu, Min Ku Jeon, Asif Mahmood and Seong Ihl Woo (Korea Advanced Institute of Science and Technology, South Korea).

Gas-Sensitive Field-Effect Devices

Gas-sensitive field-effect devices which incorporate a thin layer of a pgm such as palladium or platinum as gate material (the material used in the terminal gate area) have been developed for hydrogen and ammonia sensing. These devices, fabricated by semiconductor technology, have been employed in some specialised commercial applications.

The team at Linköping University, Sweden, led by Professor Ingemar Lundström (one of the authors of the chapter), has dominated this field for more than thirty years, and is responsible for most of the impressive work done towards the understanding and advancement of these devices. Lundström’s team has shown that for catalytic metals such as palladium, platinum and iridium, both the type of metal and its morphology (porosity and thickness) play an important role in the sensitivity, stability and selectivity of the sensors.

Chapter 5 begins with a general introduction and a brief history of gas sensors. Surprisingly, no mention is made of amperometric (toxic and oxygen) gas detectors which utilise pgm powders as electrodes and are commercially available and widely used.

This is followed by a simple but useful illustration of the hydrogen sensing mechanism for a metal-insulator-semiconductor (MIS) device. The model, proposed by the authors several years ago, suggests that for a thick Pd film, three steps are

involved: hydrogen dissociation on the gate metal surface, transportation of the hydrogen atom through the metal film, and trapping of the hydrogen atom at the metal insulator interface where polarisation occurs.

Most of the complicated theory of MIS is omitted, so this chapter would most benefit readers who have field-effect transistor (FET) expertise. However, references for the underlying semiconductor principles – much of which were developed by the authors – are provided. The focus is on a combinatorial method for the optimisation of gas sensors, in line with the main theme of the book.

Device performance can be improved by using two catalytic metal layers, each independently optimised. The first pgm metal layer is deposited at the metal-insulator interface and the second on top of the first. To achieve this using conventional FETs requires the preparation of large numbers of devices, while overcoming inconsistency between batches. The authors propose a neat and imaginative scheme that sidesteps these issues. By deploying a vacuum deposition process to vary the thickness of two metal layers independently, in orthogonal directions across a single substrate, all possible thickness combinations over a MIS capacitor device can be created. A scanning light pulse technique is employed which allows measurements of parameters analogous to FET characteristics at small illuminated points across the MIS substrate. This is used to study the gas response, so as to identify the best composition.

The concept is clearly and effectively demonstrated on a rhodium (first film)/palladium bilayer with a thickness of up to around 25 nm. Results from exposure to hydrogen and ammonia (separately) are a series of very striking voltage response images. Areas exhibiting a high hydrogen sensitivity but a low ammonia sensitivity can be clearly identified. So can areas giving a high ammonia response but a low hydrogen response. Contour plots showing areas with different sensitivities resulting from exposure to different hydrogen concentrations are particularly vivid.

The application of combinatorial methods in gas sensors is at an early stage of progress, so there is little literature for the authors to relate to. The pgms play a fundamental role in FET-based sensors. There

are also brief discussions on the effect of interference gases and accelerated ageing by heat treatment/annealing, but without inclusion of some of the pertinent values. The section on annealing might well have been expanded, as annealing appears to be capable of reversing the sensitivity. Since the device is operated at 140°C, knowing the annealing temperature and duration would help to ascertain its stability.

It is a little disappointing that there is no confirmatory study to show that the compositions identified by the experimental work really showed the sensitivities and selectivity described when applied to conventional FETs. Also most of the material was published in late 2005 (Reference 9 within the chapter, see (2)). Despite this, the chapter is authoritative and well prepared, albeit rather short – like most of the other chapters. The proposed combinatorial method is elegant and should promote further work. This chapter is essential reading for workers in this field and would also benefit scientists interested in material technology or high-throughput techniques.

Hydrogen Generation from Methanol

In Chapter 7, the authors have used hydrogen generation from methanol as an example to highlight some of the benefits and weaknesses of applying a high-throughput approach to catalyst development. They discuss how high-throughput techniques complement standard catalyst screening methods, but acknowledge that they are no substitution for the detailed work required to gain a thorough understanding of the reaction and deactivation mechanisms.

The authors start by reminding the readers that, historically, catalyst screening has followed an empirical approach. This still prevails to some extent, and they suggest that progress is normally limited by the amount of time available on test rigs. They propose that this 'brute-force' approach can be improved on by successfully combining high-throughput experimentation (HTE) with a knowledge-based catalyst design, based on a hypothetical reaction model.

In the study presented, infrared thermography is used as an initial screening tool to assess the activity of a range of copper-zinc-palladium catalysts for the

methanol partial oxidation reaction. This reaction has been studied in detail by many groups as a method for generating hydrogen to power fuel cells, although the fashion in the fuel cell industry currently favours the direct use of methanol or hydrogen fuel source. Nevertheless, the reaction is a useful illustrative example. While apparently simple, there are several side reactions that need to be taken account of in the interpretation of the HTE results.

The milligram scale thermography tests are acknowledged as a crude first screen, offering no information on the kinetics, selectivity or durability of the catalysts. The authors rely on the exothermic nature of the chosen reaction, highlighting how the technique can only be applied to reactions where a measurable thermal response (due to reaction or adsorption) can be expected. The HTE tests are followed up by parallel reactor tests on 1 to 2 g of material before the most promising samples are studied in detail, with the kinetic and durability results feeding back to validate and improve the original reaction model.

Unlike other applications where HTE is used, the performance of a heterogeneous catalyst is dependent on a range of subtle factors, over and above material composition, which affect the critical surface structure. One aspect that the authors do not highlight is that for heterogeneous catalysts, the synthesis of the materials is often the time consuming step that cannot be easily addressed by high-throughput techniques.

In summary, the authors illustrate that while HTE should not be considered as the 'Holy Grail' of catalysis, if used wisely, it can be a valuable and powerful experimental tool.

Palladium-Catalysed Carbonylation of Phenol

In Chapter 8, researchers from General Electric (GE) describe the use of high-throughput experiments to optimise the homogeneous palladium-catalysed carbonylation of phenol. This work was carried out from 1997 onwards. The chapter gives both an overview of the reaction and detailed experimental procedures.

Diphenylcarbonate is a raw material for the manufacture of polycarbonates such as Lexan[®]. It is

currently made in a two-step process: carbonylation of methanol to dimethylcarbonate followed by transesterification with phenol. A one-step process might have a lower environmental impact. However, so far, even the best processes for carbonylation of phenol to diphenylcarbonate suffer from low turnover numbers and poor rates.

The best catalysts are palladium(II) complexes such as Pd(acac)₂ (acac = acetylacetonato), Johnson Matthey's product Pd-70, and Pd(dppb)Cl₂ (dppb = 1,4-bis(diphenylphosphino)butane), Johnson Matthey's product Pd-105. The GE researchers aimed to improve their activity with additives such as other metal complexes, bases, ligands and halides. For example, Ce(acac)₃, PbO and tetraethylammonium bromide enhance activity. They used arrays of 2 cm³ gas chromatography (GC) vials inside an autoclave at 5 to 10 MPa and 100°C. The results from these high-throughput experiments correlated well with performance when scaled up 200-fold.

The results showed some complex synergistic effects when several metal additives were combined. For example, adding iron increases the turnover number of a system doped with lead and titanium from 1068 to 1631. These effects were surprising and would have been difficult to spot using traditional low-throughput methods. The performance of the Pd-70 catalyst improved from a turnover number around 500 to around 7000. GE ran some of the best catalytic systems in a one gallon bench-top continuous reactor and filed extensive patents on the process (3, 4). However, some comment on the likelihood of scaling up to a commercial process would have been welcome.

Overall, the chapter gives a comprehensive account of the catalyst screening carried out. Clear graphs and tables detail the results, along with discussion of the possible reaction mechanism. It was pleasing to see high-throughput methods applied to a long-standing and intractable problem in homogeneous catalysis. The methods give unique insights into possible future 'cocktail' catalysts for industrial processes.

Fuel Cell Technology

Chapter 14 reviews the different approaches that have been applied to date to high-throughput

screening of fuel cell electrocatalysts. Four different screening techniques are discussed: optical, electrochemical, scanning electrochemical and infra-red (IR) thermography. Examples are given for each technique, including types of catalyst array, methodologies for deposition of catalyst formulations, suitability of the techniques and their limitations.

Optical screening using fluorescence is described as a coarser technique, useful for arrays with wide compositional variations, but with some limitations in sensitivity. Electrochemical and scanning electrochemical microscopy techniques allow greater accuracy and flexibility, with possibilities to vary the electrolyte, solution and reactants, as well as the catalyst formulations studied. The examples used within the chapter cover the electrochemical reactions of oxygen reduction and evolution, methanol oxidation and hydrogen oxidation in the presence of carbon monoxide (CO) impurities. The techniques described can be used to give information on reaction pathways and the effects of catalyst particle size on catalytic activity, as well as the variation in activity with catalyst formulation. IR thermography screening is also described, as a method to determine the gas phase activity of transition and base metal oxide-doped platinum on carbon catalysts for removal of impurities such as CO under fuel cell operating conditions.

The review would be useful for those requiring an introduction to the variety of rapid screening techniques available for fuel cell catalysts. References are made to a range of relevant literature papers covering different types of catalyst array, data analysis techniques, and findings regarding improved catalyst formulations for methanol oxidation and oxygen reduction and evolution. A familiarity with the fuel cell reactions within proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) is assumed. Figures within the chapter are well chosen to illustrate the principles behind the different types of screening techniques and methods of plotting activity data for complex ternary, quaternary and even quinary catalyst compositions.

All examples discussed relate to pgm-containing catalysts, in particular platinum and ruthenium, reflecting the current requirement for these metals within PEMFC and DMFC catalysts. However,

combinatorial techniques are described as offering a clear opportunity to rapidly screen a wide range of catalyst formulations containing pgm and non-pgm elements, with a view to reducing catalyst costs without compromising activity.

Generally the catalyst materials described have been prepared by techniques such as thin film sputtering and dispensing of metal solutions to produce microdots, followed by a reduction or heat treatment step. These methods use small amounts of materials and allow a wide compositional range to be studied rapidly. Little comment is made on attempts to reproduce the most active catalyst formulations at a larger scale, and to verify the predictions made by rapid screening in operational fuel cell systems. As rapid screening techniques have only recently been applied in the area of fuel cell catalysis, the preparation and validation of active formulations from combinatorial studies at larger scales will still be in progress at this time.

Concluding Remarks

The chapters reviewed in *Platinum Metals Review* here and in a previous issue (1) cover some of the range of industrial applications of relevance to the pgms which have been studied using combinatorial and high-throughput techniques. These include data storage materials and technology (1), gas-sensitive field-effect devices, catalyst development for hydrogen generation and for the carbonylation of phenol, and fuel cell electrocatalyst technology.

A further review of the entire book: "Combinatorial and High-Throughput Discovery and Optimization of Catalysts and Materials" can be read in Reference (5).

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