

247th American Chemical Society National Meeting and Exposition: Part I

Biomass coverage from the ACS spring conference on ‘Chemistry and Materials for Energy’

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Introduction

American Chemical Society National Meetings and Expositions are held twice a year in spring and autumn and constitute the largest gathering of chemical scientists at any point in the conference calendar. This year the 247th meeting (1) was held from 16th–20th March 2014, hosted at the Dallas Convention Center, Texas, USA, a hulking concrete monolith adjacent to downtown Dallas. The overarching theme of the conference was Chemistry and Materials for Energy

which was reflected in the focus of the Plenary and Kavli Foundation sponsored Lectures.

In total almost 14,000 chemical scientists attended the meeting, of which approximately 5000 were either undergraduate or postgraduate students, many appearing undaunted by the scale of their first conference. Over 10,000 scientific papers were presented, either in one of the myriad meeting rooms or numerous poster sessions. In addition to the technical programme, the Exposition comprised over 900 exhibitors from all over the world as well as a career fair with 30 employers seeking to fill 90 vacancies, although there were almost 800 job seekers.

This selective review will focus on biomass, in which both platinum group metals (pgms) and to a lesser extent base metals feature as catalytic materials.

Kavli Foundation Lectures

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| John A. Rogers | (University of Illinois at Urbana-Champaign) ‘Biodegradable Electronics’ |
| Emily A. Weiss | (Northwestern University) ‘The Behaviour of Electrons at Nanoscopic Organic/Inorganic Interfaces’ |

Plenary Lectures

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| Jens K. Norskov | (Stanford University, USA) ‘Catalysis for Sustainable Energy’ |
| Héctor D. Abruña | (Cornell University, USA) ‘Operando Methods for Characterization of Fuel Cell and Battery Materials’ |
| Michael R. Wasielewski | (Northwestern University, USA) ‘Molecular Approaches to Solar Energy Conversion’ |

Transformation of Biomass

There were a number of talks covering various aspects of the thermochemical transformation of biomass or derived sugars and chemicals to value-added compounds. Typically, these types of transformations involve treating a slurry or solution of the biomass feedstock in an autoclave at elevated temperatures and pressures using hydrogen gas or a hydrogen transfer agent. The most common catalysts used in these reactions are supported pgm heterogeneous catalysts, although base metal variants, or more rarely homogeneous catalysts, have been shown to be effective.

One common starting platform is the C6 sugars (hexoses), readily obtained by hydrolysis of cellulose, which can then be treated in a number of ways to easily obtain other derivative chemical feedstocks. One such is 5-hydroxymethylfurfural (5-HMF), which has been touted as a promising intermediate in many biorefinery concept models but has not been studied as extensively as others. It can be easily accessed by dehydration of hexoses and has been successfully converted to chemicals such as levulinic acid, 2,5-dimethylfuran and succinic acid, for example. Jaya Tuteja (Japan Advanced Institute of Science and Technology) gave a talk on a one step conversion of HMF to 1,6-hexanediol (HDO) in greatly improved yields at atmospheric pressure compared to previous routes by using palladium supported on zirconium phosphate (Pd/ZrP) as the catalyst promoted by formic acid as a transfer hydrogenation agent. HDO is a desirable target compound due to its myriad polymer, coatings, adhesives and plasticiser applications. The hydrogenolysis of HMF into HDO is proposed to consist of two main reactions, C–O bond cleavage (ring opening) by Brønsted acid sites on the support and hydrogenation of C=O and C=C bonds by the metal sites of the catalyst. In this work, Pd was chosen as the hydrogenation metal and a range of combinations of this and different acidic supports were screened for HMF conversion activity. Pd/ZrP was found to be the most active support and gave the best carbon balances (97% HMF conversion, 42.5% HDO yield, 84% C-balance), compared to other typical acidic supports such as zeolites, silica-alumina, niobia and sulfated zirconia.

In the presence of formic acid (FA), a mixture of products were formed from the hydrogenation of HMF, including 5-methylfurfural, 2,5-hexanedione, HDO

and furans. In contrast, a reaction using Pd/Al₂O₃ led to tetrahydrofuran-2,5-dimethanol as the major product (30.6% yield, >99% HMF conversion) due to significant ring hydrogenation over hydrogenolysis (ring cleavage). This highlights the importance of a high Brønsted:Lewis acid ratio in the support to promote efficient HMF ring opening, whereas the Pd metal sites dissociate FA, leading to hydrogenation. A number of parameters were investigated including Pd loading, FA concentration and reaction time and the best conditions were found to be 7 wt% Pd/ZrP catalyst (50 mg) which afforded 43% yield of HDO from HMF (1 mmol) in ethanol solvent (3 ml) using FA (22 mmol) at 413 K for 21 h. Following this, the Pd/ZrP catalyst was easily separated from the reaction mixture and reusable at least 5 times without any significant loss of activity and selectivity. The authors proposed a reaction mechanism (see **Figure 1**) (2) consisting of adsorption of HMF onto the catalyst surface and interaction with both metal and acidic support sites (step 1), followed by ring opening and deoxygenation by the acidic support sites to form an intermediate such as the hexa-triene-diol shown in steps 2 and 3. Following FA dissociation by the Pd metal centres (step 4) and keto-enol tautomerisation of the intermediate diol (step 5), C=C bond hydrogenation occurs to yield the desired HDO product as the final step.

A more challenging target is the hydrolysis and selective depolymerisation of lignin, which makes up a considerable proportion of woody biomass and is notoriously recalcitrant to treatment. Lignin consists of complex polymer networks made up of numerous oxygenated aromatic subunits which are linked with different types of C–O ether linkage, the most common of these being the β-O-4 linkage. The number of different monomer units and range of similar C–O ether groups present make the selective conversion of lignin very challenging, as often very complex product mixtures are formed, if the catalyst is even effective at all. Ning Yan (National University of Singapore) gave an interesting talk on her recent work developing a series of highly active, stable bimetallic nickel nanoparticle catalysts which were effective for the hydrogenolysis of lignin in water and under mild conditions. They began the study by synthesising a series of pgm (ruthenium, rhodium, palladium, platinum, iridium), precious metal (silver, gold, rhenium) and base metal (copper, iron, cobalt, nickel, tin) monometallic catalysts *via* reduction of the corresponding metal precursor salt with aqueous sodium borohydride in the presence of poly(vinylpyrrolidone) (PVP) as a stabilising agent.

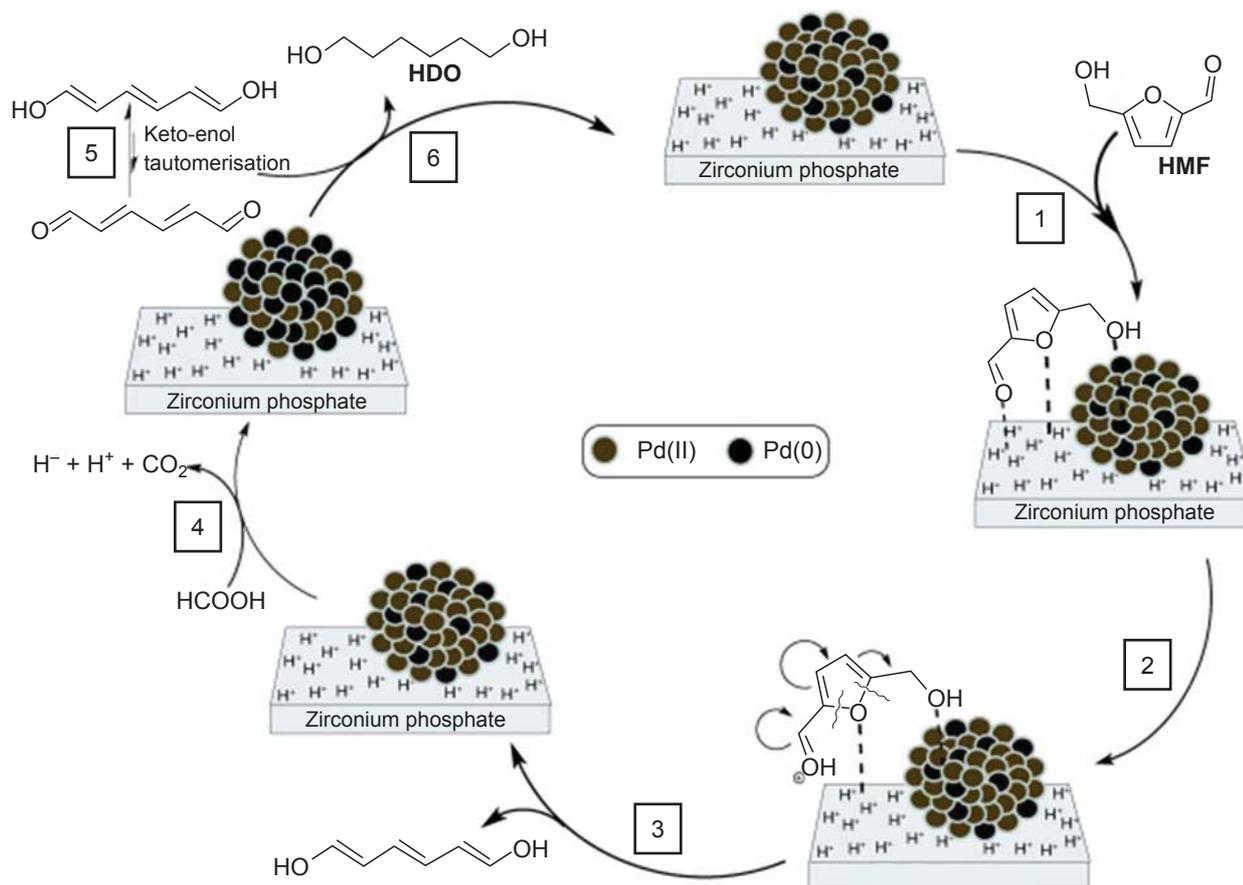


Fig. 1. Proposed mechanistic steps demonstrating the role of Pd/ZrP and FA in hydrogenolysis of HMF to HDO in the presence of FA (2) (Reproduced with permission. Copyright 2013 John Wiley and Sons)

It was postulated that the resulting colloidal catalysts may be more accessible to insoluble lignin than typical heterogeneous catalysts and so they were screened immediately after synthesis for hydrogenolysis activity against 2-phenoxy-1-phenylethanol, a typical lignin model compound containing a single β -O-4 linkage (see **Figure 2**) (3). A total of 15 compounds were identified by gas chromatography mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR) spectroscopy and categorised as dimers (compounds 1–7) and monomers (compounds 8–15) (see **Figure 2**) the yield of which gives an indication of β -O-4 hydrolysis activity. A blank reaction showed no conversion and of the 13 catalysts tested, Ni showed the highest selectivity towards monomers, indicating high selectivity for hydrolysis of the β -O-4 linkage.

Subsequently, a range of Ni based bimetallic catalysts containing 20% of the metals listed above were synthesised by a similar reduction route to the monometallic variants. The standout monomer yield of

72% was achieved with the NiAu catalyst which showed that addition of Au to Ni in this application promoted C–O bond hydrogenolysis of the model compound, which is in stark contrast to many other reactions where addition of Au to Ni typically reduces catalyst activity. The effect of the Ni: Au ratio was examined (**Figure 2(c)**) and an optimal ratio of 7:3 (Ni₇Au₃) was found to give 99% conversion of the model 2-phenoxy-1-phenylethanol compound with a monomer yield of 87% within 1 h. A physical mixture of monometallic Ni and Au catalysts in a 7:3 ratio gave only a 16% monomer yield, suggesting a significant cooperative metal effect in the bimetallic catalyst. Investigation of conversion and product distribution with respect to time showed that catalyst deactivation did not occur during the course of the reaction and that the observed dimers are reaction intermediates, with the Ni₇Au₃ catalyst showing an activity three times that of monometallic Ni.

Numerous characterisation techniques were used to probe the composition and structure of the Ni₇Au₃ bimetallic catalyst. Transmission electron

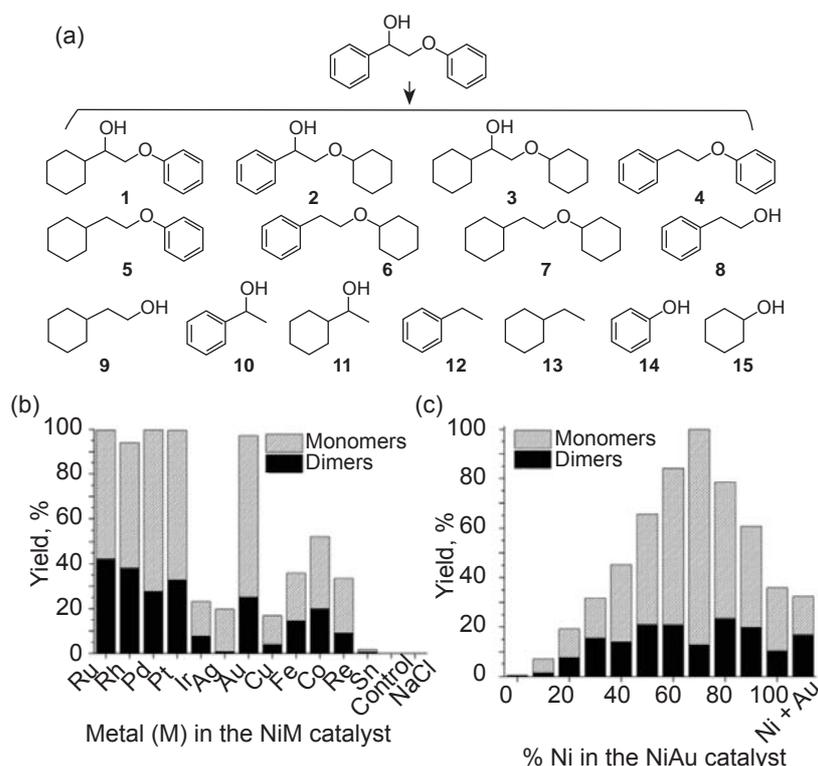


Fig. 2. (a) 15 Products identified after 2-phenoxy-1-phenylethanol hydrogenolysis; (b) dimer and monomer yields for bimetallic NiM catalysts (Ni:M = 4:1); (c) dimer and monomer yields for bimetallic NiAu catalysts for different Ni:Au ratios (3) (Reproduced with permission. Copyright 2014 Royal Society of Chemistry)

microscopy (TEM) shows spherical catalyst particles with diameter 4.1 ± 1.0 nm and consisted of metallic Ni and Au as determined by X-ray absorption near edge structure (XANES). Previous examples of NiAu catalysts consisted of a Ni core and Au surface, but the authors propose a significantly different structure here where they believe the catalyst consists of a crystalline Au core and Ni enriched shell. They support this with data from extended X-ray absorption fine structure (EXAFS) showing high Au–Au coordination numbers and low Ni–Ni coordination numbers, suggesting Ni is predominantly located at the surface; and X-ray photoelectron spectroscopy (XPS) determined an Ni:Au ratio of 3.8:1, which is higher than the stoichiometric ratio (2.3:1) and that found by inductively coupled plasma mass spectrometry (ICP-MS) of 2.8:1, suggesting the surface is Ni-enriched. UV-visible data additionally suggest that small Au⁰ clusters form and catalyse the reduction of Ni, acting as nuclei for the growth of a Ni-enriched shell. Finally the Ni₇Au₃ catalyst was assessed in the hydrogenolysis of organosolv lignin, a more realistic lignin feedstock, at 170°C under 10 bar H₂ in water

(3) **Figure 3.** A mixture of monomers were produced directly and quantified by gas chromatography-mass spectrometry (GC-MS), with the best yields of ~14 wt% monomers being produced after running for 12 h. Although this yield is low, the authors stress that the direct production of aromatic monomers from lignin, particularly under relatively mild reaction conditions, is not well known and represents a promising starting point for future work.

Alternative Processes

An alternative process for the conversion of biomass into liquid chemicals is fast pyrolysis, involving heating a biomass feedstock to 400°C–600°C in the absence of air, which produces a product referred to as bio-oil. This substance is a complex mixture of over 400 different compounds derived from the thermal breakdown of the cellulose, hemicellulose and lignin present in biomass. In addition to this, bio-oil has a low energy density, due to the high oxygen content of the constituent parts, has high viscosity and is very corrosive. These factors render crude

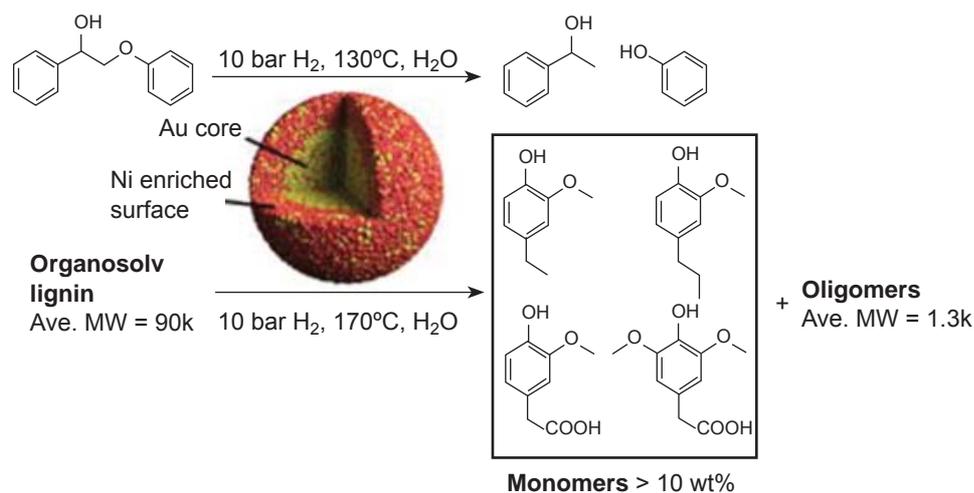


Fig. 3. Activity of Ni₇Au₃ catalyst compared to pure Ni catalyst in the hydrogenolysis of organosolv lignin at 170°C under 10 bar H₂ in water (Reproduced with kind permission from Ning Yan, National University of Singapore)

bio-oil unstable, as further reactions take place after ageing, affecting the molecular weight and viscosity of the oil. This necessitates additional catalytic upgrading before it can be processed to produce drop-in fuels and chemicals. The best approach to ameliorate these effects is to upgrade the vapours prior to condensation and this requires careful tuning of the catalyst properties to convert the most unstable components of the oil without sacrificing valuable C–C bonds.

Steven Crossley (University of Oklahoma, USA) presented work on the effect of the support phase of ruthenium on titania catalysts on the upgrading of pyrolysis vapour (4). Although more expensive than Ni or Fe, Ru has been shown to be active under conditions containing mixtures of oxygenates and water. However, the use of Ru on a large scale has been hampered due to its high mobility under high-temperature oxidative conditions and sintering during catalyst preparation, reaction or regeneration. For this study a model compound, guaiacol, has been used to represent some of the species present in bio-oil. Initial work concentrated on the effect of calcination temperature and TiO₂ phase on the activity and selectivity of the Ru/TiO₂ catalyst, studied at 400°C under H₂ at atmospheric pressure. The supports used were a pure anatase TiO₂ and P25, consisting of ~4:1 anatase:rutile phases, and the catalysts were prepared by impregnation of RuCl₃·xH₂O onto the support before

drying at 120°C for 12 h followed by oxidation at 400°C or 500°C under air for 4 h.

The BET surface areas of the TiO₂ supports and Ru catalysts were found to lie in the range 50–170 m²g⁻¹ and it was apparent that the P25 support had a surface area almost three times lower than the pure anatase but that very little surface area was lost upon doping with Ru metal compared to the anatase. This is due to the anatase phase being less thermodynamically stable than the rutile phase so increasing calcination temperature results in greater pore collapse and concomitant loss of surface area, whereas P25 contains both rutile and anatase phases and is more stable to temperature increases. The metal loadings of the catalyst samples were determined by quantitative temperature programmed reduction (TPR) and this showed that the Ru loading was not affected by an increase in calcination temperature. The metal dispersion was probed by a combination of X-ray diffraction (XRD) analysis of the support crystal planes exposed for Ru binding, TEM analysis, infrared spectroscopy and CO hydrogenation reactions. These data led the authors to conclude that Ru supported on P25 was dispersed much better than on pure anatase TiO₂. It is proposed that the rutile component of P25 serves as an anchor point for the RuO₂ species since they possess similar crystal structures and that the poorer dispersion and particle agglomeration on pure anatase was due to the mismatch between anatase

TiO₂ and rutile RuO₂. For the hydrogenation of guaiacol the authors have found a synergistic effect when combining Ru with the reducible TiO₂ support which leads to enhanced activity, compared to other non-reducible supports such as C, SiO₂ and Al₂O₃ for example. This was postulated to be due to an increase in defects on the TiO₂ surface as a result of the presence of Ru and was more active than either TiO₂ or Ru alone. The rates of guaiacol conversion to phenol, cresols, polyalkylated phenols and deoxygenated aromatics are higher on P25 supports than pure anatase and this is consistent with previous observations which suggest that the rate of hydrogen spillover onto the TiO₂ surface to produce oxygen vacancies is enhanced over the rutile polymorph.

Renewable Energy Storage

Finally, Ting Yang Nilsson (Linköping University, Sweden) gave an interesting talk on lignin modification for biopolymer/conjugated polymer interpenetrating networks as renewable energy storage materials (5). The premise behind this work is to develop low cost, renewable derived charge storage materials for use with intermittent energy sources which can match current battery technologies in terms of performance, without the use of expensive inorganic materials such as rare earth metals. In nature, redox functions contained within biopolymers are widely used in energy conversion processes in plants and make use of temporary proton storage on amino acid residues to accomplish the necessary multi-electron oxidation step. Quinones are also present in plant metabolism processes and act as soluble electron/proton transport agents. For example, the hydroquinone/dihydroquinone (Q/QH₂) couple stores two protons and electrons in a six carbon/two oxygen structure, giving an electronic charge density of 496 mAh g⁻¹. Considered alone, this charge storage capacity is superior compared to more conventional systems such as lithiated carbons (344 mAh g⁻¹) and olivine iron(III) phosphate (FePO₄) systems at 170 mAh g⁻¹. It is known that incorporating quinone groups onto the main chain of conjugated polymers leads to increased charge storage, as does the inclusion of quinones into redox active anionic counterions in doped conjugated polymers. This work has successfully produced a class of materials based on the combination of polypyrrole and lignin derivatives containing redox active functional

groups. The incorporation of lignin into a material with suitable electronic and ionic conductivity can enable charge transport to and from the quinone sites, opening up the possibility to use this redox function for charge storage. A three electrode system was used to electrochemically polymerise pyrrole at Au electrodes in an aqueous solution of lignosulfonate, generating a black [PPy(lig)] conducting product coating on the Au surface. This layer can be grown to ~3 μm thick over the course of 2 h and with a conductivity of ~1 S cm⁻¹ and elemental analysis yielded a N:S ratio consistent with a composition comprising ~1:1 ratio of polypyrrole and lignosulfonate. Cyclic voltammetry studies of the [PPy(Lig)] electrodes in 0.1 M aqueous perchloric acid (HClO₄) revealed a well-defined and narrow redox wave at ~0.5 V vs. Ag/AgCl and a poorly defined wave in the typical potential range for polypyrrole. The presence of two redox waves, compared to just one present in polypyrrole, shows that the quinone groups of the lignosulfonate are readily accessible and are responsible for the second observed wave.

Inclusion of pH buffers showed a systematic dependence of redox potential on pH with a value of 58 mV/pH unit, close to the 59 mV/pH unit anticipated for 1 electron/1 proton processes. The availability of charge stored in these materials and the rate at which it can be extracted was also studied by discharge under galvanostatic conditions in 0.1 M HClO₄ for two film thicknesses, 0.5 μm and 1.9 μm. For the thinner film little dependence on the discharge rate is seen, whereas the thicker film shows limited capacity and rate in the range 1–17 A g⁻¹. The thicker film in particular gives discharge curves with two different slopes, transitioning between 0.35–0.55 V which is likely due to contributions from the different redox potentials of the two component materials present in the film. Specifically, the transition should represent the reduction of the quinone groups from the Q to QH₂ state and any remaining capacity due to the polypyrrole present. Following further measurements and data analysis the 1:1 polypyrrole/lignosulfonate composite material was estimated to have a charge storage capacity of ~80 mAh g⁻¹ which is a very promising beginning. One area of future work with these materials is to address the issue of self-discharge, but the authors believe that this and other improvements can be achieved by examining different lignin sources and processing parameters which can have a large effect on the number of phenolic groups in the material.

Conclusions

This review has taken only a small snapshot of the work presented on biomass related topics at the conference. It was apparent from the myriad talks presented and nationality of the presenters that biomass is a burgeoning area of research across the whole world with a focus in many different application areas. By and large the pgms were featured most prominently although base metals are becoming more widespread. As shown in this review, there is also research into applications which do not utilise a metal of any sort although these are distinctly more specialised. As with most ACS meetings, whilst massive in scale and number of attendees it was very well organised and, of the talks this reviewer attended,

there were only a few issues with equipment or the speakers themselves.

References

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The Reviewer



Ian Casely graduated in Chemistry from Imperial College, London, UK, in 2005 with subsequent PhD studies at the University of Edinburgh, UK, focused on rare-earth metal *N*-heterocyclic carbene organometallic complex synthesis and reactivity. In 2009 he moved to the University of California, USA, as a postdoc to work on small molecule activation chemistry and established a project developing the organometallic chemistry of bismuth complexes. Returning to the UK in 2011 to work at University of Oxford, UK, on Group 4 metal based heterogeneous slurry polymerisation, in July 2011 he joined the PGM Applications group at Johnson Matthey Technology Centre, Sonning Common, UK. He is working on the conversion of biomass to chemicals as well as in the area of metal organic framework chemistry.