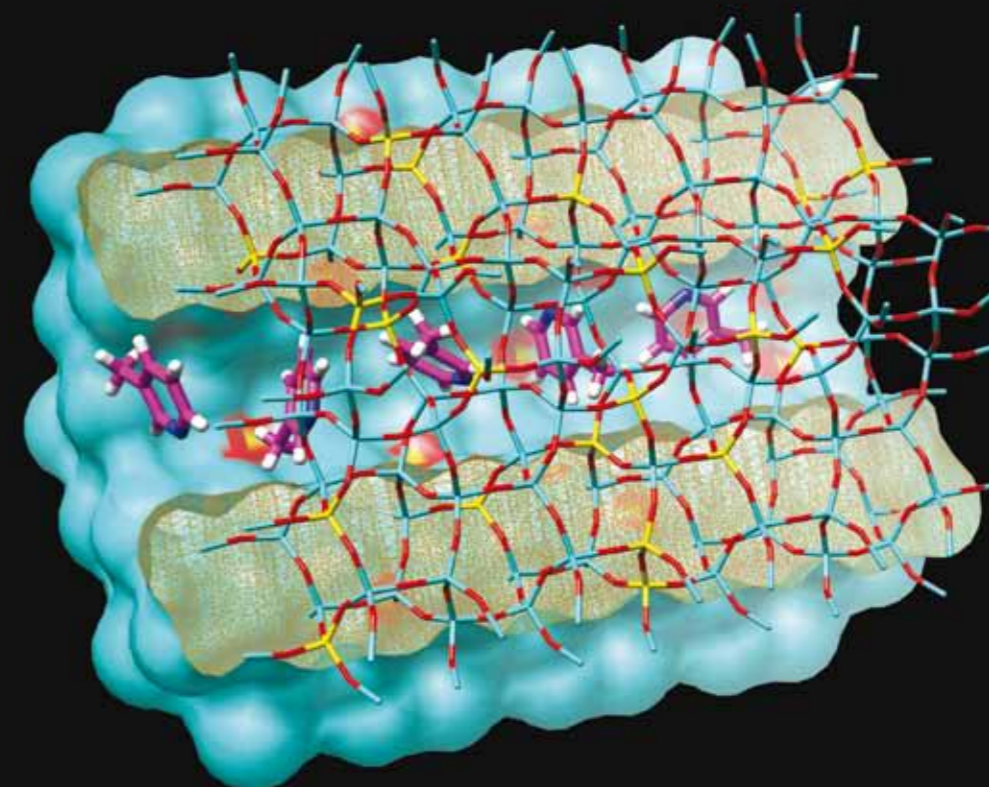


# Japan-UK Symposium

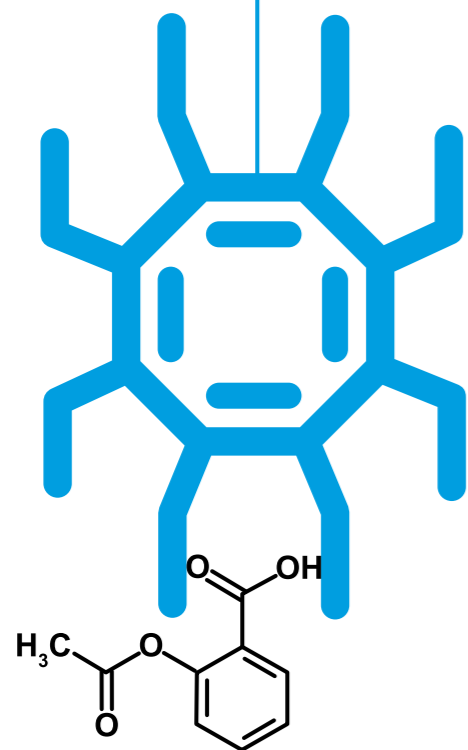
Catalysis for a Sustainable World

**Thursday 15th and Friday 16th July, 2010**

The Chemistry Centre, London, UK



# New adventures on the web



ChemSpider is a free online, structure centric community for chemists, providing fast access to millions of unique chemical entities, resources and information and the opportunity to collaborate with a world wide community of scientists. Rapidly becoming the richest single source of structure based chemistry information online, ChemSpider is a ground breaking initiative now supported by the RSC, the most innovative of chemical societies.

[www.chemspider.com](http://www.chemspider.com)

## Welcome Address

### Dear Colleagues

The Royal Society of Chemistry (RSC) and the Chemical Society of Japan (CSJ) are delighted to be the joint hosts of "Catalysis for a Sustainable World". This symposium has been organised to celebrate the signing of an International Cooperation Agreement between the RSC and the CSJ. This landmark event represents the formalisation of an already strong partnership between the two societies. We intend that this agreement and inaugural symposium will serve as springboards for future CSJ-RSC activities, facilitating and fostering other collaborative ventures.

The RSC is a learned society, concerned with advancing chemistry as a science, developing its applications, and disseminating chemical knowledge, and a professional body that maintains professional qualifications and sets high standards of competence and conduct for professional chemists. We have over 46,000 members worldwide drawn from all areas of the chemical sciences. We are active in industry, academia and education and play an important role in shaping science policy both in the UK and internationally. In addition the RSC is a major publisher of research journals, magazines, databases and books that cover all areas of the chemical sciences.

The CSJ has a history of 132 years, with a current membership of about 31,000, and is one of the most influential learned societies in Japan, covering most areas of pure and applied chemistry both in academia and industry. Our prime mission is to contribute to social development through advancing science, developing technology, promoting industry, diffusion of knowledge relating to chemistry, and developing human resources. To pursue this mission, the CSJ holds various conferences, such as an annual meeting with 8,500 participants every spring, and seven division meetings in the fall, and publishes journals and books. The CSJ also has a long history in chemical education and outreach programs to the public.

Each of the speakers in this symposium is an international expert in the aspect of catalysis that they will present. We hope that these lectures and poster presentations will stimulate the exchange of ideas and experiences between all participants with the theme of sustainability setting a clear and topical focus for the discussions.

The RSC and the CSJ thank each of the speakers, poster presenters and participants for their contributions to this symposium. Also, the members of the Japanese delegation would like to thank the Great Britain Sasakawa Foundation for supporting a part of their travel to the UK.

### Professor Dave Garner

Immediate Past-President of the Royal Society of Chemistry



### Professor Yasihuro Iwasawa

President of the Chemical Society of Japan



## Thursday 15th July 2010

10.00	Coffee and Tea / Registration
10.30	Professor Yasuhiro Iwasawa, (President, Chemical Society of Japan)
10.50	Dr Richard Pike, (CEO, Royal Society of Chemistry)
Chair: Professor James Anderson (University of Aberdeen and Chair of the RSC Surface Reactivity and Catalysis Group Committee)	
11.10	Professor Atsushi Satsuma (Nagoya University) <b>"Unique catalytic behaviour of Ag cluster in selective NOx reduction and greener chemical reactions"</b>
11.45	Dr Charlotte Williams (Imperial College London) <b>"Catalytic activation of renewable resources for polymer synthesis"</b>
12.20	Lunch and Posters
2.00	Professor Naonobu Katada (Tottori University) <b>"What controls the acid strength of zeolite? An answer from a relationship between the ammonia desorption energy and geometric parameters"</b>
2.35	Dr Robert Raja (University of Southampton) <b>"Engineering active sites for sustainable catalysis"</b>
3.10	Professor Mizuki Tada (Institute of Molecular Science, Japan) <b>"Direct phenol synthesis from benzene and oxygen on supported Re-Pt catalysts"</b>
3.45	Coffee and Tea
4.10	Professor Paul Pringle (University of Bristol) <b>"New phosphorus(III) ligands for efficient carbonylation catalysis"</b>
4.45	Dr Kazuhiko Sato (National Institute of Advanced Industrial Science and Technology) <b>"Green oxidation with hydrogen peroxide"</b>
5.30	Reception and Signing Ceremony

## Poster Presentations Thursday 15th July

	Name	Title
P01	Hiroyuki Asakura	Structural analysis of group V, VI, VII metal compounds by means of XANES and DFT calculation
P02	Farid Aiouache	Screening temperature and concentrations by near-infrared tomography
P03	Dr Daisuke Imao	Environmentally benign selective oxidation of $\alpha,\beta$ -unsaturated aldehydes to the corresponding carboxylic acids with hydrogen peroxide
P04	Geoffrey Akien	Improving the production of 5-hydroxymethylfurfural from fructose using microwave heating
P05	Dr Yoshihiro Kon	Pt black-catalyzed selective oxidation of allylic alcohols with aqueous hydrogen peroxide under organic solvent-free conditions
P06	Sarah Burnham	Oxidation of glycerol over titania supported gold catalysts
P07	Shuichi Koso	Chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol over Rh/SiO <sub>2</sub> catalysts modified with metal oxide species
P08	Mark Coleman	The Salamander – A versatile tubular reactor for continuous flow chemistry
P09	Simon Collinson	PRIME – polymer reprocessing by innovative metal-catalyzed enterprises
P10	Carmine D'Agostino	In-situ <sup>13</sup> C DEPT NMR spectroscopic studies of aerobic oxidation of benzyl alcohol over heterogeneous Pd/Al <sub>2</sub> O <sub>3</sub> catalyst

## Friday 16th July 2010

10.00	Coffee and Tea
Chair: Dr John Birtill (Glasgow University and Member of the RSC Applied Catalysis Group Committee)	
10.30	Professor Mark Ormerod (University of Keele) <b>"Catalytic conversion and utilisation of waste biogas over supported nickel catalysts and solid oxide fuel cell anodes: Catalyst deactivation, carbon deposition, sulphur tolerance and characterisation of surface species"</b>
11.05	Professor Keiichi Tomishige (Tsukuba University) <b>"Catalyst development for the production of biomass-derived chemicals"</b>
11.40	Dr Karen Wilson (University of Cardiff) <b>"Designer catalysts for biodiesel synthesis"</b>
12.15	Lunch and Posters
Chair: Professor Andy Whiting (Durham University and Member of the RSC Applied Catalysis Group Committee)	
2.00	Professor Tetsuya Shishido (Kyoto University) <b>"Photooxidation of alcohol over niobium oxide"</b>
2.35	Professor Chris Hardacre (Queen's University, Belfast) <b>"Theory designed catalysts for the hydrogenation of carboxylic acids and amides at low pressure and temperature"</b>
3.10	Coffee and Tea Break
3.35	Poster Awards
3.45	Dr Naoya Kumagai (The University of Tokyo) <b>"Atom-economical catalytic asymmetric reactions and their application to efficient synthesis of therapeutics"</b>
4.20	Professor Michael North (University of Newcastle) <b>"Synthesis at cyclic carbonates from waste CO<sub>2</sub>"</b>
4.55	Close

## Poster Presentations Friday 16th July

	Name	Title
P11	Dr Satoshi Muratsugu	Design of a molecularly-imprinted Ru catalyst for regulating regioselective epoxidation of limonene
P12	Elizabeth Eterigho	Synthesis, characterization and evaluation of two forms of sulphated zirconia for triglyceride cracking
P13	Tatsuya Nitabaru	Anti-selective catalytic asymmetric nitroaldol reaction via heterobimetallic heterogeneous catalysis and application to asymmetric synthesis of therapeutics
P14	Naimah Ibrahim	Enhancing EPOC through catalyst surface modification
P15	Keiichiro Oshima	Direct dehydrogenative amide synthesis from alcohols and amines by Ag/Al <sub>2</sub> O <sub>3</sub>
P16	Becky Leithall	Highly selective oxidations using synergistic nanoporous catalysts
P17	David Xuereb	Silica supported amino acids as heterogeneous catalysts
P18	Hafizuddin Yussof	Comparison of homogeneous and heterogeneous forms of quaternary ammonium as transesterification catalysts.
P19	Takahiro Kubo	Selective oxidation of silanes to silanols over Pd/C
P20	W M C Sameera	Mechanistic and computational studies of the atom transfer radical addition of polyhalogenated alkanes to olefins catalyzed by copper-homoscorpionate complexes



## Professor Chris Hardacre

Queen's University, Belfast,  
c.hardacre@qub.ac.uk

Professor Chris Hardacre is currently Head of the School of Chemistry and Chemical Engineering in Queen's University, Belfast. He obtained a PhD from Cambridge University in 1994 in the area of emission control catalysis and the use of surface science techniques to probe metal-support interactions. This work was awarded the International Institute of Precious Metals award. Following the award of an SERC research fellowship and a junior research fellowship at Emmanuel College, Cambridge, he moved to Queen's in 1995 as a lecturer in Physical Chemistry.

In 2003, he was appointed as Professor of Physical Chemistry and took on the role of Director of Research leading the catalysis group in the multidisciplinary Centre for the Theory and Application for Catalysis (CentACat) and in 2004 he was awarded a USAF, window on Science visiting research fellowship. Through his work in ionic liquids research, he was awarded the Royal Society of Chemistry Encouraging Innovation Award with Merck Chemicals Ltd and was part of the team to win the Queen's Anniversary Prize for Further and Higher Education.

Current projects in his group range from water gas shift catalysis and the use of transients to determine gas phase mechanisms to liquid phase hydrogenation and the conversion of biomass to fine chemicals. He has developed a strong research group in ionic liquids within the QUILL research centre with interests in heterogeneously catalysed reactions, structural determination of ionic liquids, and species dissolved therein, analytical aspects, electrochemistry and prediction of physical properties of ionic liquids. He has published over 210 papers and 7 patents in total.

### Theory designed catalysts for the hydrogenation of carboxylic acids and amides at low pressure and temperature

Chris Hardacre, CentACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, UK

Catalytic hydrogenation is one of the most useful synthetic tools in chemical industry, in particular for the synthesis of alcohols and amines, from their corresponding carboxylic acids and amides.<sup>[1]</sup> Alcohols and amines are widely used in lubricants, resins, perfumes, cosmetics, shampoos, conditioners, dyes, solvents, additives, anti-foam agents, corrosion inhibitors, detergents and drugs.<sup>[2]</sup> In comparison with many carbonyl hydrogenations, the hydrogenation of carboxylic acids and amides is difficult due to the fact that the carbonyl group has weak polarizability and has, consequently, lower reactivity. This results in the manufacturing processes requiring very high pressures and temperatures (200–400 bar hydrogen, 200–400 °C).<sup>[3]</sup> Under these conditions, control of the selectivity of the process is difficult. Theoretical gas phase DFT calculations were used to design a catalyst capable of operating under much milder conditions and provide selectivity to amines and alcohols. Experimentally selective hydrogenation of carboxylic acids and amides at 5 bar hydrogen, 60 °C using Pt/TiO<sub>2</sub> monometallic and Pt-Re/TiO<sub>2</sub> bimetallic catalysts have been examined as predicted by the DFT calculations. For example, the hydrogenation of small aliphatic amines using a 4%Pt-4%Re/TiO<sub>2</sub> resulted in >90% conversion and >99% selectivity to the corresponding amines. This has significant implications in the replacement of high energy and stoichiometric processes in the fine, pharma and bulk chemical industries.

Literature:

[1] Ucciani E., in Heterogeneous Catalysis and Fine chemicals, ed. Guisnet M., Barrault J., Bouchoule C., Duprez D., Montassier C., Pérot G., Elsevier, Amsterdam, **1988**, p. 33.

[2] Tan Tai L. H., Rataj V. N., in Handbook of detergents part E: Applications, ed. Zoller U., CRC press, Taylor and Francis group, Boca Raton, **2009**, p. 110.

[3] Pohl J., Carduck F.-J., Goebel G., U.S. Patent, **1990**, 4935556.



## Professor Naonobu Katada

Tottori University  
katada@chem.tottori-u.ac.jp

Naonobu Katada received the MS degree in Nagoya University under the supervision of Professor Yuichi Murakami in 1990. After a period of researching for Nippon Shokubai Co. Ltd. in 1990 - 1992, he was appointed a research associate in Tottori University in 1992. He received the PhD degree from Nagoya University in 1996. He has been an Associate Professor in Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University since 1998. Throughout the periods in Nagoya and Tottori Universities, he has collaborated with Professor Miki Niwa. He received Award of Encouragement for Young Researchers by the Catalysis Society of Japan in 2004, and Award of Encouragement for Young Researchers by The Japan Petroleum Institute in 2005 for the development and application of ammonia TPD (temperature-programmed desorption) method to measure the acidic properties of solid catalysts. His current interest is on the analysis and design of acid sites on zeolites and other combined metal oxides, applications of solid acid catalysts to alternative fuels and resources, and chemical vapor deposition of a molecular-sieving silica overlayer using a molecular template to generate shape selectivities on catalysts and sensors.

### What controls the acid strength of zeolite? An answer from a relationship between the ammonia desorption energy and geometric parameters.

Naonobu Katada, Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori 680, Japan

An ammonia IRMS-TPD (infrared/mass spectroscopy - temperature-programmed desorption) method was developed to precisely measure the acidic properties (number and strength distribution of Brønsted and Lewis acid sites) of solids. In the case of zeolite, the acid strength (ammonia desorption energy) of each OH group can be quantified. It was applied to various zeolites to demonstrate that the strength of acid site due to a framework SiOHAl unit was controlled by the crystallographic position and crystal phase of zeolite. DFT (density functional theory) gave the ammonia desorption energy values in good agreement with the IRMS-TPD experiments.

Analysis of correlations between the desorption energy and geometric parameters assumed in the DFT study showed;

- 1) The shorter the AlO distance, the more positive the charge of OH giving the stronger acidity.
- 2) The stronger the compression from both sides of SiOHAl unit, the shorter the AlO distance.
- 3) Other effects were negligible.

Thus, the stronger compression from both sides of SiOHAl unit brought the stronger Brønsted acidity. The origin should be the electron withdrawing nature of Lewis Al centre connecting to SiOH. What controls the acid strength of zeolite has been clarified based on quantitative discussion.





## Dr Naoya Kumagai

*The University of Tokyo*

**nkumagai@mol.f.u-tokyo.ac.jp**

Naoya Kumagai was born January 11, 1978 and raised in Ibaraki, Japan. After receiving a B. A. degree at the University of Tokyo in 2000, he carried out graduate studies at the University of Tokyo under the supervision of Professor Masakatsu Shibasaki. Following completion of his doctoral studies in 2005, he joined the research group of Professor Stuart L. Schreiber at Harvard University as a postdoctoral associate. He was appointed as an assistant professor at the University of Tokyo in 2006, where he pursues the development of novel strategies in asymmetric catalysis with particular emphasis on atom-economy. His current research interests are in the development of new methodology in asymmetric catalysis and its application to the efficient synthesis of therapeutics and bio-inspired dynamic process. He is a recipient of the Japan Society of Pharmaceutical Science Award for Young Scientists.

### **Atom-economical catalytic asymmetric reactions and their application to efficient synthesis of therapeutics**

*Naoya Kumagai, Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Recent advances in modern organic synthesis allowed for an efficient access to a broad range of complex molecules in a highly stereocontrolled manner. The methodologies, however, usually require the stoichiometric use of activating reagents to achieve high reactivity and chemo/stereoselectivity, thereby co-producing the unwanted wastes. In this context, we envisioned the development of atom-economical catalytic asymmetric reactions, where stereogenic centers are produced via a proton-transfer between unactivated substrates by the action of designed catalysts, affording enantioenriched products without any waste. With regard to recent demand for sustainable chemistry, the above-mentioned catalytic process is ideal and has received increasing attention for the utility in environmentally benign synthesis of optically active therapeutics. Currently, our research group is aiming at the development of atom-economical asymmetric reactions based on 1) rare earth metal/amide-based ligand catalysts; and 2) soft Lewis acid/hard Brønsted base cooperative catalysts. Some of them are under final optimization for the prospective use in the industrial production of promising therapeutic candidates.



## Professor Michael North

*University of Newcastle*

**michael.north@ncl.ac.uk**

Michael North was born in Blackburn, England in 1964. He obtained his BSc. in 1985 from the University of Durham and his D.Phil in 1988 from the University of Oxford for work on the synthesis of non-racemic amino acids, carried out in the group of Professor Sir J.E. Baldwin. After a two-year postdoctoral position in Professor G. Pattenden's research group at the University of Nottingham, he was appointed to his first academic post at the University of Wales at Bangor. In 1999 he moved to King's College London and was promoted to Professor of synthetic organic chemistry in 2001. In 2004, he moved to his current position as Professor of organic chemistry and joint director of the University Research Centre in Catalysis and Intensified Processing at the University of Newcastle upon Tyne. Professor North has published over 130 original papers and also holds six patents. His research interests are centred on the design and mechanistic study of new catalysts with applications including asymmetric carbon-carbon bond formation, carbon dioxide chemistry and polymer chemistry. In 2001 he was awarded the Descartes Prize by the European Commission for his work on asymmetric cyanohydrin synthesis using metal(salen) complexes.

### **Synthesis of cyclic carbonates from waste CO<sub>2</sub>**

*Michael North, School of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK*

World-wide production of oil and gas is expected to peak before 2020. Therefore, since over 90% of all commercially available organic chemicals are sourced from crude oil, a major challenge for chemistry over the next 10 years is to find alternative, sustainable feedstocks for the chemicals industry. One particularly attractive reaction in this respect is the 100% atom economical reaction between CO<sub>2</sub> and epoxides leading to cyclic carbonates. Cyclic carbonates are already manufactured commercially and have a number of applications including as electrolytes for lithium ion batteries. In this presentation, the mechanism led development of bimetallic aluminium(salen) based catalysts which in the presence of a tetraalkylammonium cocatalyst allow this reaction to be achieved at atmospheric pressure and room temperature will be discussed. In addition, the synthesis of one-component versions of the catalysts, their immobilisation on inorganic supports and the use of the resulting immobilised catalysts in gas-phase flow reactors at temperatures and pressures suitable for direct utilization of flue-gas will be described. The tolerance of the catalysts to the NO<sub>x</sub> and SO<sub>x</sub> impurities present in flue-gas will be reported.



## Professor Mark Ormerod

*University of Keele*

**r.m.ormerod@keele.ac.uk**

Professor Mark Ormerod graduated in Natural Sciences from the University of Cambridge in 1986, and then undertook his PhD in the Department of Chemistry at Cambridge in the area of surface chemistry. He was subsequently awarded the Cambridge University Oppenheimer Research Fellowship in 1989. He was appointed to a Lectureship in Physical Chemistry at Keele University in October 1992. In 1997 he was awarded an EPSRC Advanced Research Fellowship and was promoted to Professor of Clean Technology. He was made Dean of Research for Natural Science in 2000, and became Head of the School of Chemistry and Physics in 2003. He currently leads the Sustainable Technology and Materials Chemistry Research Group within the Institute for the Environment, Physical Sciences and Applied Mathematics, and has been Head of the School of Physical and Geographical Sciences since 2005. His current research interests are centred on sustainable processes, heterogeneous catalysis and inorganic materials chemistry, in particular on solid oxide fuel cells, hydrocarbon conversion catalysis and utilisation of waste biomass and biogas. He has received substantial funding for his research from both government sources and industry, and has published over 120 papers in peer-reviewed journals since 1990 and given many invited lectures at international conferences and national meetings. Professor Ormerod has also been actively involved in promoting public engagement in and awareness of science, particularly in the area of sustainability, clean and renewable energy and developing sustainable approaches to our future needs, for over 10 years, with significant funding to support this work. In 2007 he formed the Science for Sustainability group at Keele, which has a nationally leading reputation for its highly innovation work in engaging and educating young people and communities in environmental and sustainability issues and increasing public awareness and engagement in these issues. He has given over 80 public lectures and been involved in many public science events.

### **Catalytic conversion and utilisation of waste biogas over supported nickel catalysts and solid oxide fuel cell anodes: Catalyst deactivation, carbon deposition, sulphur tolerance and characterisation of surface species**

*Professor Mark Ormerod, Sustainable Technology and Materials Chemistry Group, Institute for the Environment, Physical Sciences and Applied Mathematics, Keele University*

Nickel-based catalysts are relatively cheap and have excellent reforming activity. They are commonly used in catalytic reforming of hydrocarbons and in Solid Oxide Fuel Cells (SOFCs), but unfortunately their tendency to promote carbon deposition and susceptibility to sulphur poisoning can present serious problems with catalyst deactivation. Biogas obtained from various waste sources, including landfill sites and agricultural waste, is predominantly a methane-rich mixture of methane and carbon dioxide, containing up to 2000 ppm of gaseous sulphur compounds, as well as other impurities. Conversion of waste biogas into synthesis gas, with subsequent conversion of syn gas into useful chemicals or utilisation in SOFCs, can potentially be achieved through dry reforming. However, there are several obstacles to overcome, including the variable composition of waste biogas with source and time, carbon deposition which can be severe, especially with methane-rich biogas where excessive methane decomposition occurs, and major issues of sulphur poisoning. Thus, development of this potentially very attractive process for utilising waste biogas is subject to minimisation of both carbon deposition and sulphur poisoning. The reforming characteristics of biogas mixtures over supported nickel and doped-nickel catalysts and SOFC anodes, in terms of catalyst performance, stability and deactivation, carbon deposition and sulphur poisoning characteristics have been investigated in detail, including studying the species formed on the catalyst surface during reforming.



## Professor Paul Pringle

*University of Bristol*

**paul.pringle@bristol.ac.uk**

Professor Paul Pringle was born and bred in Liverpool, did a BSc at Leicester followed by PhD with Professor Bernard Shaw at Leeds. He was a Lecturer at Warwick followed by Bristol and has been a Professor since 2000. His research focus is on the design and synthesis of phosphorus(III) ligands for homogeneous catalysis of reactions with industrial applications including hydroformylation, hydrocyanation, asymmetric hydrogenation, alkene carbonylation and oligomerisation. Of particular interest to his group is the chemistry of ligands in which the P-donor atom is in an unusual stereoelectronic environment. This work has resulted in over 120 publications and 25 patents and the award of the Royal Society of Chemistry Awards for Precious Metal Chemistry (2000) and Homogeneous Catalysis (2004).

### **New phosphorus(III) ligands for efficient carbonylation catalysis**

*Paul Pringle, School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*

Synthesis gas is currently made from coal and gas and has been an important feedstock for the organic chemicals industry for over 70 years. The ready conversion of biomass to synthesis gas means that it will continue to be a key resource for the foreseeable future. Therefore the development of increasingly efficient catalysts for CO / H<sub>2</sub> conversions is a high priority. In this lecture, recent results from our laboratory on the design of phosphines for the improvement of two industrial catalytic carbonylation processes will be described.



**Dr Robert Raja**  
*University of Southampton*  
**r.raja@soton.ac.uk**

Robert Raja completed his doctoral degree (Ph.D.) in 1997 at the National Chemical Laboratory (India) and was awarded a Royal Commission for the Exhibition of 1851 Fellowship to pursue an independent postdoctoral research program, at the Royal Institution of Great Britain. He worked with Bayer Chemicals, Leverkusen, Germany (2000-2003) as a Research Chemist and was instrumental in developing one of the first series of heterogeneous, organometallic chiral catalysts for fine-chemical and pharmaceutical applications. He moved to Cambridge University in 2004 as a Senior Research Associate and his research efforts were focussed on the discovery and design of novel single-site heterogeneous catalysts. In June 2006, he was appointed as Reader/Associate Professor in Chemistry at the University of Southampton where the focal theme of research within his Group has been devoted to engineering active sites for effecting industrially significant catalytic transformations, using environmentally benign reagents, energy-renewable feedstocks and sustainable processes. Research efforts within his Group in the last four years have led to the successful commercialization of 2 catalytic technologies.

He has won several awards and prizes, the most notable being the Erskine Fellowship (2008) awarded by the University of Canterbury (New Zealand) and the Barrer Award (2005) by the Royal Society of Chemistry 'in recognition of outstanding contributions to preparative materials chemistry and their application to industrial catalysis'. He is the author of over 135 publications and lead inventor on 35 International Patents.

#### **Engineering active sites for sustainable catalysis**

*Robert Raja, School of Chemistry, University of Southampton, Highfield, Southampton SO16 1BJ, UK*

Engineering active sites in porous architectures affords a widely applicable strategic principle that offers adequate scope for the rational design of single-site heterogeneous catalysts. Open-structure microporous solids, organometallic cluster-derived precursors for generating nanoparticles and amino acid and protein-derived catalytically active sites for creating bio-inspired organocatalysts, can be ingeniously designed for effecting a number of important sustainable chemical transformations that are of high relevance in the fine-chemical, energy and pharmaceutical sectors. The diverse array of synthetic and design strategies that we have evolved, has led to the creation of a unique range of single-sites that enable one to access mechanistic pathways that are otherwise difficult and facilitate structure-property relationships to be established.

This lecture will outline and elucidate some of the fundamental principles of our approach for engineering active sites that play an important role in enhancing the synergy in many catalytic oxidations, dehydrations, hydrogenations and cascade reactions. A range of novel heterogeneous catalytic systems that facilitate shape-selective, regioselective, enantioselective and bifunctional catalytic conversions with benign oxidants and reagents will be illustrated. Large fractions of these catalysts are ideally suited for the era of clean technology as, they minimize the production of waste thereby maximising the atom efficiency, which results in enhanced turnovers and exceptional selectivities in many industrially significant catalytic transformations.



**Dr Kazuhiko Sato**  
*National Institute of Advanced Industrial Science and Technology*  
**k.sato@aist.go.jp**

Kazuhiko Sato was born in Fukushima, Japan, in 1963. He received his Ph. D. degree from Tohoku University in 1990 under the supervision of Professor Hideki Sakurai and joined the Professor Ryoji Noyori's group at Nagoya University as an Assistant Professor. In 2000, he was invited to the National Institute of Materials and Chemical Research (one of the predecessors of National Institute of Advanced Industrial Science and Technology (AIST)) as a Senior Research Scientist. He became the leader of Organic Reaction Control Group in 2005, and now is a Principal Research Scientist at AIST. Since 2008, he has been the Research Leader of national project for green chemistry, aiming for the development of an innovative process for chemical oxidation. His current research interest is the development of environmentally benign oxidation reactions. In 2001, he received the Incentive Award in Synthetic Organic Chemistry, Japan, and the Award 2008 of Tsukuba Foundation for Chemical and Bio-Technology in 2008.

#### **Green oxidation with hydrogen peroxide**

*Kazuhiko Sato, Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, Tsukuba, Ibaraki, 305-8565, Japan*

Oxidation is a core technology for converting petroleum-based materials to useful chemicals of a higher oxidation state. The oxidation procedure must be high-yielding and highly selective without any by-products through a simple, safe operation using a clean, well-behaving, and cheap oxidant. Aqueous hydrogen peroxide ( $H_2O_2$ ) is an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole co-product. However,  $H_2O_2$  can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds. Thus, the discovery of an efficient catalyst and the choice of reaction conditions are the keys to realizing an ideal oxidation procedure. In this context, we developed various oxidation reactions with aqueous  $H_2O_2$  under organic solvent- and halide-free conditions, including alcohols to ketones, aldehydes, and carboxylic acids,  $\alpha$ ,  $\beta$ -unsaturated aldehydes to corresponding carboxylic acids, epoxidation of olefins, 1,2-dihydroxylation of olefins, and oxidative cleavage of cyclic olefins and ketones. These oxidation methods are high-yielding, clean, safe, operationally simple, and cost-effective, and therefore meet with the requirements of contemporary organic synthesis. Furthermore, we have successfully developed a non-phenolic, halide-free resin which has both excellent insulation performance and flexibility by clean epoxidation process with  $H_2O_2$ .



**Professor Atsushi Satsuma**  
*Nagoya University*  
 satsuma@apchem.nagoya-u.ac.jp

Atsushi Satsuma received his PhD in engineering in 1989 from Nagoya University in Japan. He was a research associate (1989-1995), an assistant professor (1995-1998), an associate professor (1998-2003), and has been a professor at Graduate School of Engineering, Nagoya University, Japan since April 2003. He was a postdoctoral fellow of University of New South Wales and Macquarie University in Sydney, Australia, from 1997-1998. His current research interests are in automobile catalysts, gas sensors, and environment-friendly chemical reactions.

**Unique catalytic behavior of Ag cluster in selective NO<sub>x</sub> reduction and greener chemical reactions**

*Atsushi Satsuma and Kenichi Shimizu, Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan*

This presentation reports unique catalytic behavior of nano- and subnano-sized Ag cluster in selective catalytic reduction of NO by hydrocarbons (HC-SCR) and greener chemical reactions based on oxidant-free selective dehydrogenation. HC-SCR is one of the promising technologies for removal of NO<sub>x</sub> in exhausts from diesel and lean-burn gasoline engines, and Ag/alumina is thought to be the most promising candidate for practical use. The HC-SCR activity of Ag/alumina can be significantly boosted by the addition of hydrogen into the reaction atmospheres. By means of in-situ measurements of UV-Vis, FT/IR, and EXAFS, the important role and reaction mechanism of Ag cluster on the hydrogen-assisted HC-SCR are clarified. The formation of Ag clusters and the higher catalytic activity were related to formation of Ag-hydride and that of hydrogen peroxide-like species on Ag cluster, respectively. Knowing these unique catalytic behaviour of Ag cluster, our research group applied Ag cluster supported on alumina as solid recyclable catalyst for greener chemical reactions, such as oxidant-free dehydrogenation of alcohols, direct C-C cross-coupling of alcohols, and direct dehydrogenative amide synthesis.



**Professor Tetsuya Shishido**  
*Kyoto University*  
 shishido@moleng.kyoto-u.ac.jp

Dr Tetsuya Shishido was born in Yokohama in 1970 and completed his MSc in 1994 and PhD Engineering in 1997 both from Hokkaido University. From 1997-2003 he was a Research Associate at Hiroshima University before moving to Tokyo Gakugei University in 2003 as an Associate Professor. In 2005 he took up his current position as Associate Professor at Kyoto University. His research interests cover acid-base catalysts, oxidation catalysts, supported metal catalysts and *in situ* XAFS analysis. In 2009 he was awarded The Incentive Award of the Catalysis Society of Japan and The Incentive Award of the Japan Petroleum Institute.

**Photooxidation of alcohol over niobium oxide**

*Tetsuya Shishido, Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan*

Photooxidations of alcohols to carbonyl compounds proceed selectively at a low temperature over niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) without organic solvents. Although Nb<sub>2</sub>O<sub>5</sub> is not able to absorb light at > 390 nm wavelengths, the photooxidation of 1-pentanol proceeded under irradiation up to ca. 480 nm. This observation indicates that the photo-activation mechanism of alcohol over Nb<sub>2</sub>O<sub>5</sub> is different from the classical electron transfer mechanism found in semiconductor photocatalysis (the formation of an excited electron in the conduction band and the positive hole in the valence band). On the basis of FT-IR and ESR measurements, the following mechanism is proposed: alcohol is adsorbed onto Nb<sub>2</sub>O<sub>5</sub> as an alcoholate species in the dark. Alcoholate adsorbed on Nb<sub>2</sub>O<sub>5</sub> is activated by transferring an electron to the conduction band reducing Nb<sup>5+</sup> to Nb<sup>4+</sup>, and leaving a hole on the alcoholate. The formed alkenyl radical is converted to a carbonyl compound. The product is desorbed and then the reduced Nb<sup>4+</sup> sites are re-oxidized by the reaction with molecular oxygen. The rate-determining step of the photooxidation of alcohol over Nb<sub>2</sub>O<sub>5</sub> is the process of desorption of the formed carbonyl compound.





## Professor Mizuki Tada

*Institute of Molecular Science*

**mtada@ims.ac.jp**

Prof. Mizuki Tada was born in 1979 in Tokyo, Japan. She received her Ph.D. from the Department of Chemistry at The University of Tokyo in 2005 under the supervision of Prof. Yasuhiro Iwasawa. In 2004, she became an assistant professor in Department of Chemistry at The University of Tokyo and promoted to an associate professor in 2008. In 2008, she moved to the Institute for Molecular Science in Japan. Her current research interests are the molecular-level design of heterogeneous catalyst surfaces using supported metal complex, molecular imprinting, in-situ characterization of heterogeneous catalysts, and time-resolved XAFS.

### **Direct phenol synthesis from benzene and oxygen on supported Re-Pt catalysts**

*Mizuki Tada, Institute of Molecular Science, Myodaiji Area, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan*

Phenol is one of the most important chemicals in industry and it has been produced by three-steps reaction cumene process. Direct phenol synthesis from benzene and oxygen is one of the most desirable catalytic reactions but there have been no catalysts to exhibit good phenol yield.

In 2006, we have found that the chemical vapor deposition of  $\text{CH}_3\text{ReO}_3$  and subsequent treatment with  $\text{NH}_3$  produced a N-interstitial Re10 cluster in the pore of HZSM-5 zeolite, which was highly selective for the direct phenol synthesis using  $\text{O}_2$  as an oxidant. Recently, we have succeeded in preparing novel Re-Pt catalysts supported on  $\text{NH}_4$ -ZSM-5 zeolite and achieving a remarkable catalytic performance (benzene conversion: 28% and phenol selectivity: 93%). The preparation of the supported Re-Pt catalysts, the structures of catalytically active species, and catalytic performances for the direct phenol synthesis will be presented.



## Professor Keiichi Tomishige

*Tsukuba University*

**tomi@tulip.sannet.ne.jp**

Keiichi Tomishige received his B.Sc., M.S. and Ph.D. from the Graduate School of Science, Department of Chemistry, University of Tokyo with Prof. Y. Iwasawa. During his Ph.D. course in 1994, he moved to the Graduate School of Engineering, University of Tokyo as a research associate and worked with Prof. K. Fujimoto. In 1998, he became a lecturer, and then he moved to Institute of Materials Science, University of Tsukuba as a lecturer in 2001. Since 2004 he has been an associate professor, Graduate School of Pure and Applied Sciences, University of Tsukuba. In addition, since 2008, he also has been a principal investigator, International Centre for Materials Nanoarchitectonics Satellite (MANA), National Institute for Materials Sciences (NIMS) and University of Tsukuba, and a research director, Core Research Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST). His research interests are in the development of heterogeneous catalysts for the conversion of biomass, natural gas, and  $\text{CO}_2$ .

### **Catalyst development for the production of biomass-derived chemicals**

*Keiichi Tomishige, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8573, Japan*

Utilization of biomass as a renewable raw material will gain importance in the industrial production of chemical substances for sustainability and as a substitute for petroleum for energy production. Since biomass-related raw materials usually have high oxygen content, useful oxygenates such as diols will be one of the target chemicals derived from biomasses. In particular, the diols with a linear carbon-carbon chain and carbons at both edges with the OH group have been used as monomers for production of polyesters and polyurethanes. Here, development of catalysts and catalytic reactions for the production of the diols from renewable resources is reported. The target diols are 1,3-propanediol, 1,5-pentanediol and 1,6-hexanediol, and we are developing the heterogeneous hydrogenolysis catalysts for glycerol to 1,3-propanediol, tetrahydrofurfuryl alcohol to 1,5-pentanediol, and tetrahydropyran-2-methanol to 1,6-hexanediol.



**Dr Charlotte Williams**  
Imperial College London  
c.k.williams@imperial.ac.uk

Charlotte K Williams is a senior lecturer in chemistry at Imperial College London and an EPSRC advanced research fellow. Her research interests are in coordination chemistry (Zn(II), Y(III) and Al(III)), homogeneous catalysis, polymerisation catalysis, degradable polymer synthesis, the activation and use of renewable resources. Her research has been recognized by the RSC Energy, Environment and Sustainability Early Career Award 2009, The RSC Meldola Medal for 2005 and the RSC Laurie Vergnano Award in 2001.

She was appointed at Imperial in 2003 after working as a postdoctoral research associate at Cambridge University (with Profs. A.B. Holmes FRS and R.H. Friend FRS) on the synthesis of electroactive polymers and at the University of Minnesota (with Profs. M.A. Hillmyer and W.B. Tolman) on the synthesis of biodegradable polymers. She received her PhD (Profs. V.C. Gibson and N.J. Long) and BSc in Chemistry from Imperial College London

#### Catalytic activation of renewable resources for polymer synthesis

Charlotte Williams, Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

Using renewable resources, such as biomass or carbon dioxide, as feedstocks for the chemical industry offers exciting opportunities due to concerns regarding the sustainability, supply, environmental impact and cost of petrochemicals. Currently, almost all commodity plastics derive from petrochemicals; and after use, the vast majority end up in landfill sites where they are bulky and pervasive. There is, therefore, a significant drive to prepare replacement degradable, commodity polymers from renewable resources. This lecture will describe the preparation and application of catalysts to enable the activation of carbohydrates or carbon dioxide for use as monomers in polymer synthesis. In particular the preparation of new catalysts, based on yttrium complexes, which are highly active and controlled (including Stereocontrolled) initiators for lactide ring opening polymerisation will be described. Lactide derives from lactic acid which is harvested from corn or sugar beet. More recently, methods to activate D-glucose to prepare functionalised lactones and polyesters have been developed. Finally, investigations into new catalysts for the copolymerization of carbon dioxide and epoxides will be described. We have recently prepared a series of bimetallic catalysts which show very high activities at low pressures of carbon dioxide. Furthermore, some of these species show high air and moisture tolerance.



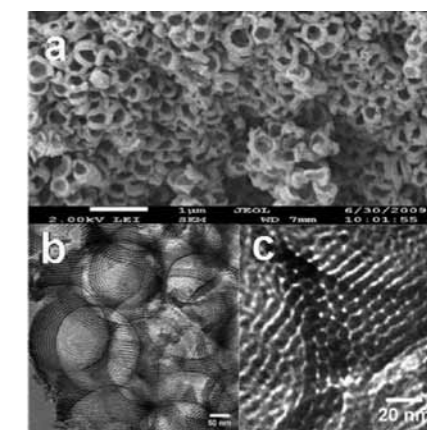
**Dr Karen Wilson**  
University of Cardiff  
wilsonk5@cardiff.ac.uk

Karen is a Reader in Physical Chemistry in the School of Chemistry at Cardiff University, where she is a member of the Cardiff Catalysis Institute. Karen was first appointed to a lectureship in 1999 at the University of York, following PhD and post-doctoral research in Cambridge (1993-98) in heterogeneous catalysis with Prof Richard Lambert. She is co-founder of the Surface Chemistry and Catalysis group which relocated from York to Cardiff in October 2009. Karen has authored over 100 papers, and in 2001 her work on new mesoporous solid catalysts for fine chemicals syntheses was recognised by the 'Research of the Future Award' from the Nanotechnology in Catalysis Symposium at the 221st ACS National Meeting. She is particularly interested in alternative clean chemical technologies and the use of renewable resources in industrial liquid phase processes. She has been active in the design of new catalysts for biodiesel synthesis, for which her work was noted as a Nature research highlight (Nature 2004, 430, 416), and in 2006 Karen was a recipient of an EPSRC Chemistry-Chemical Engineering discipline hop award. In recognition of her work in clean technology she was also one of 5 top UK young Green Chemists invited by the RSC in 2007 and 2008 to present her work in this area at the joint Japanese Chemical Society/EPSC-RSC organised Green and Sustainable Chemistry Symposium in Osaka and Belfast.

#### Designer catalysts for biodiesel synthesis

Karen Wilson, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

The combination of dwindling oil reserves and growing concerns over carbon dioxide emissions and associated climate change is driving the urgent development of clean, sustainable energy supplies. Biodiesel is non-toxic and biodegradable, with the potential for closed CO<sub>2</sub> cycles and thus vastly reduced carbon footprints compared with petroleum fuels. However, current manufacturing routes employing soluble catalysts are very energy inefficient and produce copious amounts of contaminated water waste. This presentation will highlight the significant progress made in recent years towards developing tuneable solid acid and base catalysts for biodiesel synthesis, which offer several process advantages by eliminating the need for quench steps (and associated waste water), while allowing operation in a continuous reactor. Issues to be discussed include the introduction of non-food based feedstocks and technical advances in catalyst and reactor design required to ensure that biodiesel remains a key player in the renewable energy sector for the 21st century. In particular the benefits of designing porous networks comprising interconnected hierarchical macroporous mesoporous channels (Figure 1) to enhance mass-transport properties of viscous plant oils during biodiesel synthesis will be addressed.



**Figure 1.** (a) SEM and (b, c) low and high magnification TEM images for hierarchical macro-mesoporous SiO<sub>2</sub>.