BRITISH COUNCIL

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“Sustainable Chemistry”

ÁVILA, 6 –10 MARCH 2011

CO-ORDINATORS:

Mª ROSA INFANTE
INSTITUTO DE QUÍMICA AVANZADA DE CATALUNYA (IQAC-CSIC), BARCELONA

JAMES CLARK
UNIVERSITY OF YORK, YORK

SCIENCE

SUSTAINABLE CHEMISTRY

Opening Doors

Scientific workshops for young researchers

Ávila, Spain, 6 - 10 March 2011

INTRODUCTION

The British Council in Spain, in collaboration with the Spanish National Research Council (CSIC) is organising a series of scientific workshops to provide opportunities for young researchers from the UK and Spain to meet face-to-face for the exchange of ideas, knowledge and information on priority topics and to explore future areas of research and collaboration.

This workshop on “Sustainable Chemistry” was the nineteenth in the series.

PRESENTATION

Coinciding with the **International Year of Chemistry 2011** the workshop brought together senior and young scientists, mostly chemists, to talk and discuss on **Sustainable Chemistry**. The main topics were: 1) industrial waste as renewable resources; 2) green solvents; 3) bio-based products from renewable resources: surfactants, lubricants, flavours, fragrances, and fuels; 4) clean technologies for the decreasing waste production and 5) catalysis and biocatalysts.

The workshop programme included 10 key lectures of 30 minutes in length and 23 presentations of 20 minutes by a total of 33 researchers in the field preceded by a short welcome introduction by British Council and CSIC representatives.

The last 5 minutes of each presentation were reserved for discussion. Further opportunities for dialogue were provided at the end of each session. The workshop finished with a final discussion and possibilities for future collaboration.

The workshop was coordinated by Prof James Clark, director and founder of the Green Chemistry Centre of Excellence at the University of York and Prof Mª Rosa Infante from de Instituto de Química Avanzada de Cataluña at the CSIC.

LIST OF PARTICIPANTS

Andy Abbott, *University of Leicester, Leicester* apa1@le.ac.uk

Miguel Ángel Bañares, *Instituto de Catálisis (CSIC), Madrid* banares@icp.csic.es

Carolina Belver, *Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid* carolina.belver@uam.es

Kamelia Boodhoo, *School of Chemical Engineering & Advanced Materials, University of Newcastle, Newcastle* k.v.k.boodhoo@ncl.ac.uk

Simon Breeden, *University of York, York* Simon. Breeden@york.ac.uk

George Britovsek, *Imperial College London, London* g.britovsek@imperial.ac.uk

Pedro Castaño, *Facultad de Ciencia y Tecnología, Universidad del País Vasco, Bilbao* pedro.castano@ehu.es

Antonio Chica, *Instituto de Tecnología Química (UPV-CSIC), Valencia* achica@itq.upv.es

Pedro Cintas, *Facultad de Ciencias, Universidad de Extremadura, Badajoz* pecintas@unex.es

Simon Collinson, *Cranfield University, Cranfield* s.collinson@cranfield.ac.uk

Jaume Cot, *Instituto de Química Avanzada de Catalunya (IQAC-CSIC), Barcelona* jcceco@iqac.csic.es

Matthew Davidson, *Department of Chemistry, University of Bath, Bath* m.g.davidson@bath.ac.uk

Silvia Díez-González, *Department of Chemistry, Imperial College London, London* s.diez-gonzalez@imperial.ac.uk

Marcelo Domine, *Instituto de Tecnología Química (UPV-CSIC), Valencia* mdomine@itq.upv.es

Mª Teresa García Ramón, *Instituto Química Avanzada de Catalunya (IQAC-CSIC), Barcelona* teresa.garcia@iqac.csic.es

Eduardo García-Suárez, *Instituto Nacional del Carbón (CSIC), Oviedo* eduardo@incar.csic.es

Eduardo García-Verdugo, *Universidad Jaume I, Castellón* eduardo.garcia-verdugo@qio.uji.es

Olga Guerrero-Pérez, *Escuela de Ingenierías, Universidad de Málaga, Málaga* oguerrero@uma.es

Andrew Hunt, *University of York, York* ajh134@york.ac.uk

María Rosa Infante, *Instituto de Química Avanzada de Catalunya (IQAC-CSIC), Barcelona* rimste@cid.csic.es

Peter Licence, *School of Chemistry, University of Nottingham, Nottingham* pete.licence@nottingham.ac.uk

Fernando López Gallego, *Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Madrid* flopez@icp.csic.es

Beatriz Lora, *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid* belora@quim.ucm.es

Pedro Lozano, *Facultad de Química, Universidad de Murcia, Murcia* plozanor@um.es

Rafael Luque, *Departamento de Química Orgánica, Universidad de Córdoba, Córdoba* q62alsor@uco.es

Ángeles Manresa, *Facultad de Farmacia, Universidad de Barcelona, Barcelona* amanresa@ub.edu

Michael North, *University of Newcastle, Newcastle* michael.north@ncl.ac.uk

Jesús Palenzuela, *University of Leicester, Leicester* jpc34@leicester.ac.u

Lourdes Pérez Muñoz, *Científico Titular, Instituto Química Avanzada de Catalunya (IQAC-CSIC), Barcelona* Lourdes lpmste@cid.csic.es

Gemma Villorbina Noguera, *Escuela Técnica Superior de Ingeniería Agraria, Universitat de Lleida, Lleida* gemmav@quimica.udl.cat

Colin Webb, *University of Manchester, Manchester* colin.webb@manchester.ac.uk

Richard Wells, *Department of Chemistry, University of Aberdeen, Aberdeen* r.wells@abdn.ac.uk

Karen Wilson, *School of Chemistry, Cardiff University, Cardiff* wilsonk5@Cardiff.ac.uk

PROGRAMME

Sunday 6	Monday 7	Tuesday 8	Wednesday 9
	9:00 *Welcome by British Council Director in Spain and Vicepresident CSIC (Spanish National Research Council)* **9:20-11:15** ***INDUSTRIAL WASTE AS RENEWABLE RESOURCES*** • Simon Breeden • Pedro Castaño • Matthew Davidson • Jaume Cot	**9:00-11:00** ***BIO-BASED PRODUCTS FROM RENEWABLE RESOURCES*** • Colin Webb • Kamelia Boodhoo • Gemma Villorbina • Olga Guerrero • George Britovsek	**9:00-11:00** ***CATALYSIS AND BIOCATALYSTS*** • Miguel Bañares • Beatriz Lora • Karen Wilson • Antonio Chica
	11:15-11:45 coffee break	**11:00-11:15 coffee break**	**11:00 - 11:30 coffee break**
	11:45-13:30 ***GREEN SOLVENTS*** • Pedro Lozano • Richard Wells • Peter Licence • Teresa García	**11:15-13:00** ***CLEAN TECHNOLOGIES FOR THE DECREASING WASTE PRODUCTION*** • *Pedro Cintas* • *Simon Collinson* • *Andrew Hunt*	**11:30-13:30** ***CATALYSIS AND BIOCATALYSTS*** • Marcelo Domine • Fernando López • Silvia Díez-González • Rafael Luque
	13:30-15:30 lunch	**13:00-14:30 lunch**	**13:30-15:30 lunch**
	15:30-17:00 ***GREEN SOLVENTS*** • Andy Abbott • Eduardo García-Suárez • Eduardo García-Verdugo	**14:30-16:00** ***CLEAN TECHNOLOGIES FOR THE DECREASING WASTE PRODUCTION*** • Michael North • Carolina Belver • Karen Wilson on behalf of Adam Lee	**15:30-16:00** ***General Conclusions and Perspectives***
	17:00-17:30 coffee break		**16:00-16:30 coffee break**
	17:30-19:00 ***BIO-BASED PRODUCTS FROM RENEWABLE RESOURCES*** • Ángeles Manresa • Lourdes Pérez • Jesús Palenzuela	**16:00-19:00** *Ávila guided tour*	
20:30	**20:30**	**20:30**	**20:30**
Welcome drinks and informal welcome dinner at the Parador de Ávila	*Dinner at the Parador de Ávila*	*Dinner at a local restaurant*	*Dinner at the Parador de Ávila*

SUMMARY OF DISCUSSIONS

■ The workshop began with a session on "Industrial Waste as Renewable Resources" focussed on how to treat or reuse waste resources to reduce waste or to use them as raw materials to obtain useful new compounds. The opening lecture was given by *Simon Breeden*, a colleague of *James Clark*, who focused on different aspects (legislation, industrial, environment, demand, ...) of the use of waste as resource as a future green solution. He proposed an industrial symbiosis approach consisting to make the chemical life-cycles greener and more sustainable. Wastes from the disposal of the same or different chemical products can be used as feedstocks for further manufacture. Biomass or wastes must be transformed efficiently to fuels or chemicals in a sustainable way by the use of new catalysts. *Pedro Castaño* proposed us a new approximation to understand the chemical pathways of deactivation of the catalysts used to obtain light alkenes. One of the nice examples on how to make chemicals from sustainable resources was described by *Mathew Davidson* who presented a new benign, robust and stereoselective catalyst initiators to produce renewable and biodegradable polylactic acid polymers as a viable alternative to traditional petrochemical based commodity polymers. Finnaly, *Jaume Cot* described the ecological problems of the waste leather industry and how to convert the leather wastes in high value biopolymers. A complete methodology for the extraction and production of new biopolymers (collagenic biopolymers of different molecular weight) from tannery solid waste was described. It has been demonstrated that those biopolymers can be produced in form of gels, films, sponges and/or fibres.

■ The need for alternative environmentally friendly solvents was the subject of the second session. The use of liquid and supercritical CO_2 provides an alternative to conventional organic solvents in a wide range of applications including extraction and fractionation of botanical materials, reactions with conventional or bio-catalysts, product cleaning and production of micro particles. *Pedro Lozano* focused in the use of ionic liquids as reaction media in enzymatic catalyst processes. He described a biphasic systems based on ionic liquids and supercritical CO_2 as integral green bioprocesses to be used in biocatalytic methods in non-aqueous media. *Richard Wells* presented the use of water as a solvent in directing selective hydrogenation of aromatics over Pd/Carbon catalysts. Enhanced activity in water for ring hydrogenation of aromatic acids & amides was observed in comparison with conventional hydrogenation methods. A nice talk was executed by *Peter Licence* on the study of ionic liquids in-vacuo. Ionic liquids, ILs are liquids below 100°C consisting solely of ions. They exhibit a combination of properties, for example, electrical conductivity, involatility and tuneable solvent behaviour, which has led to a large number of potential applications. He presented a series of new analytical experiments that could be made possible because these ionic liquids have negligible vapour pressure and consequently they do not evaporate even under vacuum. *Teresa Garcia* presented biological properties of ionic liquids, in particular biodegradation and aquatic toxicity. These issues are extremely important to the prevention of environmental pollution and provide information about the "green" nature of ionic liquids as alternative to the industrial organic solvents. She concluded that ionic liquids with a pyridinium cation bearing an ester containing substituent at positions 1 or 3 show excellent biodegradability. In contrast, 1-alkylpyridinium ILs with linear C4, C10 and C16 showed relatively low levels of biodegradability. The talk by Andy Abbot was devoted to processing metals and metal oxides using ionic liquids based on choline chloride a non-toxic and biodegradable IL. Metal oxides are insoluble in most molecular solvents so the solution based processing of metals is done in either melts or very acidic or basic conditions. Ionic liquids based on choline chloride are useful for large-scale waste and recycling metal applications. *Eduardo Garcia Suarez* showed that ILs can be designed to accommodate functional groups which can provide the liquids with auxiliary reactivity like, e.g. Brønsted acidity to environmentally produce ethene methoxycarbonylation. Ethene methoxycarbonylation is an important reaction in the chemical industry and a new attractive route to produce MP as a source for MMA for poly-MMA production. PMMA is a transparent thermoplastic alternative to glass (aquariums, exteriors lights of cars, protection in ice hockey, helmet visors, etc.) and medical technologies and implants (intraocular lenses, bone cement, cosmetic surgery, etc.). The immobilisation of ILs onto a support or structured material is a highly attractive strategy to minimize the amount of ILs used, maintaining their properties. *Eduardo García Verdugo* reported an elegant strategy to immobilize ILs onto a support or structured materials by covalent linking transferring the IL properties to the solid phase.

■ The third session of the workshop was focused to bio based products. Biobased compounds from renewable resources such as waste food, oils, glycerol, amino acids and starch plastics to obtain useful building blocks, surfactants and new compounds was described. The session commenced with *Angeles Manresa* who showed us several biosurfactant examples. These natural surfactants are produced by microorganisms. Biotechnology allows us to take advantage of the natural properties of micro-organisms and facilitates the natural recycling process, which is the bioconversion of waste. Different residuals have been used to produce different mixture of rhamnolipids homolog's and open the opportunity to the design of integrated process. In summary, Bacteria are a working force with a great potential; Metabolic plasticity to deal with complex substrates and they are an important source of new products and new enzymes Another type of biobased surfactants were described by *Lourdes Pérez* in particular the amino acid based surfactants with interesting biocompatible and antimicrobial properties. The utility of waste starch to produce new starch-based bioplastics with strength similar to a conventional and synthetic plastic such as nylon was presented by Jesus Palenzuela. Each of us uses about 300 g of plastics on average per day; this is unsustainable due to the reduction in oil production and most plastics degrade very slowly in the environment. Jesus concluded that starch-based bioplastic materials could be made using biocompatible materials. A versatile range of materials could be made. Composites produced had greatly enhanced properties. *Colin Webb's* talk was about chemicals from food waste. There is a growing recognition that the twin problems of waste management and resource depletion can be solved together through the utilisation of waste as a resource, using green and sustainable chemical technologies. Food waste digestion as nutrient for bioprocesses solid fermentation to reduce the waste content and downstream process was described. The more important conclusions were: Waste bread can successfully be used to produce high quality hydrolytic enzymes to process further waste bread into an excellent fermentation substrate. The stability of enzymes produced from waste bread is significantly greater than those produced from other raw materials. Nowadays the interest of glycerol as starting material to prepare useful chemical compounds is increasing together with biodiesel industry development and the interest in utilising renewable materials. The excess glycerol generated may become an environmental problem. There are different applications. One is its use as carbon energy source for microbial growth. In other hand glycerol is present in a huge number of natural products integrating part of their structure. Moreover, it presents great synthetical potential for creation of stereogenic centers since it functionalization in its three carbons. In this sense there were two contributions. *Gemma Villorbina* talked about new uses of glycerol to obtain halohydrins esters and derivatives from polyols and acylglycerides from biodiesel industry. A new approach to synthesize allyl esters from these raw materials was described. *George Britovsek* presented new approaches for carbonylation of glycerol in presence of Iridium and Rhodium, resulting in a mixture of butyric and isobutyric acid. Iridium showed better selectivity than rhodium. Guerrero offered us a nice talk about new synthetic strategies (nanocasting, hydrothermal, electrospining and chemical activation.) for the generation of carbon materials from different raw materials including biomass residues; this derives to a revalorization of the waste in a high valuable product.

■ Clean Technologies for the decreasing waste production was the subject of the fourth session. It consisted of seven talks. *Kamelia Boodhoo* contributed with the description of opportunities and challenges of process intensification methods for sustainable chemical and bioprocessing in order to get potential benefits to business, process and environment: smaller more efficient equipment (potentially less costly plant), improved mixing and heat/mass transfer; higher selectivity, reduced waste, improved process safety. She described several examples. A key lecture was presented by *Pedro Cintas* who described process intensification technologies with soft radiations such as ultrasound and/or microwave-based. Polymer waste from bottles and textiles causes a high environmental impact given its difficulty to be recycled. An interesting alternative to plastics was described by *Simon Collinson.* Renewable bioplastics such as polylactide (PLA) could be an even more sustainable option with effective recycling. *Andrew Hunt* talked about legislation issues and new technologies for the recycling of liquid crystal displays (LCD). He presented the project REFLATE as a solution for an emerging problem on LCs. It consisted of four operations: Di-assembly of the LCD panel, Extraction with carbon dioxide, Analysis, and Re-use. A novel strategy to reduce waste CO_2 was presented by *Prof North*. He presented CO_2 as alternative sustainable feedstock material for the synthesis of cyclic carbonates in a flow reactor in presence of several catalysts. In the frontier between waste reduction and catalyst Carolina Bellver presented the use of photocatalytic behaviour of polimetalates for degradation of waste materials. The session was concluded by Adam Lee who talked about selective oxidation.

■ Catalysis and Biocatalysis were key topicsin this workshop. In the context of sustainable chemistry a key challenge is to efficiently convert molecules. This is the job of catalysts. The key benefits from catalysis are multifold: optimize material use (selectivity), optimize number of steps (less waste), optimize energy use (lower temperature). But there are major opportunities for catalysis. 1) Process intensification (reactor design); 2) alternative activation (microwave, ultrasounds, photocatalysis). These two points were discussed in the session before. 3) Catalysis in new solvents media; 4) Synthesis of new green catalyst and 5) reaction and catalyst investigation/monitoring. Prof Bañares opened the session showing us an “operando”/ “in situ” methodology necessary to understand how catalysis work and which is the reaction pathway. He illustrated this methodology with an efficient glycerol conversion example. Lora talked about development of supported hydroxyamide-based chiral catalysts as sustainable catalytic system for green chemistry; Synthesis and screening of hydroxyamides functionalized for their grafting to polymers and NPs. Synthesis and screening of hydroxyamide- functionalized polymers and NPs. Study on the reusing and optimization of the developed supported ligands. *Karen Wilson* gave a complete overview of some recent developments in catalytic bio-fuel synthesis and highlights some of the technical hurdles for efficient chemical transformation of biomass to fuels. *Antonio Chica* presentd delaminated zeolites as support of active Co metals as efficient catalytic system for the production of hydrogen. *Marcelo Domine* in his presentation described the development of multi-functional catalysts to afford some challenging cascade type transformations for bio-based platform chemicals valorisation. Several examples were shown. For example the direct and selective reductive amination of alcohols and/or ketones to produce substituted amines and N-heterocycles starting from bio-based compounds (i.e. glycerol, 1,2-propanodiol) were shown by the use of Me-based solid materials as efficient catalysts. *Lopez Gallego* presented with some examples the sustainable advantages to use enzymes as catalysists in the frontier between chemistry and biology. *Silvia Diez-Gonzalez* presented their last results on developing novel and more efficient catalytic systems for the [3+2] cycloaddition reaction of alkynes and azides. Rafael Luque gave an introduction to the field of designer nanomaterials, primarily focused on supported metal nanoparticles (SMNPs) on porous materials, in view of their applications for the production high value-added chemicals and biofuels.

COLLABORATIONS

Colin Webb:

I am hoping to develop a collaboration with Angeles Manresa from Universidad de Barcelona, directly as a result of the workshop. We discussed her work on surfactant production and mine on solid-state fermentation during the meeting and some interesting ideas emerged.

Peter Licence:

I will soon host a student from Eduardo Garcia Verdugos Lab (Universidad Jaume I). We are still finalising the details but it will be about chiral ionic liquids.

Miguel Ángel Bañares:

We have an incipient collaboration with Adam Lee (who finally couldn't attend the meeting) and Karen Wilson at Cardiff University. We are sending them some samples and we are going to apply for a project.

In addition, I talked with Simon Breeden from the University of York to run some glycerol reaction at their facilities with my catalysts.

Rafael Luque:

I expect to carry on collaborating with James Clark and Andy Hunt from the University of York on various aspects related to waste and biomass valorization and supercritical CO2 as reaction media.

I am also collaborating with Eduardo Garcia Suarez (Instituto del Carbón) on Pd catalysed reaction with some of his materials as well as with Jaume Cot from Instituto de Química Avanzada de Catalunya in the preparation of a review article on waste valorization for the journal *Energy and Environmental Science*.

Mª Rosa Infante:

We are going to collaborate with Prof. James Clark's Group from the University of York on a new Cost Action proposal on bio-waste valorisation.

Pedro Castaño:

Olga Guerrero from Universidad of Málaga and I are going to research on catalytic applications of activated carbon (with metals supported) during the production of fuels from tires through pyrolysis and hydrotreating.

Michael North:

We have discussed testing some catalysts made by Mat Davidson's group from the University of Bath and also to work with Pete License from the University of Nottingham on using ionic liquids as solvents for cyclic carbonate synthesis.

Pedro Cintas:

We are going to collaborate with Mª Rosa Infante from Instituto de Química Avanzada de Catalunya on design and applications of surfactant-like molecules.

We have previously collaborated with Rosa's group and have already a joint paper with members of her group. During this meeting we have contacted again and certainly plan to continue in the near future.

Regarding a new potential collaboration, I could also envisage joint efforts with Angels Manresa (Faculty of Pharmacy, University of Barcelona). Further business, but still premature, with Miguel Angel Bañares and/or another British colleague remain open.

ABSTRACTS

Simon Breeden (substituting for James Clark), Green chemistry and industrial symbiosis – using waste as a resource

Pedro Castaño, Deactivation pathways of the catalysts used for producing fuels and chemicals from renewable sources

Jaume Cot, Minimization of collagenic waste: Isolation of high value-added biopolymers

Pedro Lozano, Continuous green biocatalytic processes in neoteric solvents: From one phase to multiphase systems

Richard Wells, The use of water as a solvent in directing selective hydrogenation of aromatics over pd/carbon catalysts

Peter Licence, Ionic liquids in vacuo: liquid surface science

Mª Teresa García Ramón, Biodegradability and aquatic toxicity of ionic liquids

Andy Abbot, Processing of metals and metal oxides using ionic liquids

Eduardo García-Suárez, Application of bronsted acid lionic Liquids in Pd-Catalyzed ethene methoxycarbonylation

Eduardo García –Verdugo, Supported ionic solvents

Ángeles Manresa, Biosurfactants, bioemulsifiers: a common occurrence in nature

Lourdes Pérez, Biocompatible surfactants from natural resources

Jesús Palenzuela, High strength starch-based plastics

Colin Webb, Chemicals from foodwaste

Kamelia Boodhoo, Process Intensification for sustainable chemical and bio processing: opportunities & challenges

Gemma Villorbina, New uses for glycerol

Olga Guerrero, Catalytic materials and adsorbents obtained thought biomass waste revalorization

George Britovsek, Selective carbonylation of Ggycerol

Pedro Cintas, Process intensification with soft radiations: the use of ultrasound and/or microwave-based technologies

Simon Collinson, New recycling options for polymer waste from bottles and textiles

Andrew Hunt, Elemental sustainability, through the recycling of liquid crystal displays

Michael North, Synthesis of cyclic carbonates from waste CO_2

Carolina Belver, Photocatalytic behaviour of polimetalates: future prospects to use solar irradiation

Adam Lee, Selective oxidation of allylic alcohols: tuning the active site

Miguel Bañares, New trends for efficient glycerol conversion: co-reactants and/or microwave-activation to produce acrylonitrile and to produce glycerol carbonate

Beatriz Lora, New sustainable hydroxyamide-based catalysts for the addition of organozinc reagents to aldehydes

Karen Wilson, Tailored heterogeneous catalysts for biodiesel synthesis

Antonio Chica, Delamiated zeolites as support of active metals for the preparation of highly active and selective catalysts for hydrogen production

Marcelo Domine, Solid metal catalysts for new cascade type transformations of biomass-derived compounds

Fernando López Gallego, Sustainable catalysis at the interface between chemistry and biology

Silvia Díez-González, Well-defined metal systems for true click chemistry

Rafael Luque, Designer nanomaterials for the production of high added value chemicals and biofuels

Green chemistry and industrial symbiosis – using waste as a resource

James Clark/ Simon Breeden
Green Chemistry Centre of Excellence, University of York

Chemicals are vital components of many consumer goods including furniture, floor coverings, cosmetics, plastics and paints but the manufacture and use of chemicals faces unprecedented pressures for change. New legislation across the globe will force chemicals to be safe to people and to the environment; chemical manufacturing is inefficient and produces hazardous waste which is increasingly expensive to treat and dispose of; and traditional raw materials are becoming more scarce and expensive. Green chemistry is about making chemical processes and products more environmentally compatible and sustainable.

At the beginning of the life-cycle the raw materials – the sources of carbon and other essential elements – need to be renewable, the chemical processes used in manufacturing need to be simpler, safer and less wasteful, and the products need to have low toxicity, not bioaccumulate and not persist in the environment. An industrial symbiosis approach to chemicals can help make their life-cycles greener and more sustainable. Wastes from the disposal of the same or different chemical products can be used as feedstocks for further manufacture. For example, the components of waste carpet tiles can be recovered and recycled by using switchable bio-adhesives. In other examples, the waxy surface chemicals of bio-wastes can be extracted and used in personal care product formulations; and silicates and other species in the ashes from burning biomass for power can be used as binders for straws to create genuinely green and sustainable furniture boards.

Deactivation pathways of the catalysts used for producing fuels and chemicals from renewable sources

Pedro Castaño
Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología, Universidad del País Vasco

As the crude-oil and natural gas becomes more scarce, other sources of (chemical) energy become more competitive, e.g. organic wastes (fats, tars, waxes, plastics and tires). The resulting scenario forces refineries revamping their facilities in order to treat biomass or wastes. The catalytic cracking of polyolefins achieves two objectives simultaneously: (i) the valorisation of wastes and (ii) the production of chemicals and fuels. Using an acid catalyst, a conical spouted bed reactor, tailored conditions, and feeding high-density polyethylene (HDPE) and polypropylene (PP) we obtained yields of light alkenes (olefins that can be used as monomers) of 60-70 wt%, however the catalyst suffer from deactivation by coke fouling. I will review the pathways of deactivation of this process, the current state-of-the-art technology for investigating the deactivation, and how to deal with it.

Minimization of collagenic waste: isolation of high value-added biopolymers

Jaume Cot
Instituto de Química Avanzada de Catalunya

The whole world is bending over backwards the achievement of a more environmentally friendly and sustainable policy. The concept of "Sustainable Development" transmits the idea of the rational use of the resources, the improvement of life quality and the maintenance of the ecosystems without jeopardizing future generations.

The present project has two objectives: firstly, to help solve an important environmental problem faced by the leather industry, and secondly, to enable acceptable financial gains in terms of obtaining chemical products designed for the tanning industry (basic chromium (III) salts) and high value-added biopolymers.

Chromium in leather waste is a major environmental problem since it has considerable potential for producing hazardous pollution. The first stage of the process is to dechrome those tanned solid wastes in order to reduce potential risks associated with their disposal. The second stage is based on the extraction of biopolymers from the resultant dechromed leather. Those biopolymers are cost-effective in terms of time, chemicals, waste minimisation and therefore environmental impact. The experience gained by our research team in recent years has led to the optimization of a quick and effective procedure for the complete dechromation of chromium waste (based on the oxidation of chromium (III) to chromium (VI) through the action of hydrogen peroxide in an alkaline medium) and subsequent biopolymer extraction by chemical and/or thermal hydrolysis.

An industrial transformation plant has been designed for the treatment of solid leather waste. This plant consists of the following equipment: defibering machine, hydroextractive centrifuge, two reactors (dechromation and biopolymer extraction), tank for storage and reduction of chromium (VI), atomizer (optional), and transportation truck.

Those collagenic biomaterials are at the forefront of potential new applications, and can be perfectly adapted to those future uses. Those “Tailor-made” biopolymers will be designed, with the desired molecular weight, polymorphic formulation (form), optimized properties and characteristics.

Continuous green biocatalytic processes in neoteric solvents: from one phase to multiphase systems

Pedro Lozano
Departamento de Bioquímica y Biología Molecular, Facultad de Química, Universidad de Murcia

Chemistry necessitates a paradigmatic shift from traditional concepts of chemical process efficiency, which focus largely on chemical yield, to ones that assign economic value to eliminating waste at source, reusing solvents and avoiding the use of toxic and/or hazardous substances. Enzymes clearly constitute the most powerful green tools for catalyzing chemical processes, because their activity and selectivity (stereo-, chemo- and regioselectivity) for catalyzed reactions are far-ranging. However, the use of these biocatalysts in aqueous media is limited (e.g. low solubility of most chemicals in water, non-inert character of water, etc). Switching from water to non-aqueous solvents, as reaction medium for enzyme-catalyzed reactions, is not always easy, because the native structure of the enzyme can easily be destroyed, resulting in deactivation.

Ionic liquids (ILs) and supercritical fluids (SCFs) are the non-aqueous green solvents which have received most attention worldwide for use in biocatalysis, because of their excellent characteristics to design enzymatic processes. Research on enzymatic catalysis in ILs was firstly focused on the potential of these neoteric solvents as reaction media, then on understanding the exceptional behaviour of enzymes in some kinds of ILs, and finally on the development of integrated biotransformation / separation systems. In such enzymatic processes, the unique properties of supercritical carbon dioxide ($scCO_2$) to extract, dissolve and transport chemicals, are tarnished by the denaturative effect it has on enzymes. Biphasic systems based on ILs and $scCO_2$ have been proposed as the first approach to integral green bioprocesses in non-aqueous media, where both the biocatalytic and extraction steps are coupled in an environmentally benign and efficient reaction/separation process in continuous operation.[1] Several types of continuous reactors based on enzymatic [2] or chemoenzymatic [3] catalysis have been tested with excellent results. As example, the dynamic kinetic resolution (DKR) of rac-1-phenylethanol was carried out in a chemoenzymatic packed-bed reactor, based on both immobilized lipase (Novozym 435) and acid zeolites catalysts, in IL/scCO2 biphasic system at 50°C and 100 bar (see Fig.1). The system provided an excellent yield (up 98.0 %) for R-phenylethyl propionate product and enantioselectivity (up 97.3 %), and without any activity loss for 14 days of operation.4

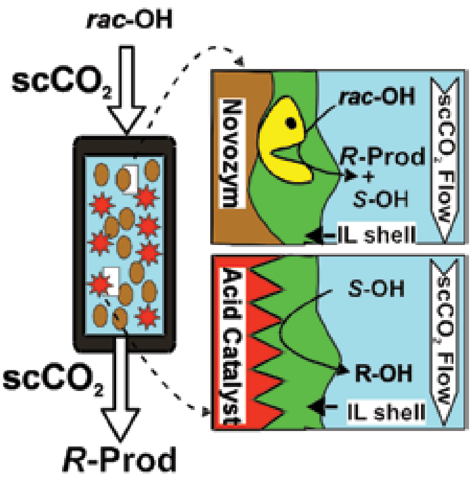

Fig. 1. Enzymatic reactor in IL/$scCO_2$

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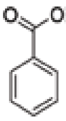
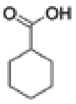
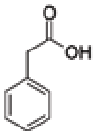
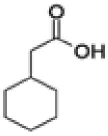
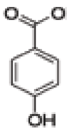
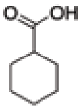
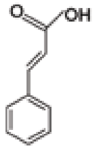
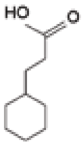
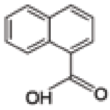
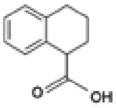
The use of water as a solvent in directing selective hydrogenation of aromatics over pd/carbon catalysts

Richard Wells
Department of Chemistry, University of Aberdeen

1. Introduction

The desire to produce more environmentally acceptable chemical processes has led to increased interest in replacing stoichiometric regents with reusable heterogeneous catalysts which are capable of producing high selectivities to a desired product. Further improvements are possible where commonly used volatile organic compounds (VOC) may be replaced by solvents with lower vapour pressures or which are deemed to be environmentally benign. The use of water as solvent has received attention and there are cases in which additional benefits, such as increased reaction rates have been found when this replaces organic solvents. Water may be used in hydrogenation reactions since its moderate Henry's constant permits reactions to proceed at relatively low hydrogen partial pressures. In this report, we outline the use of steam activated carbon and nitric acid treated carbon nanofibres, both of which show high miscibility with water, allowing the hydrogenation of water-soluble aromatic acids with exceptional selectivity to the corresponding cyclohexane carboxylic acid. In

Table 1. Results of catalytic hydrogenation tests.

Reagent	Product(s)	Conversion / % and (Selectivity) / %
Benzoic acid 	**Cyclohexanecarboxylic acid** 	**80** **(100)**
Phenyl acetic acid 	**Cyclohexaneacetic acid** 	**65** **(100)**
p-Salicylic acid 	**Cyclohexanecarboxylic acid** 	**93** **(51)**
Cinnamic acid 	**Cyclohexylpropanoic acid** 	**100** **(97)**
Naphthoic acid 	**1,2,3,4-tetrahydro-1-naphthoic acid** 	**80.5** **(61.5)**

general, aromatic ring hydrogenation requires more severe conditions than those required to hydrogenate other functional groups thereby leading to their preferential reaction relative to the former.

2. Experimental

Pd loaded samples were attained by combing the support with a volume of an aqueous solution of $Pd(NO_3)_2$ equivalent to its adsorption capacity and containing a predetermined quantity of salt to prepare a 5% loading of Pd on reduction. Prior to use, catalysts were activated by exposure to a 1:1 H_2/N_2 mixture (50 $cm^3\ min^{-1}$) at 423 K for 1 h followed by cooling to 298 K under nitrogen. Catalytic reactions were carried out using 50 cm^3 of a 0.1 M aqueous solution of the aromatic acid. All reactions were performed over a 24 h at 358 K and 15 Bar H_2 pressure.

3. Results and discussion

To determine whether the catalyst was capable of selective hydrogenation, benzoic acid was used as a test substrate. At 80% conversion, 100% selectivity to the hydrogenated ring product (cyclohexane carboxylic acid) was obtained. To determine whether the proximity of the acid function to the ring was important, the reaction was repeated using phenylacetic acid. Although the reaction rate was less for this substrate, the system continued to show 100% selectivity to the saturated acid. Selective hydrogenation of the ring was only attained when ring substitution by an acid function was present. When the same reaction conditions were applied to acetophenone, it was the external aldehyde function which was hydrogenated preferentially (94% selectivity at 100% conversion). The influence of other substituents, together with the morphological nature of the support and a potential model to explain the high selectivity to ring hydrogenation, will be presented.

4. Conclusions

A model will be presented that suggests the key to the unusual selectivities observed is a combination of the water-reagent-metal surface interaction. The more polar side groups prefer interacting with the surrounding water molecules, leaving the aromatic moiety to adsorb on the metal surface leading to its subsequent hydrogenation

Biodegradability and aquatic toxicity of ionic liquids

Mª Teresa García Ramón
Instituto de Química Avanzada de Catalunya

Ionic liquids (ILs) are low melting organic salts that have an enormous potential for industrial use as “green” chemicals. They have a negligible vapour pressure making them an attractive alternative to volatile organic solvents. However, before the likely release of ILs into the environment a more complete understanding of their fate and potential effects on environmental systems is required. Therefore, responsible product design should always bear in mind not only technological demands but also risks arising out of possible persistence in the environment and toxicity of the ionic liquids. Research in this field has to be carried out in order to provide the required knowledge on the biodegradability and aquatic toxicity (ecological properties) of ILs, prior to their widespread use and release. The results can aid to the prevention of environmental pollution and provide information about the “green” nature of ionic liquids as alternative to the industrial organic solvents. This approach can be regarded as a complementary element in the design and selection of technically efficient ionic liquids with lower toxicity that at the end of their function they do no persist in the environment. The structural variability of ionic liquids as well as the abundance of theoretically accessible ionic liquids make necessary to assess the effect of specific structural parameters on their ecological properties.

Processing of metals and metal oxides using ionic liquids

Andrew P. Abbott*, Gero Frisch, Jennifer M. Hartley
Department of Chemistry, University of Leicester

The dissolution and deposition of metals and metal oxides is key to a range of important processes such as metal winning and recycling, corrosion remediation and catalyst preparation. Metal oxides are insoluble in most molecular solvents and are generally soluble in aqueous acid or alkali. High temperature molten salts are used extensively for the production and recovery of refractory metals. The oxidative dissolution of metals often requires harmful reagents such as cyanides or strong acids and alkalis.

We have recently shown that substituted quaternary ammonium salts such as choline chloride form liquids at ambient temperatures when mixed with hydrogen bond donors such as amides and carboxylic acids. These liquids have properties similar to ionic liquids viz. high conductivities, viscosities and surface tensions. Most of the hydrogen bond donors used to date are common bulk commodity chemicals such as urea [1] and oxalic acid [2], which are readily available and hence could be economically applied to large-scale processes.

Analogous to high temperature molten salts, low temperature chloride eutectics demonstrate high solubilities for a wide range of solutes including metal oxides. Redox potentials in these solvents can shift significantly compared to aqueous solution. This allows designing the redox properties of the solute for a particular application by judicious choice of the solvent.

In this work we quantify the solubility of a range of metal oxides in different ionic liquids and present a method to oxidize metal waste using benign reactants such as iodine. We show how these metals can subsequently be precipitated and/or electrowon from solution. We demonstrate that this methodology can be applied to practical applications such as the recycling of zinc from electric arc furnace dust. [3]

Application of brønsted acid ionic liquids in pd-catalyzed ethene methoxycarbonylation

Eduardo J. García-Suárez,[a] Ana B. García,[a] Anders Riisager,[b] Jianmin Xiong,[b] Rasmus Fehrmann[b]

[a] *Instituto Nacional del Carbón (CSIC), 33011 Oviedo, Spain*

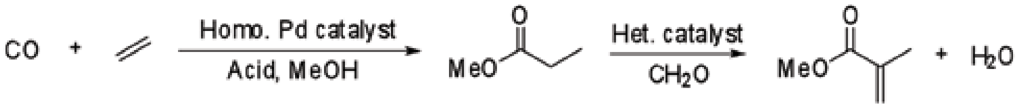
[b] *Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

The selective alkoxycarbonylation of olefins with carbon monoxide and alcohols is a versatile, atom-efficient reaction which is applied industrially for production of commodity alkyl esters and derivatives [1] (Scheme 1). Homogeneous catalyst systems based on palladium-phosphine complexes and strong acid-promoters are most frequently applied for the reaction in order to provide high activity and selectivity towards esters instead of polyketones under relatively mild conditions [2,3].

Scheme 1

Use of ionic liquids (ILs) as reaction media in liquid-liquid biphasic reactions make in many cases processes more green compared to when using traditional organic solvents, due to the IL advantages of unusually low vapour pressure, good thermal stability and tunability of solubility and acidity/coordination properties [4]. Additionally, ILs can also relatively easy (in contrast to organic solvents) be designed to accommodate functional groups which can provide the liquids with auxiliary reactivity like, e.g. Brønsted acidity [5].

In this work we present highly active, selective and reusable catalyst systems with palladium-phosphine complexes dissolved in sulfonic acid-functionalized ILs for methoxycarbonylation of ethene to produce methyl propionate (MP) [6]. MP is a highly valuable precursor for production of methyl methacrylate (MA) utilized in manufacture of acrylic plastics (Scheme 2).



Scheme 2

In batch reactions low solubility of the product resulted in spontaneous phase-separation of the organic MP from the IL catalyst phase after reaction, thus allowing facile product recovery and catalyst reuse. Accordingly, the catalyst system remained stable and revealed no significant loss of activity and selectivity upon reuse in three consecutive cycles, thus clearly demonstrating the versatility of the system.

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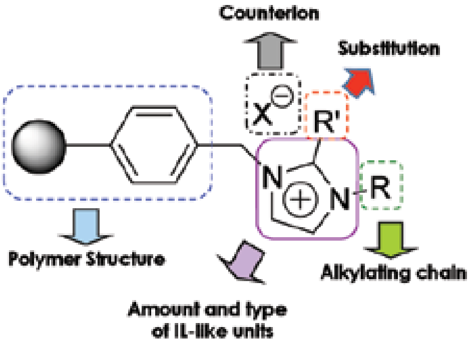
Supported ionic solvents (solisol)

Eduardo García-Verdugo
Department of Inorganic and Organic Chemistry, University Jaume I, Castellón

ILs are an excellent 'green' solvent with significant potential for both synthesis and separation of chemicals. Although ILs have become commercially available, they are still relatively expensive compared to traditional solvents. Besides, some of them show evidence of low biodegradability and (eco) toxicological properties. Hence, the immobilisation of ILs onto a support or structured material is a highly attractive strategy to minimize the amount of ILs used, maintaining their properties. Here, we reported our strategy to immobilisation of ILs onto a support or structured materials by covalent linking transferring the IL properties to the solid phase leading to either monolithic or gel supported ionic liquid phase (*m- or g*-SILLP) allowing us: i) to minimize the amount of ILs used, ii) an easy separation and recyclability and iii) develop mini-flow reactors for continuous processes in SCF. Besides, the use of polymeric materials as supports allows the introduction of an additional design vector base on the structure and type of polymer resin use. Thus, a wide range of polymeric supported ionic liquid-like phases (SILLPs) or "Solid Ionic Solvents" with tuneable properties can be easily prepared.



Scheme 1. Design vectors used in the preparation of Supported Ionic Liquid-like Phases (SILLPs)

We have quantitatively demonstrated that the change on polarity of the microenvironment of these SILLPs as compared to the standard PS-DVD supports. Moreover, those results reflect that the functional surfaces on the polymers containing IL-like moieties essentially maintain the same polarity of the bulk room temperature ILs. Our results have proved that very significant variations in the physico-chemical properties of SILLPs can be obtained by varying the anion or the cation of the ionic-liquid-like moieties grafted onto a polymeric matrix. Properties of high interest, such as the thermal stability, hygroscopicity, swelling, and polarity, can be finely tuned by varying the anion or the cation and by appropriately adjusting the loading and morphology of the matrix. Rather interestingly, highly thermally stable materials can be prepared in this way.

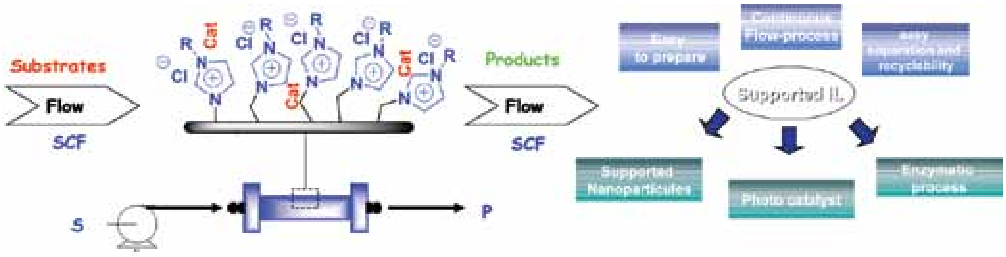


Figure 2. Applications of SILLPs in catalytic continuous flow processes.

Hence, SILLPs might be regarded as "solid ionic solvents" or as nanostructured materials with microenvironments of tunable polarity, which can be used in the following ways: 1) to generate novel catalytic species, 2) to improve the stability of the catalyst, 3) to optimize immobilizationand recyclability, 4) to assist the activation of the catalyst, 5) to facilitate product isolation, and 6) to influence the selectivity of the reaction, which are some of the essential roles of conventional solvents.

The greenness of chemical transformations concerns also the catalyst. These SILPs allow us to immobilise the required catalysts for different type process, for instance: nanoparticules of Pd for Heck processes in ncEtOH, enzymes for bio-catalytic process in $scCO_2$, photocatalyst for photooxygenation processes and organocatalytic processes have been successfully demonstrated. The catalytic performances obtained with these systems are similar or even better than those obtained for batch conventional systems. Furthermore, and taking into consideration the principles of Green Chemistry, the former catalysts are also tested using supercritical fluids as solvent. In this case, catalysts also showed a better performance than that obtained in flow systems by using conventional organic solvents. In conclusion, we are developing a simple methodology that allows the environmental friendly use of supported catalytic system onto immobilised IL in continuous flow systems with excellent performance for different synthetic processes.

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Biosurfactants, bioemulsifiers: a common occurrence in nature

Ángeles Manresa.
Unitat de Microbiologia. Facultat de Farmàcia.
Universitat de Barcelona

Biosurfactants and emulsifiers are among the strategies micro-organisms have developed to survive in boundaries. Their rapid growth allow for the production of large communities to colonize any habitat known. Micro-organisms have designed a variety of compounds to fill with cellular functions such as quorum sensing, nutrient uptake, antibiosis, etc. Microbes are able to produce high-value compounds; one major challenge is the use of renewable biomass or by-products, in the new horizon in which the world is depleted of natural resources and the problem of wastes from processing operations and their disposal has gained public recognition. Biotechnology allows us to take profit of the natural skills of micro-organisms and facilitates the natural recycling process, which is the bioconversion of waste. Different residuals have been used to produce different mixture of rhamnolipids homologs and open the opportunity to the design of integrated process. The nanotechnological behaviour of these remarkable biomolecules has been also explored specially their interaction with membranes.

Finally, the discovery of particulate emulsifiers produced by a new described micro- organisms to survive in cold- environments, open a new frame in producing new effective emulsifiers.

Biocompatible surfactants from natural resources

Lourdes Pérez Muñoz
Instituto de Química Avanzada de Catalunya

Biocompatible surfactants from renewable raw materials such as amino acids will be described. Our multidisciplinary approach include design, synthesis, adsorption at interfaces and self-assembling behaviour, antimicrobial activity, study of biocompatibility including ecotoxicity, biodegradability and irritation effects. Considering the green chemistry principles the synthesis contemplates the preparation of more efficient and safer surfactants using chemo-enzymatic methodologies and designing for biodegradation.

High strength starch-based plastics

Jesús Palenzuela Conde
Department of Chemistry, University of Leicester

Traditional bioplastics occupy only a small part of the materials market at the moment due to their poor mechanical properties and their high cost of production. The employment of the environmental friendly Ionic Liquids as plasticizers, in conjunction with natural and biodegradable materials or recycled waste substances, produces new starch-based bioplastics with strength similar to a conventional and synthetic plastic such as nylon. These materials were produced by compression moulding, achieving materials with a wide range of physical and mechanical properties, e.g.: translucent plastics, flexible plastics, rigid plastics and fibre composite materials with a high tensile strength. The employment of biodegradable materials achieved fully compostable and biodegradable plastics, once they are in the landfill.

Chemicals from food waste

Colin Webb
Satake Centre for Grain Process Engineering, School of Chemical Engineering and Analytical Science, The University of Manchester

Industrial production of chemicals from sustainable feedstocks will require a balance to be achieved between the supply of food and the non-food processing of bio-based raw materials. Research at the Satake Centre for Grain Process Engineering has resulted in the production of various generic fermentation feedstocks that can be converted into a range of platform chemicals, biodegradable polymers, and biofuels via microbial bioconversion from a range of starch based raw materials. One of the major untapped resources for such processes is waste cereal based foods and in particular bread.

Bread possesses the characteristics of an ideal substrate for solid state fermentations and waste bread possesses little or no commercial value. However, when disposed in landfill sites it is converted into methane, an extremely potent greenhouse gas, by anaerobic fermentation. This talk reports studies of a proposed bioprocess for the utilisation of waste bread for the production of value-added products, in particular a multi-enzyme solution of amylolytic and proteolytic enzymes. Preliminary solid state fermentations demonstrated that waste bread pieces are suitable for the growth of the filamentous fungus Aspergillus awamori and for the production of glucoamylase and protease at high concentrations.

Production of over 130 U(glucoamylase)/g bread, and more than 80 U(protease)/g bread, were achieved in a small scale packed bed bioreactor under the optimum conditions. Kinetic studies showed that the glucoamylase produced via solid state fermentation had a much longer shelf-life than the same enzyme produced under submerged conditions. It appears that using solid state fermentation enhances the thermostability of the enzyme significantly.

The multi-enzyme solution produced from waste bread was used in subsequent hydrolysis reactions to produce nutrient rich hydrolysates. These were then used for ethanol production. The yield for these fermentations was found to be equivalent to 255 litres of ethanol per tonne of waste bread. Consequently, 300 million litres of ethanol, with a current market value of £100 million could be produced annually in the UK if all of the waste bread could be recovered and processed in this way.

Process intensification for sustainable chemical and bio processing: opportunities & challenges

Kamelia Boodhoo
School of Chemical Engineering & Advanced Materials, Universityof, Newcastle

The successful delivery of green, sustainable chemical technologies at industrial scale will inevitably require the development of innovative processing technologies by chemical engineers. In bioprocessing, for example, genetic engineering of micro-organisms will obviously play a major part in the efficient use of biomass but development of novel reactor technologies giving high reactor productivity will be equally important for commercial success. Process Intensification (PI) can provide such sought-after innovation of equipment design and processing to enhance process efficiency. This presentation will explore the general approaches involved in achieving intensification and the potential benefits of such PI technologies in the business, process and environment contexts. Selected case studies will be presented to highlight the opportunities and challenges involved in implementing intensified reactors such as a spinning disc reactor and a rotating packed bed reactor for chemical and bio processing applications.

New uses for glycerol

Gemma Villorbina Noguera
Universidad de Lleida

The main objectives are to prepare useful chemical compounds from renewable sources. We have developed new chemical reactions to prepare chlorohydrin esters in high yields from polyols and acylglycerides. Allyl and glycidyl esters have been also prepared from those esters. Usually starting materials will include glycerol from biodiesel industry and acylglycerides from agrifood industries. The chemical reactions used to prepare these products have been carried out in batch, in continuous flow system and in microwaves reactors. The chlorohydrins esters obtained and their derivatives can be used as starting material to prepare multifunctionalised molecules with a high added value. Some of them contain a stereogenic centre constituting a synton for obtaining chiral compounds.

Catalytic materials and adsorbents obtained thought biomass waste revalorization

M. Olga Guerrero Pérez
Departamento de Ingeniería Química, Universidad de Málaga

Carbon materials found many applications, mainly as catalysts, catalytic supports and adsorbents. Thus, actually there is an increasing demand for carbons with well controlled structure and uniform pore size. The motivation of our research has been the development of new synthetic strategies for the generation of carbon materials with controllable chemical surface and morphology. In addition, the materials have been obtained from different raw materials including biomass residues; this derives to a revalorization of the waste in a high valuable product. The four synthesis methods that have been deeply investigated in our group are nanocasting, hydrothermal, electrospining and chemical activation.

The nanocasting procedure implies a direct replication of the pore system from the template. The method generally involves three steps: (i) infiltration of the carbon precursor into the pores of a template inorganic matrix,

(ii) carbonization at high temperature under non-oxidizing conditions to obtain a composite (template+carbon), and finally (iii) removal of the template by acid washing (HF, HCl) to generate porous carbons. In our group we have described the use of industrial waste or byproducts as carbonaceous precursors for obtaining these template carbons.

With the hydrothermal process the biomass can be transform into carbonaceous nanostructures and/or liquid oils at moderate conditions. The process is environmentally friendly and the use of water as a solvent presents many advantages. For example, we have reported the use of hemp cane as raw material for the synthesis of larger dispersed spherical carbon particles. Another synthesis technique in which we have focus is the electrospining, for the preparation of fibers and spheres from electrified liquid jets generated by the injection of conductive liquids through concentric needles to which a high electrical voltage is applied.

Another simply and economical revalorization of the biomass consists in the preparation of activated carbons, that can be used as adsorbents and as catalytic supports. We have used different lignocellulosic materials (as citrus skin or olive stone) to obtain these materials by chemical activation with phosphoric acid. This activation procedure lead to phosphorus surface complexes in form of COPO3, CPO3 and C3P groups, which remain very stable on the carbon surface at relatively high temperatures and confer to the carbons a high oxidation resistance, acting as a physical barrier and blocking the active carbon sites for the oxidation reaction. Thus, these phosphoric-activated carbon materials, with high oxidation resistance, opens new possibilities for the use of carbon materials as catalysts or catalytic supports for reactions that take place at high temperatures under oxidizing conditions.

Selective carbonylation of glycerol

George Britovsek
Department of Chemistry, Imperial College London

The catalytic carbonylation of methanol to acetic acid (Equation 1) has been a major industrial process since the development of the cobalt catalysed BASF process in the 1960s.[1] Since then, research into metal-catalysed methanol carbonylation has resulted in the development of the multi-million dollar Monsanto[2,3] and BP Cativa®[4] processes using rhodium and iridium catalysts, respectively. Further research continues today to improve selectivity and stability of methanol carbonylation catalysts under the relatively harsh conditions employed in industry.[3]

$$\mathrm{MeOH + CO \rightarrow MeCO_2H} \quad (1)$$

A series of complexes of the general formula $[RhL(CO)_2]SbF_6$ where L is 6,6'-substituted-2,2'-bipyridine have been synthesised and characterised.

The complexes were tested as methanol carbonylation catalysts against a standard of $[RhI_2(CO)_2]^-$ (Monsanto Catalyst). It was observed that as the size of the 6,6-susbtituents was increased the stability of the complexes decreased.[5]

The second part of this presentation involves the carbonylation of glycerol. For every 9 kg of biodiesel, 1 kg of glycerol is produced as a by-product, which on a European scale at current production rates, equates to a little more than 200,000 tonnes annually and on a global scale. The global consumption of glycerol lies currently at 700,000 tonnes annually. Increased biodiesel production is expected to further increase the amount of glycerol produced to the extent that it will become a waste product, with its own environmental problems. Research into the development of green conversion processes for glycerol to fuels or other consumer products is therefore, both from an economical and from an environmental point of view, highly desirable and should be carried out now.

Initial studies have shown that the catalytic carbonylation of glycerol in acetic acid as the solvent generates butyric and isobutyric acid. Further catalyst development is required to increase the catalytic activity and the product selectivity.

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Process intensification with soft radiations: the use of ultrasound and/or microwave-based technologies

Pedro Cintas
Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura

The use of microwaves and ultrasound in environmentally friendly syntheses of chemical compounds as well as organic and inorganic materials has come of age. Perhaps the most empowering skill of these waves is their ability to enhance dramatically heat and/or mass transfers, thereby contributing to fast transformations with little or no side products. Both radiations are essentially innocuous and represent real options in some laboratory and industrial applications, in terms of minimization of energy and optimization of reaction control.

This presentation will briefly highlight some fundamentals associated with microwave heating and acoustic cavitation. As we shall see later, such techniques are suitable for the intensification of chemical processes yielding efficient and scalable protocols. Major emphasis will be put on the combined use of microwaves and ultrasound to enhance their effects still further. Thus, simultaneous irradiation in a single reactor or sequential combination in a continuous flow system provide more satisfactory results than the individual techniques alone or conventional activation by thermal methods.

Applications to organic synthesis, the preparation of ionic liquids, and organic-based materials, performed by our group and others, will illustrate the pluses and potentiality of novel hybrid technologies.

New recycling options for polymer waste from bottles and textiles

Simon R Collinson,[1]* A Carné Sánchez1 and O Duplá García1

[1] *Centre for Energy & Resource Technology, School of Applied Sciences, Cranfield University*

1. Polymer Recycling

Polymers are an environmental concern due to their consumption of non-renewable resources and accumulation in the countryside and landfills. Biopolymers from renewable sources, e.g. polylactic acid (PLA), will help tackle these issues as they degrade quicker than conventional polymers. However PLA production is energy intensive and its biodegradation must be carried out in industrial composting facilities to be efficient. The even more sustainable chemical recycling of PLA must be considered if PLA is to be widely used and so disposed of on a large scale. Here alcoholysis is used to chemically recycle both PLA and polyethylene terephthalate (PET) waste.1 These reactions produce lactate esters (which have good solvent and environmental properties as an alternative to traditional more toxic organic solvents) and glycol esters (which can be repolymerized).2 It was found that the methanolysis catalysed by zinc acetate yields a good conversion of waste PLA to methyl lactate. However, with the same reaction conditions PET is unconverted and so is easily separated (Scheme 1). This provides a new process to selectively recycle a mixture of both plastics, which could occur as a mixture in typical waste packaging streams.

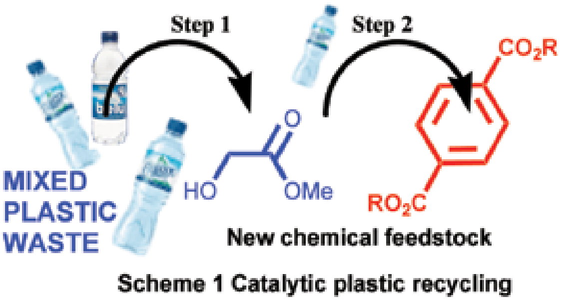

Figure 2. Catalytic plastic recycling

2. Recycling waste carpet as adsorbents for metal ions and nutrients to mitigate pollution

There is a need for cost effective water treatment to satisfy the Water Framework Directive e.g. the Environment Agency reported in 2008 that of the rivers in England 32% had high nitrate and 52% had high phosphate and so farmers need to avoid pollution and recycle fertilisers. In the UK, currently 8% of household waste comprises textiles (including carpets). Here wool rich carpet was successfully employed as a sorbent for metal ions e.g. copper and anions e.g. phosphate.3 To reversibly bind phosphate it was found that the best modification carpet was with hydrated ferric oxide particles (Figures 1 & 2).

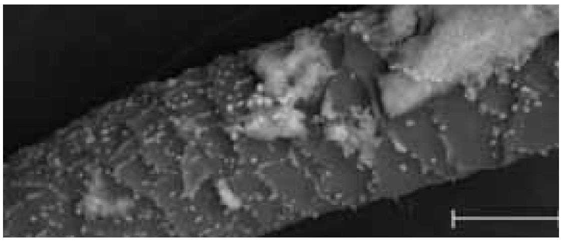

Figure 1 1SEM image of hydrated ferric oxide particles on a carpet fibre

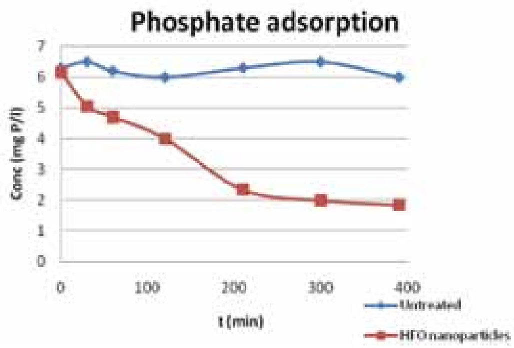

Figure 2 Removal of phosphate from water by HFO modified carpet

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Elemental sustainability through the recycling of liquid crystal displays

Andrew Hunt
University of York

Influence of Liquid Crystal Displays (LCDs) on modern society is dramatic. Its estimated that 2.5 billion LCDs are approaching their end of life and LCDs are the fastest growing waste in the European Union. With increasing concerns for our fragile environment, legislative measures are in place to reduce electronic waste sent to landfill or incineration, as such recycling of LCDs is now a global concern.

By adopting a holistic approach to LCD utilization significant value can be added to this waste. It has been demonstrated that liquid carbon dioxide is efficient at extracting high purity liquid crystals from defunct LCDs. Fractionation, characterization and reuse of the recovered liquid crystals have demonstrated that extracted components have significant potential value.

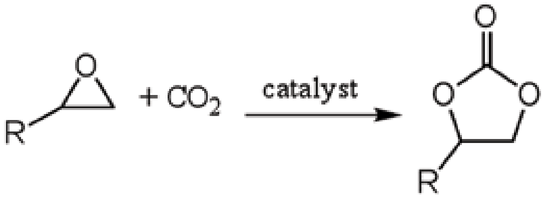
Low value polymers such as polyvinyl alcohol (PVA) from polarizers can also be obtained. By heating the recovered PVA in water (gelatinization), cooling (retrogradation) and dehydration with ethanol, its possible to produce a high surface area structured mesoporous material. Addition of iodine to virgin PVA is essential in changing the micro-structure of PVA and thereby allowing expansion to take place. Use of recovered PVA required no additional iodine, producing expanded materials with high surface areas (95.0 m^2 g^{-1}) and total pore volumes (0.56 cm^3 g^{-1}). These materials may find use in many applications including tissue scaffolds, due to the high surface area and compatibility with the human body. The antimicrobial properties of these materials were enhanced by the simple reaction of silver nitrate with the PVA/iodine complex to form silver nanoparticles encapsulated within the polymer matrix. These materials demonstrated excellent antimicrobial properties against both *Staphylococcus aureus and Escherichia coli*.

Unfortunately, there is a serious problem with traditional supplies of some elements. Reserves of indium for example a vital component in LCD screens and semiconductors, may be used up in 13 years. These unique and finite elements are quickly being dispersed throughout our environment, making it more costly and difficult to recover them. This project has successfully extracted and concentrated indium from LCD waste. It is vital for the future of this technology and others that full recovery of indium and other valuable elements is achieved.

Synthesis of cyclic carbonates from waste CO_2

Michael North
School of Chemistry and University Research Centre in Catalysis and Intensified Processing, Newcastle University

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_2 and epoxides leading to cyclic carbonates (Scheme 1). Cyclic carbonates are already manufactured commercially and have a number of applications including as electrolytes for lithium ion batteries.



Scheme 1

In this presentation, the 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. Mechanistic studies on cyclic carbonate synthesis using these catalysts will be presented, which subsequently led to the synthesis of one–component versions of the catalysts. The immobilisation of the one–component catalysts on inorganic supports and their use in gas–phase flow reactors at temperatures and pressures suitable for direct utilization of power station flue–gas will be described. The tolerance of the catalysts to the NOx and SOx impurities present in simulated flue–gas will be reported as will the results of studies in which the catalysts were exposed to real flue gas from a combustion test–rig burning natural gas or coal.

In view of the scale of the possible use of the catalysts (up to 50 tonnes of catalyst per reactor), it is essential that the cost of catalyst production is as low as possible. Therefore, a cost analysis of the catalysts will be presented along with a modified synthesis which avoids all of the expensive reagents and solvents.

Photocatalytic behaviour of polimetalates: future prospects to use solar irradiation

Carolina Belver
Facultad de Ciencias, Universidad Autónoma de Madrid

Recently, the development of visible light-driven photocatalysts has attracted much attention, especially in the application of water splitting and organic contaminants degradation. TiO2 has been the most popular photocatalyst, but its low absorption efficiency under solar radiation (max. 5 %) has forced the development of systems with high activity under a wide range of visible-light wavenumbers.

Many reports aim to improve the textural and bulk properties from TiO2, although many researches are focussed on looking for new photocatalysts. Diverse oxides and metallates have been reported as photoactive under solar radiation, although have only been a few reports on the development of new materials for detoxification processes.

The synthetic way of these materials has been initially centred on solid state reactions. Nevertheless, recent advances in the development of nanoparticles have allowed their synthesis by soft chemical routes. Several metallates have been recently optimized, approaching the improvement of their optical and physical properties. The systems are promising photocatalysts to water detoxification by using solar light as energy source.

Selective oxidation of allylic alcohols: tuning the active site

Adam F. Lee
Cardiff Catalysis Institute, School of Chemistry, Cardiff University

There has been great recent interest in the development of heterogeneously catalyzed, aerobic selective oxidation (selox) routes to transform alcohols to aldehydes and ketones [1]. Allylic aldehydes are valuable chemical intermediates and high - value components used in the perfume and flavourings industries; for example, crotyl alcohol (($CH_3CH=CH-CHOH$ or CrOH) is an important agrochemical and valuable precursor to the food preservative sorbic acid, while cinnamaldehyde confers a cinnamon aroma. Their commercial synthesis often proceeds via atom-inefficient alcohol oxidation by toxic or hazardous stoichiometric oxidants, which are economically disadvantageous. A number of promising heterogeneous catalysts derived from nanocrystalline Au [2] and/or Pd [3] have been discovered, however their optimization is hampered by limited understanding of the active site responsible for the oxidative dehydrogenation step, and its associated response to reaction conditions.

We recently demonstrated that highly dispersed Pd nanoparticles on a mesoporous Al2O3 support are particularly active towards allylic alcohol selox [3], with Turnover Frequencies proportional to the concentration of surface Pd^{2+} (as PdO) sites. Operando (under working conditions) liquid phase X-ray absorption spectroscopy (XAS) also revealed that catalyst deactivation coincides with PdO reduction to Pd metal [4]. Here we utilise the powerful combination of energy dispersive XAS), diffuse reflectance Fourier Transform IR spectroscopy (DRIFTS) and on-line mass spectrometry (MS), for a dynamic, in-situ study of the vapour phase selox of CrOH over a Pd/mesoporous Al_2O_3 catalyst. Crucially, by working in the vapour phase we are able to minimize artefacts arising from diffusion limitations or solvent effects common in liquid phase selox, and interrogate the nature of adsorbates present on the surface of the catalyst (DRIFTS), and any associated restructuring (XAS), while monitoring the global reactivity via the gaseous exhaust stream composition with 1 Hz time resolution. This represents the first application of time-resolved synchrotron XAS to simultaneously follow dynamic catalyst re-structuring, and the evolution of both surface and gas-phase products during any organic reaction.

Figure 1a shows a schematic of the in-situ reaction cell for simultaneous energy dispersed DRIFTS/MS/XAS measurements. At low temperature, crotonaldehyde is reactively-formed over oxidic Pd nanoparticles upon exposure to CrOH **(Figure 1b)** and is subsequently liberated from the catalyst surface following O_2 adsorption. Elevated reaction temperatures facilitate reversible nanoparticle restructuring, and concomitant catalytic selectivity loss, in response to reaction conditions. These discoveries highlight the importance of stabilising surface PdO and minimising catalyst reducibility in order to achieve high selox yields, and will hopef sts.

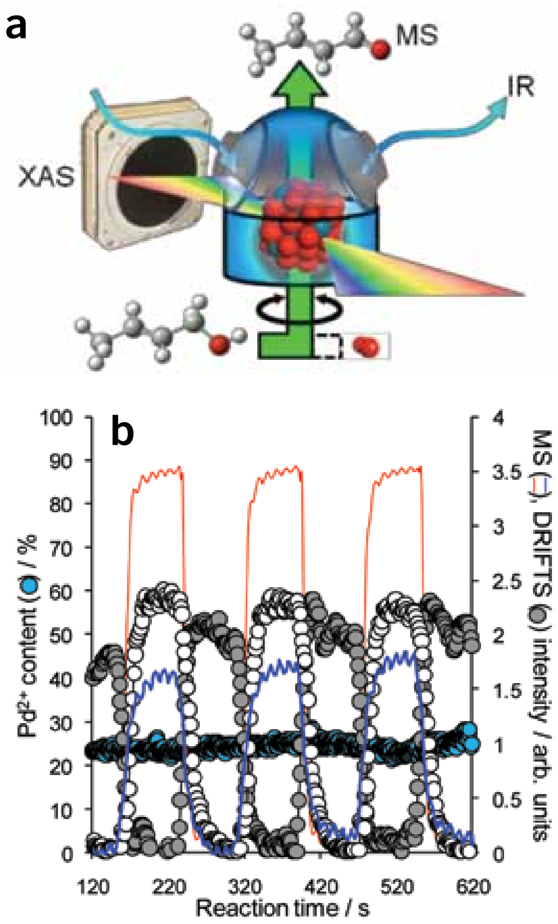


Figure 1. (a) Cartoon of in-situ catalytic reactor; **(b)** synchronous DRIFTS/MS/XANES intensities as a function of alternating CrOH/O_2 cycles over 2.37 wt% Pd/meso-Al_2O_3 catalyst at 80 °C: ● 1712 cm-1; H_2O (m/z = 18), O_2 (m/z= 32), ○ crotonaldehyde (m/z = 70), ● XANES Pd^{2+} concentration.

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New trends for efficient glycerol conversion: co-reactants and/or microwave-activation to produce acrylonitrile and to produce glycerol carbonate

Miguel A. Bañares 1, M. Olga Guerrero-Pérez 1, Vanesa Calvino-Casilda 1, Fernando Rubio-Marcos 2, Jose F. Fernandez-Lozano 2

1 *Instituto de Catálisis y Petroleoquímica, CSIC, Madrid*

2 *Instituto de Cerámica y Vidrio, CSIC, Madrid (Ver documento adjunto)*

SCOPE

Glycerol is a major by-product from methanolysis during the production of biodiesel. Thus, it is an increasingly important molecule in the context of renewable biomass resources to provide energy and chemical intermediates. However, the development of selective glycerol-based catalytic processes is a major challenge as a result of their low selectivity [1,2]. Here, we report on the use of an additional reactant to narrow the product distribution in two cases, with ammonia, to produce acrylonitrile and with urea to produce glycerol carbonate. Both approaches result in a significant increase in selectivity and afford very high conversion values. In addition, the use of microwave activation results in significant enhancement of catalytic performance at significantly milder reaction conditions.

GLYCEROL TO ACRYLONITRILE

Alumina supported nanoscaled rutile VSbO4 crystallites were prepared using impregation of V and Sb precurors and calcination [3] We report a new process for valorization of glycerol to acrylonitrile on $VSbO_4/Al_2O_3$ catalysts with very promising selectivities at high conversions and moderate reaction temperatures under thermal activation (83 % conversion, 58 % selectivity at 400 °C) [3]. Performance by alternative activations affords further improvements. Solvent-free microwave-activation yields efficient conversion (47 %) of glycerol into acrylonitrile under mild conditions (100 °C), short reaction times (1 h) and in the absence of any solvent; with high selectivity (> 80 %) [4], its performance can be further tuned by niobium doping [5].

CARBONYLATION OF GLYCEROL INTO GLYCEROL CARBONATE

Cobalt oxide nanoparticles (40–50 nm) were hierarchically dispersed on ZnO microparticles (0.2 – 1 μm) using a low-energy dry mixing method, resulting in a zinc–cobalt interaction that stabilizes Co^{2+} sites. Raman spectroscopy is used to evidence the nature of the interphase reaction between ZnO and Co_3O_4 particles. The system evolves toward the formation of the spinel phase, ZnCo2O4, with further temperature thermal treatment at 400 °C. The catalytic activity of these materials was tested in the transformation of renewable materials via the carbonylation of glycerol by urea. Room-temperature-prepared Co_3O_4/ZnO systems exhibit catalytic behavior in the production of glycerol carbonate reaching conversions up to 69 % in 4 h with close to total selectivity [6]. So, this approach allows the transformation of renewable materials via the carbonylation of glycerol by urea at moderate reaction conditions (140 °C / 4 h). The methodology here proposed offers invaluable insight into catalysts design and for their mass production due its simplicity [6].

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New sustainable hydroxyamide-based catalysts for the addition of organozinc reagents to aldehydes

B. Lora, T. de las Casas, E. Sokolovskaya,§ S. de la Moya*
Universidad Complutense de Madrid, Madrid, Spain.

The development of new catalysts for asymmetric processes is a research topic of current interest nowadays. The catalysts must be, not only efficient and versatile, but also easy to obtain and, if possible, reusable, for the best exploitation of resources, i.e. chemically-sustainable reusable catalysts.[1]

One of the most important asymmetric methods to create new C-C is the enantioselective addition of organozinc reagents to aldehydes. The interest of the process lies in the importance of the obtained enantioenriched secondary alcohols, which are useful synthetic intermediates of valuable chiral molecules, including natural products, drugs and new materials.[2]

We have recently reported some camphor-derived bis(hydroxyamides), *e.g.* **1**, as cheap chiral ligands for this reaction.[3] The good results achieved with **1** inspired us towards the design of reusable catalysts based on this structure. Thus, we show in this communication that functionalized catalyst **2** can be anchored to solid matrixes, to enable the easy recovery of the catalysts after the enantioselective reaction.

Tailored heterogeneous catalysts for biodiesel synthesis

Karen Wilson
Cardiff Catalysis Institute, School of Chemistry, Cardiff University

Keywords: Biofuels, Biodiesel, Hierarchical materials, Heterogeneous catalysis.

Abstract. Concerns over dwindling oil reserves, carbon dioxide emissions from fossil fuel sources and associated climate change is driving the urgent need for clean, renewable energy supplies. While a number of sustainable technologies (e.g. Wind, Solar and Hydroelectric) are currently receiving heavy investment for stationary energy sources, the most easily implemented and low cost solutions for transportation needs are those based upon biomass derived fuels [1]. To be sustainable so called 'second generation' bio-fuels should be sourced from non edible components of crops (stems, leaves and husks), forestry waste or alternative non-food crops such as switch grass or Jatropha curcas which require minimal cultivation. In addition there is growing potential for using oil triglycerides from algae which can annually yield 80-180 times the amount of oil per hectare compared to plants [2].

While there is growing interest in refining plant and algae oil to transportation fuel via hydrotreating routes [3], conversion of triglycerides to biodiesel via catalytic transesterification remains an energetically efficient and attractive means to generate fuel [1]. However, current biodiesel manufacturing routes employing soluble alkali based catalysts are very energy inefficient producing copious amounts of contaminated water waste. Technical advances in catalyst and reactor design and introduction of non-food based feedstocks are thus required to ensure that biodiesel remains a key player in the renewable energy sector for the 21st century.

This presentation will give an overview of some recent developments in catalytic bio-fuel synthesis and highlight some of the technical hurdles for efficient chemical transformation of biomass to fuels. A particular focus of the presentation will be the design of solid acid and base catalysts for biodiesel synthesis [4-7], with the benefits of designing interconnected hierarchical macro-mesoporous channels **(Figure 1)** which enhance mass-transport of viscous plant oils during biodiesel synthesis discussed [8].

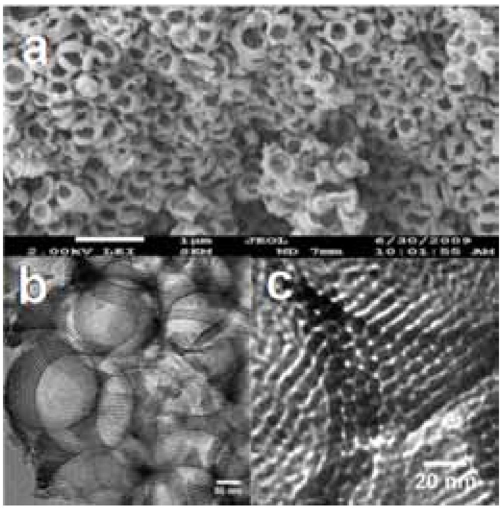

Figure 1. (a) SEM and (b, c) low and high magnification TEM images for hierarchical macro-mesoporous SiO_2.

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Delamiated zeolites as support of active metals for the preparation of highly active and selective catalysts for hydrogen production

Antonio Chica Lara
Instituto de Tecnología Química UPV-CSIC, Valencia

Hydrogen production by catalytic steam reforming of bioethanol highly depends on the type of metal catalyst, preparation methods, type of support, and operating conditions. Support plays an important role since it helps in the dispersion of metal catalyst and enhances its activity via metal-support interactions. The singular structure of delaminated zeolites, and particularly the very high and well-defined external surface area, makes these materials attractive to be used as supports for dispersing active metal phases. We have explored the activity, selectivity, and stability of Co metal particles supported over delaminated zeolites (ITQ-2 and ITQ-6) in the steam reforming of bioethanol. The characterization of these materials by DRX, BET area, TPR, SEM and TEM, has allowed to establish interesting relationship between their catalytic and physico-chemical properties.

Solid metal catalysts for new cascade type transformations of biomass-derived compounds

Marcelo E. Domine
Instituto de Tecnología Química (ITQ – CSIC), Universidad Politécnica de Valencia

A wide range of renewable raw materials can be easily obtained from ligno-cellulosic biomass in both polymeric (i.e. cellulose, starch, lignin) and monomeric (i.e. sugars, polyols, phenols) forms [1]. These bio-based platform compounds could be converted in a large variety of chemical products (specialty and fine chemicals) to replace non-renewable fossil raw materials (oil, coal, natural gas) [1-3]. Up to now, the bio-based products are more eco-friendly than the fossil-derived ones, but also more expensive due to the lack of practical and efficient synthetic processes. Thus, the development of new catalytic processes to competitively and efficiently produce these biomass-derived chemicals is largely needed. In this sense, bio-based platform compounds, such as sugars, polyols, furfural, succinic acid, among others, can be transformed into valuable chemicals via new eco-friendly processes in which the number of steps in synthesis are reduced by performing cascade type catalytic reactions. To accomplish this target, the development of new multi-functional (or multi-component) catalytic materials becomes a key point, bridging the gap between two or more reaction steps and "one-pot" synthesis [4-6].

In this presentation, the development of multi-functional catalysts to afford some challenging cascade type transformations for bio-based platform chemicals valorisation will be described. In this sense, the direct and selective reductive amination of alcohols and/or ketones [7] is a well known process that offers the opportunity to produce substituted amines and N-heterocycles starting from bio-based compounds (i.e. glycerol, 1,2-propanodiol). In order to selectively perform the consecutive oxidation-condensation-reduction steps of this process under mild reaction conditions the development of Me-based materials combining redox and acid/base properties becomes crucial [8,9]. Herein, the synthesis of Pd and Pt nanoparticles supported on amorphous metal oxides (i.e. γ-Al_2O_3), Beta zeolite, and MCM-41 mesoporous materials will be reported, as well as their catalytic performance in reductive amination processes of ketones and alcohols always comparing with commercial catalysts. The influence of the metal type, as well as the structural and functional properties of the catalysts will be described. Additionally, the possibilities offered by these Me-based solid materials as efficient catalysts for other interesting biomass-derived transformations will also be stated.

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Sustainable catalysis at the interface between chemistry and biology

Fernando López-Gallego
Instituto de Catálisis y Petroleoquímica (CSIC), Madrid

Waste production is one of the main issues of the current synthetic chemistry that must be addressed. This problem is even more dramatic at Pharmaceutical industry, being the industrial segment with highest E factors (25->100). Biocatalysis has been revealed as one of the most effective solutions to afford more environmental friendly and economically pharmaceutical synthetic processes (1). This is a consequence of the intrinsic features of enzymes like their performance in aqueous media at mild reaction conditions, their high chemio-, regio- and stero- selectivities and their biodegradability. However, all these excellent properties have been naturally evolved to accomplish physiological necessities which are often quite far of the requirements for an industrial chemical process. In order to take advantages of the enormous potential of enzymes as catalyst, their low stability in non biological media, their low range of substrates and their low activity towards non natural substrate must be addressed to circumvent their limited industrial application. Since the last twenty years, genetic engineering has been a powerful tool to make enzymes much more active and promiscuous for non natural substrates. However, both rational design and random mutagenesis do not sometimes achieve the level of enzymatic feature desired. Since the last two year we have been pursuing a synergy between protein engineering and organic chemistry to expand chemical diversity on aminoacid side chains to tailor-made shape the substrate bindings pockets of enzyme2. We have customized the enzyme active centers with exogenous synthetic groups easing the binding of non natural substrates that would not be bound at the biologically designed active site. Several thiol-containing synthetic groups were tethered at different positions of the binding pocket of lipase (2) from Bacillus thermocathenolatus (BTL2). We call these new synthetic groups "binding modifier groups (BMG)" because their special properties would directly affect to the substrate binding, altering both enzyme activity and selectivity towards non natural substrates. We have demonstrated how those groups modify the interfacial activation mechanism that is clue for substrate binding. Moreover, the nature of the BMGs has directly impacted on the final chemo-enzyme performance, resulting in catalysts with different selectivities and/or activities towards different non natural substrates regarding to the non-modified enzyme.

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Well-defined metal systems for true click chemistry

Silvia Díez-González
Department of Chemistry, Imperial College London

Since the discovery of copper(I) species as remarkable catalysts for the [3+2] cycloaddition reaction of alkynes and azides, this transformation has become the most prominent Click reaction[1] to date and found a plethora of applications.[2] Despite its incontestable success, little efforts have focused on developing novel and more efficient catalytic systems for this transformation. Herein, our latest results on well-defined complexes for this cycloaddition reaction, including the reaction of internal alkynes in this context under Click conditions.

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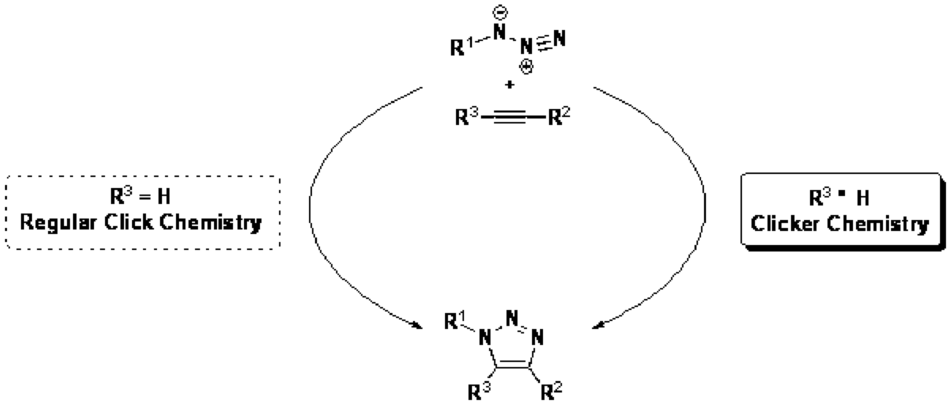


Designer nanomaterials for the production of high added value chemicals and biofuels

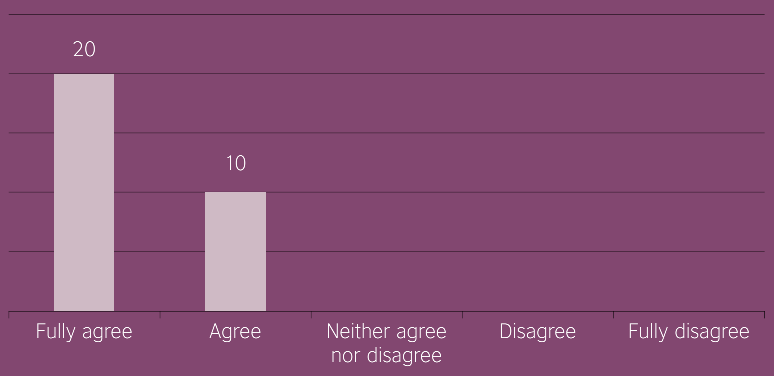
Rafael Luque
Departamento de Química Orgánica, Universidad de Córdoba

Nanomaterials are regarded as a major step forward to achieving the miniaturisation and nanoscaling effects and properties that have been utilised by nature for millions of years. Such materials are receiving extensive attention across a broad range of research disciplines. Among them, the fusion between nanoparticles and nanoporous materials technology represents one of the most interesting of these rapidly expanding areas. The harnessing of nanoscale activity and selectivity, potentially provides extremely efficient catalytic materials for the production of commodity chemicals, and energy needed for a future sustainable society. In this chapter, the aim is to present an introduction to the field of designer nanomaterials, primarily focused on supported metal nanoparticles (SMNPs) on porous materials, in view of their applications for the production high value-added chemicals and biofuels.

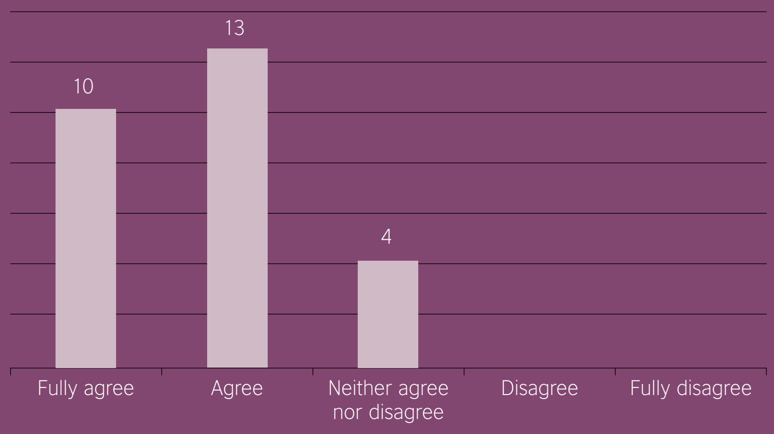
Keywords: *nanomaterials, supported metal nanoparticles, biofuels, fine chemicals*

EVALUATION QUESTIONNAIRE

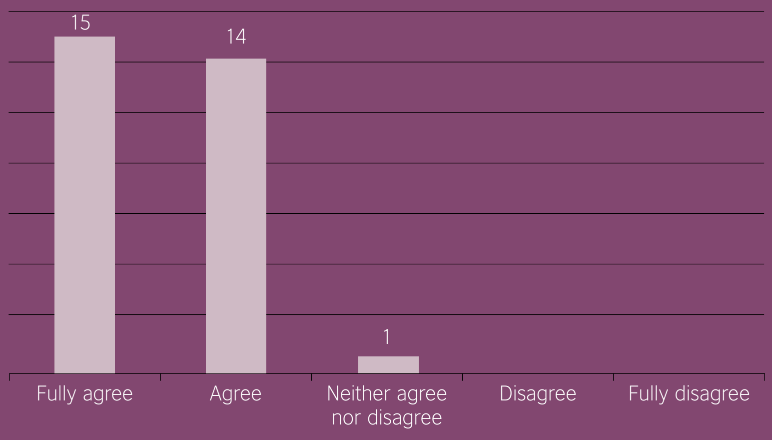
1. It was a well balanced programme



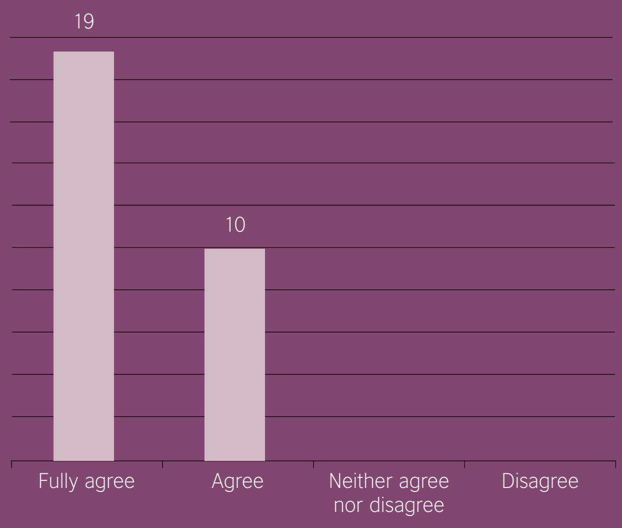
2. The discussion timing was right



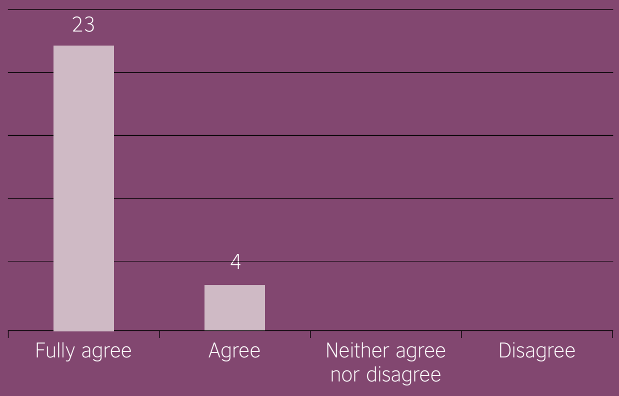
3. The length of the seminar was correct



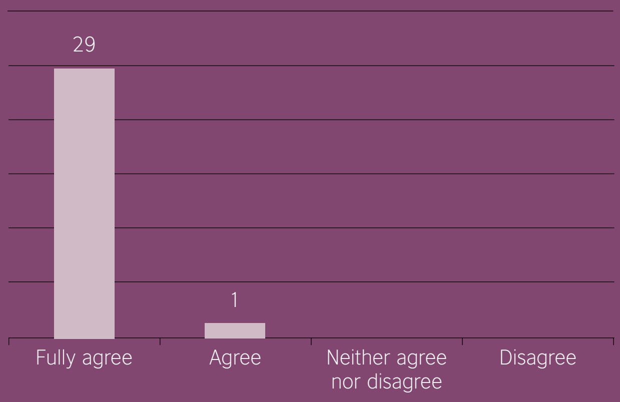
4. The mix of participants was right



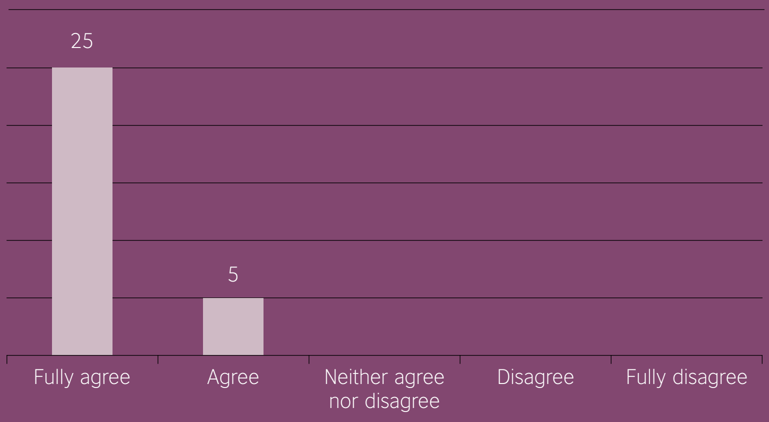
5. The conference facilities were good



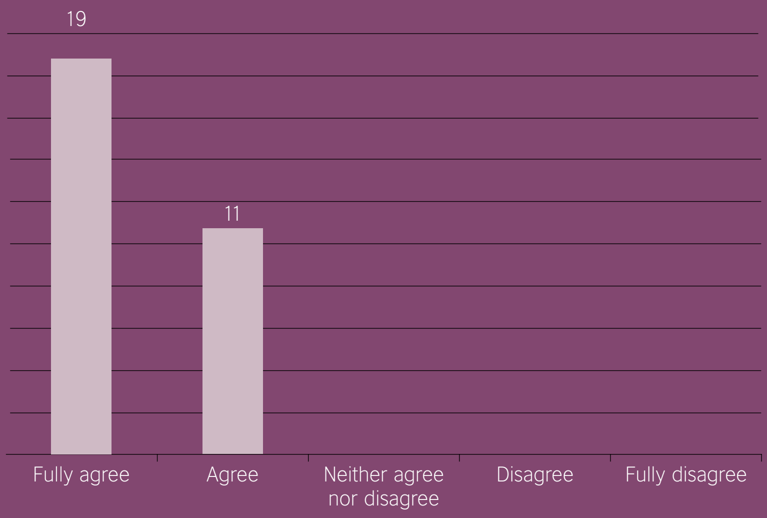
6. The standard of accommodation was good



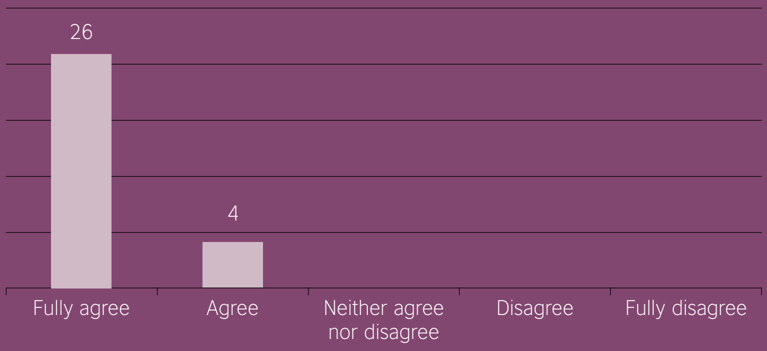
7. The food was good



8. The seminar meet my expectations?



9. Overall, this was a high quality seminar



10. Overall, how would you rate the quality of our services?

Results of Event Evaluation Questionnaires

General data

Number of participants	33
Number of questionnaires received	30
Percentage	90%

GENERAL COMMENTS

Very high scientific level, excellent organisation. (Jaume Cot)

A really interesting and inspiring workshop and I enjoyed discussing a lot of science. (Simon Collinson)

It was an excellent meeting and I think we all thoroughly enjoyed it. (Andy Abbott)

It was all fantastic (Eduardo García-Suárez)

A great conference and very well organised (Andrew Hunt)

The meeting was brilliant!! (Rafael Luque)

A great opportunity both at a personal and professional level.
(Olga Guerrero)

A very enjoyable conference. (Michael North)

A high quality meeting. (Ángeles Manresa)

A great workshop, I really enjoyed it, both the science and the social side, it was great to meet so many new people. (Richard Wells)

ACKNOWLEDGEMENTS

We would like to thank the Consejo Superior de Investigaciones Científicas and the British Council for organizing this excellent and thoroughly enjoyable scientific meeting. The event has provided a great deal of opportunities for dialogue and discussion whilst demonstrating the strength of our young scientists. Furthermore, we are especially indebted to Belén Fortea of the British Council for her very important contribution to the success of the workshop. Belen's friendliness, good humour and social skills alongside her efficiency and hard work have helped create a wonderful environment in Ávila.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Paseo del General Martínez Campos, 31
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Calle Serrano, 117
28006 Madrid. Spain

www.britishcouncil.es

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