Green Chemistry—one year on

As *Green Chemistry* enters its second year we can look back on the successful launch of this new journal. The timing for this venture appears to have been just right, since in 1999 there have been numerous international conferences devoted to the topic. This has generated considerable discussion with regard to what green chemistry embodies and even whether, or not, the name itself is appropriate.

Although it is not easy to succinctly describe what green chemistry encompasses, the following is a reasonable working definition:


Professor Roger Sheldon

> *Green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.*

Green chemistry eliminates waste at source, *i.e.* it is primary pollution prevention. Waste remediation (end-of-pipe solutions) may be very useful and necessary, particularly for the short-term, but it does not constitute green chemistry.

Industry appears to prefer the terms *sustainability* or *sustainable development*, defined as development that meets the needs of the present, without compromising the ability of future generations to meet their needs. The word ‘green’ apparently has too many political associations in many countries. This is a pity because green chemistry is probably more meaningful to the general public. Moreover, perhaps the two terms are not mutually exclusive: sustainability is the goal and green chemistry is the means to achieve it.

Green chemistry embodies two components. One is concerned with efficient utilisation of raw materials and the elimination of waste. The other focuses on the health and safety aspects of chemical manufacturing. The two aspects were admirably illustrated by Guy Ourisson, President of the French Academy of Sciences and doyen of synthetic organic chemistry, in his opening address at a conference entitled “Clean Processes and the Environment: The Catalytic Solution”, which was held in Lyon from 6-8 December 1999. He invoked the terms black chemistry and red chemistry to describe these two shortcomings of many traditional processes. Black chemistry stands for waste = pollution and conjures up images of the industrial revolution, black smoking chimneys and Blake's "dark satanic mills". Red chemistry, on the other hand, denotes danger and evokes associations with incidents such as Bhopal and Seveso. Many chemical processes in use today are black or red, or both. Hence, the goal of the chemical industry is, or should be, the replacement of red and/or black chemistry with green alternatives.

Ourisson suggested that the following chemicals should, in addition to the desired product, be allowed to leave a chemical plant: O_2, N_2, H_2O (potable), NaCl and $CaCO_3$ (and, presumably CO_2). It is worth noting, however, that a salt such as NaCl, although quite innocuous, can be a problem depending on the scale. If 10 kg of NaCl is produced per kg of product this is not likely to be a problem in the production of ten tons per annum of a pharmaceutical. The concomitant production, however, of one million tons of NaCl with 100,000 tons of a bulk chemical is a different matter.

Subsequent lectures at the conference in Lyon generated considerable discussion with regard to what does and does not fall within the scope of green chemistry. This was perfectly illustrated by two back-to-back lectures on phosgene chemistry and dimethyl carbonate, presented by J. P. Senet (SNPE) and F. Rivetti (Enichem), respectively. In the production of polycarbonates, for example, phosgene is reacted with bisphenol A and NaOH to give a polycarbonate and NaCl. If the latter is recycled, *via* electrolysis to NaOH and Cl_2, and the Cl_2 is used to regenerate $COCl_2$, then the process is in principle waste-free. Is this green chemistry? Not really. Even if we stretch our definition of primary pollution prevention to include recycling (always better than remediation), phosgene chemistry remains red. However, phosgene can be converted to 1,1-dichloromethyl ether (Chloromyl®), by reaction with methylformate. If a pharmaceutical company uses Chloromyl® as a non-hazardous phosgene substitute is this green rather than red chemistry? The answer obviously depends on the vantage point from which we are looking.

Most people would agree that the use of dimethyl carbonate as a phosgene substitute constitutes a greener solution. Dimethyl carbonate is produced by catalytic carbonylation of methanol and is a non-toxic substitute for phosgene and dimethyl sulfate in carbonylations and methylations, respectively. Moreover, no salt is produced; the co-products are methanol and CO_2 and the former can be recycled. But does recycling of methanol and emission of CO_2 better qualify as primary pollution prevention than recycling of NaCl? Well, for one thing methanol is a lot easier to recycle and recycling of NaCl is only viable on a very large scale. And is carbon monoxide green, red or possibly pink?

These examples illustrate that it is neither simple nor clearcut to define what is or is not green. The problem is that black, red and green are relative rather than absolute descriptors. What is needed, as was noted in a lecture by M. Misono, is a semi-quantitative measure of the greenness of a process, that is the environmental impact based on energy and raw materials consumption, waste generation and health and safety aspects. This is easier said than done.

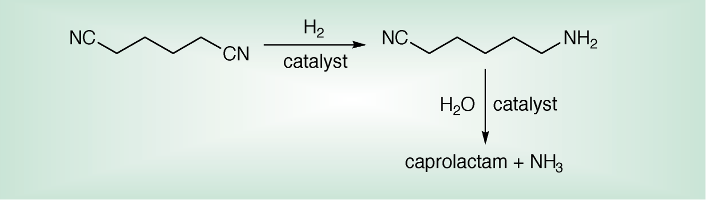
As reflected in the title of the conference, the solution to replacing black and/or red chemistry with green alternatives is often a catalytic one. This and other issues within the context of clean processes and the environment were underlying themes in the lectures and poster sessions:

- selective catalytic organic chemistry
- waste minimisation by selective catalysis and waste treatment
- enhanced atom utilisation
- replacement of stoichiometric or hazardous reagents by use of homogeneous or heterogeneous catalysis
- new trends in polymerisation and depolymerisation
- new solvents and reaction media
- alternative feedstocks

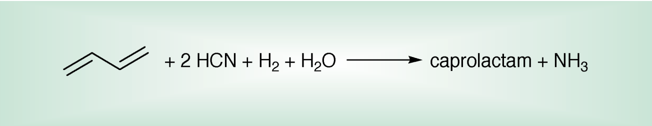
Apart from the words “waste treatment” this looks very much like a list of topics suitable for publication in *Green Chemistry*.

One of the highlights of the conference was the lecture by J. P. Brunelle of Rhodia, on a new eco-friendly caprolactam process, in the session on enhanced atom utilisation. Caprolactam (CPL) is mainly produced from cyclohexanone *via* oximation and Beckmann rearrangement of the oxime, a process that generates *ca.* 4.5 kg of ammonium sulfate per kg of CPL (*E* factor = 4.5). Rhodia’s objectives were ambitious: a new process that was salt-free, had lower costs than the existing process, gave CPL of high quality and was ready for commercialization in 2000.

To cut a long story short, they rapidly concluded that it would not be possible to achieve these objectives via a cyclohexanone oxime-based route. An evaluation of different routes led to the following choice:



The key to success was the development of a highly efficient (>99.5% selectivity at >99% conversion) hydrolysis/cyclization of the intermediate aminonitrile to CPL and NH_3 over an alumina catalyst in the vapour phase at 300 °C. The ammonia is not produced as a salt and can be re-used. The raw material, adiponitrile, is produced by DuPont *via* catalytic hydrocyanation of butadiene, giving an overall stoichiometry:



The process meets the objectives set by Rhodia. It is salt-free, lower cost and quality approval was achieved on a 60-ton scale in 1999. The current goal is a 100,000 ton plant in Europe in 2003.

A truly elegant example of high atom utilisation thanks to catalysis. This is surely the quintessence of green chemistry. But what about HCN? Does its use not constitute red chemistry? Here again it depends on your vantage point. From the viewpoint of Rhodia the process is green, as the starting material is adiponitrile. If one looks further upstream, however, the process begins to take on a red tinge. The situation is similar to the phosgene/Chloromyl® story (see above).

Alternative processes based on catalytic carbonylation would, in principle, be greener since CO is less red (and less expensive) than HCN. For the quintessential green route to caprolactam what about a cost-effective, glucose (biomass)-based route? Perhaps this is a challenging goal for the new millennium.

And so it goes. The discussion of technological and social aspects of green chemistry continues on a broad basis and *Green Chemistry* is an ideal forum for this discussion. A happy and green new year to all our readers.

Roger Sheldon (Chairman, *Green Chemistry* Editorial Board)
Delft University of Technology
The Netherlands

A novel continuous reactor for UV irradiated reactions

Bill Dunk and Roshan Jachuck from Newcastle University, UK, describe how use of a spinning disc reactor allows bulk polymerisations under UV irradiation

The reduction of organic solvent use in several industries is a topic of great concern to environmentalists, and throughout the world efforts are being made to bring about drastic reductions in their use. In the chemical industry an important advance in this direction would be the introduction of means whereby many of the reactions currently conducted in solvents could be conducted at, or near to, 100% reactant concentration.

In the synthetic polymer industry the free-radical mechanism is favoured for the preparation of addition polymers, since the robust nature of the reaction lends itself to a variety of reaction conditions. However the properties of most monomers having commercial importance require that their polymerisation be carried out at relatively low concentrations, very often in organic solvent solution. High heats of polymerisation combined with rapid rates of propagation dictate against the use of 100% monomer unless bulky and complex installations are available. The patent literature contains numerous disclosures of plant for bulk polymerisation, but only methyl methacrylate and styrene have been polymerised in this way, in the liquid phase, on an industrial scale. Multi-unit tubular reactors and heat exchange zones that utilise heat exchange fluids are typical for these monomers, whilst a variety of other systems, *e.g.* conveyor belts or hollow shafts[1] have been disclosed for a wider range of polymerisation procedures. None of these approaches seem to have reached industrial realisation.

Only in recent years has any concerted effort been expended to reduce the scale of chemical plant, not only for conventional chemical reactions, but also for polymerisation. At Newcastle University the process Intensification and Innovation Centre (PIIC) has been at the forefront of such endeavours, and amongst several novel reactor designs and concepts, has introduced spinning disc technology to both organic and polymer synthesis. A very recent development, in which a spinning disc reactor (SDR) has been applied to the bulk polmerisation of ethylenically unsaturated monomers using UV radiation initiation, has been pioneered by Dr Bill Dunk and Dr Roshan Jachuck who believe that the procedure has great potential for processes based on green chemistry.

Figure 1. Spinning disc reactor.

The spinning disc reactor, which can be seen in Figure 1, produces thin highly sheared films. It has been shown that the hydrodynamics of such films encourages high heat and mass transfer rates whilst providing excellent mixing (Figure 2). The centrifugal force created by the rotation of the reactor surface is used to produce very thin sustainable films of 100–300 μm. As the film is thin it is possible to maintain good and uniform penetration of UV radiation. The reactor studied and developed is 180 mm in diameter and has the ability to produce approximately 40 kg h^{-1} of polymer on a continuous mode. Currently even smaller reactors are being developed for laboratory-scale studies. Since the reactor has very good heat transfer characteristics it is particularly suitable for performing fast exothermic reactions.

The use of photoinitiation was chosen for a number of reasons, not least the wide temperature range available for effective initiation. In addition there were other advantages:

- Novelty. Little progress has been made in the use of photochemistry for the synthesis of linear, high-molecular-weight polymers.

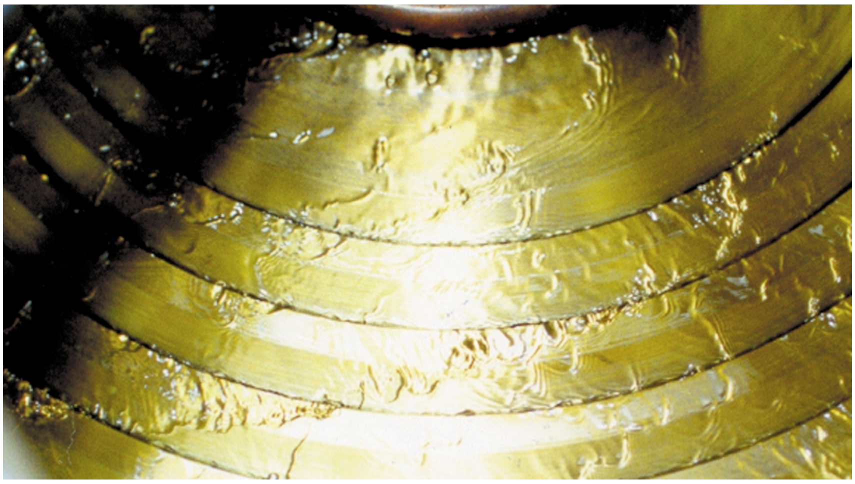


Figure 2. View of the surface waves in a spinning disc reactor.

- Control of polymerisation, since the free-radical initiator could only give initiating species when the UV lamp was turned on.

- The zero activation energy for the free-radical initiator decomposition means that there would be little effect of temperature on the rate of polymerisation.

- Rapid rate of initiation under SDR conditions would be expected to be comparable to rate of propagation, thus polydispersity of the formed polymer should be low.

We may remark that the use of UV radiation in polymerisation chemistry is far from new, Hoffmann having reported the formation of a glassy solid when styrene was exposed to sunlight (1849), whilst as long ago as 1912 Ciamician[2] foresaw possible applications of photochemistry in industry. However in 1927 IG Farbenindustrie rejected the suggestion that sunlight be used to polymerise vinyl acetate on the ground that “there would not be sufficient sunlight and they could only operate on a small scale with other light sources”.[3] Little progress was made in this direction and some 35 years later we read of a photo-polymerisation of isopropyl acrylate on a 500 ml scale which required four identical UV lamps positioned around the reactor.[4] Subsequently patents appeared,[5] disclosing conveyor belts moving under banks of UV lamps, but problems of plant size and homogeneity of light source have hindered exploitation of these procedures.

For the purposes of exploiting the advantages, of excellent micro mixing, short residence times and effective heat exchange that are features of the spinning disc reactor, the use of photo-initiation seemed most attractive, particularly as polymerisations could be conducted at or near to ambient temperatures. The monomer chosen was *n*-butyl acrylate which is transparent to the radiation to be used, with a heat of polymerisation of 77.4 kJ mol^{-1} and a rate coefficient for propagation of 16300 l mol^{-1} s^{-1} at 30 °C. Benzoin methyl ether or dimethoxyphenyl acetophenone were used as photoinitiators, the latter proving more effective, at a UV wavelength of 365 nm. Polymerisations were carried out with nitrogen purged monomers in the temperature range 30–60 °C. As a control static film polmerisations were conducted under similar conditions.

The results of the experiments indicated that there is a definite potential for adaptation to photo-initiated polymerisations. A particular observation concerning polymer micro structure was that even at 66% conversion there were no signs, by NMR, of any branching. As is well known this is a common feature in conventionally prepared poly(*n*-butyl acrylate). As a result of these results it is hoped to develop a predictive model for this polymerisation procedure, and extend investigations to other monomers and other polymerisation mechanisms, *e.g.* cationic.

We believe that the characteristic features of the SDR which have been described earlier in this article have proved to be of importance in the performance of UV-initiated polymerisation reactions. However the enhanced degree of mixing at the molecular level (micro-mixing) should lead to improvements in reaction times and efficiencies of currently utilised photochemical reactions, even where production costs are already reduced by using photoreactions, *e.g.* the synthesis of caprolactam for nylon-6 production. The synthesis of vitamin D components by application of the photo-Cope reaction might benefit from the use of SDR characteristics, as may other organic reactions that involve UV-irradiated steps, *e.g.* Rose oxide from citronellol.

In any photochemical reaction that involves appreciable conversion of reactants to products it is very likely that the absorbance of the system will change significantly as the reaction proceeds, consequently the validity of the Beer–Lambert Law is in question since the presence of a time-dependent concentration gradients do not allow one to assume the law to be valid. The thin film regime on the spinning disc may well reduce these problems.

The use of UV radiation in the sterilisation of water represents an area of technology where increased efficiency may be achieved where the water is present in a thin film. A similar area of water treatment makes use of semiconductor photocatalysts (R)[6] for the removal, by oxidation or reduction, of trace toxic chemicals, *e.g.* phenol or chlorinated solvents present in industrial water effluents. The economic viability of slurry reactors has been questioned for such use, and although some progress has been reported by the use of fixed bed catalysts (R),[7] low surface area to volume ratios and inefficiency due to absorption and scattering of the applied radiation by the reaction medium seem to be limiting factors in their adoption. Conditions on a spinning disc should reduce these drawbacks considerably, perhaps using immobilised semiconductor catalysts.

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Since retiring from Courtaulds Coatings **Bill Dunk** (Tel. +44 (0)191 222 5206) has collaborated with the Process Intensification & Innovation Centre (PIIC) at Newcastle University, UK, to develop polymerisation techniques for use in novel reactors, with special reference to photo-initiation. **Roshan Jachuck** (r.j.j.jachuck @ncl.ac.uk; Tel. +44 (0)191 222 5202), a Lecturer in the Department of Chemical & Process Engineering at Newcastle University, is involved in promoting the concepts of Process Intensification through his involvement with PIIC.

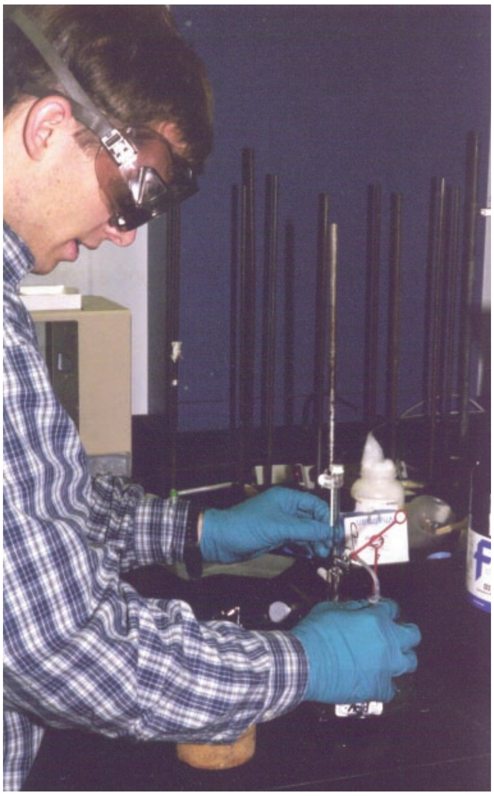
University of Oregon Green Chemistry Laboratory

Professors Jim Hutchison (left) and Ken Doxsee (right), developers of the green organic chemistry curriculum at the University of Oregon, USA.

A new teaching laboratory which focuses on reducing waste and chemical hazards in organic chemistry has been opened at the University of Oregon, USA. Professors Jim Hutchison and Ken Doxsee have developed the "green" organic chemistry curriculum over the last few years. Their experiments teach the same principles as a traditional organic laboratory, but use solvents and reagents that are less toxic, and teach students to consider the environmental cost of the chemistry they are learning. Students learn how to evaluate potential hazards of chemical processes, and suggest creative ways to minimise their human and environmental impact.

Students substitute less-toxic solvents and reagents, and minimise waste by recycling the products into future experiments. One experiment, soon to be published in *Journal of Chemical Education*, teaches students how to synthesise adipic acid, a chemical used to make nylon. Typically, nitric acid is used as the oxidant. An unfortunate byproduct of the experiment is nitrous oxide, a chemical that contributes to ozone depletion and global warming. Instead, students substitute hydrogen peroxide and a simple catalyst, significantly reducing the hazard.

Because green chemistry focuses on using environmentally benign chemicals, students can perform experiments using the larger quantities typical of industrial and research settings; hence green chemistry allows the student to move closer to reality in their chemical experiments. Professor Hutchison believes that the new laboratory will prepare students to contribute environmentally responsible solutions to chemical problems in their future careers. "They will act," he says, "as green ambassadors when they enter the job market". Many companies are now focusing attention on green considerations as they struggle to keep abreast of regulations and satisfy environmentally aware consumers and investors; examples include Intel, 3M and DuPont, who are all seeking to phase out harmful chemicals, reduce water consumption, reduce waste generation, *etc.*



Student working in the green chemistry laboratory at the University of Oregon, USA.

To further promote green chemical education, Professor Hutchison hopes to see the University of Oregon become a national centre for green chemical education, where educators from colleges, universities and high schools learn green methods and curriculi to take back to their schools and laboratories.

For further information contact Lynde Ritzow, Graduate Recruiting Coordinator, Chemistry Department, 1253 University of Oregon, Eugene OR 97404-1253, USA. Email lynde@oregon.uoregon.edu

Sustainable development report

A report has been presented by UNICE, the union of industrial and employers' confederations of Europe, called Agenda for Promoting Sustainability, to the EU environment commissioner and the president of the European environment council. In the report European businesses reiterate their commitment towards taking a growing role in promoting sustainable development. Commissioners are to receive a paper containing more focused suggestions in the near future, once UNICE's directors give approval. According to UNICE, sustainable development is only possible through the integration of environmental, economic and social policies and urges clearly defined European environmental objectives involving both producers and consumers. Its recommended approach is for more scope for companies' own environmental initiatives, more emphasis on partnership agreements, and more cost-effective legislation (http://www.unice.org).

Power plants from short-rotation coppice

Several UK companies are building new power plants utilising renewable energy resources such as short-rotation coppice. RRBRE is building the first at Eggborough, Yorkshire, to be completed in March 2000, to produce 10 MW of electricity from wood chips, 75% from short-rotation coppice grown on 2000 ha within 40 miles of the plant. Others include Border Biofuels whose Carlisle plant, producing 20 MW in the first phase and a further 10 MW in the second, is due to start up in spring 2002; plans for a second plant at Newbridge on Wye await planning permission. Ambient Energy plans to open 5.5 MW plants at Eye, Suffolk, and at Cricklade, Wiltshire, by June 2001.

Green Chemistry in Japan

Japan will launch an Alliance for Green and Sustainable Chemistry in spring 2000. This will include a new centre for a Green/Sustainable Chemistry Network. There will be a strong emphasis on international collaboration.

These initiatives follow from the workshops on green chemistry in Tokyo held in November 1999, along with a survey of the news of academic and industrial chemists. The workshop involved 67 invited delegates from academia, industry and other interested organisations.

The survey on green chemistry revealed a number of interesting points:

- 71% recognised the term "green chemistry"
- the majority of respondents believe that the major driver towards the greening of chemical processes is societal
- 11 key areas of development were identified, including alternative reagents and renewable feedstocks

The importance of recognising the declining public image of chemistry was also highlighted by another survey among 5th grade elementary schoolchildren. This revealed that while the majority (57%) believed that science and technology improved their quality of life, a majority (53%) also believed that science and technology cause many problems for society. A major initiative to promote chemistry at school level, "Dream Chemistry 21" (Chemistry will make our dreams come true in the 21st Century), is now running with sponsorship from several organisations.

EU to clamp down on hormone-mimicking chemicals

The EU has pledged to clamp down on a group of chemicals believed to damage both animal and human health by mimicking the effects of hormones in the body. So-called endocrine disruptors have been linked to a range of health problems in animals, including the development in fish of both male and female reproductive organs. They have also been linked to hormone-related cancers, lowered sperm counts and birth defects in humans. Some of the chemicals suspected of having these effects include those used in certain paints and in some pesticides, as well as the phthalates used to soften plastics.

Environment Agency joins forces with Fire Service

A new partnership has been formed in the UK between the Environment Agency, the Fire Service and Local Authorities. This will ensure that all fire-fighters are properly trained and equipped to reduce the environmental impact of an accident before Environment Agency officers are able to attend to provide technical support and assistance. The early actions of fire-fighters at a pollution incident are very important and can significantly limit the environmental impact of many incidents such as fires and road traffic accidents. (*Environment News Service*, December 1999).

Centre of excellence for the UK chemical industry

A major boost for Britain's largest export industry was launched on 19 October 1999 by Yorkshire Forward. The Chemical Industries Regional Centre of Excellence (CIRCE) is a unique facility within the UK provided to help new and established businesses and universities. The £3M facility has been built beside Hickson & Welch's site in Wheldon Road, Castleford, but will operate independently to encourage innovation and improve the business performance of companies in the chemical and related sectors. It has been funded by a £685,000 grant from the Department for Education and Employment's Centre of Excellence Fund and £665,000 from European Regional Development Funds. Hickson has also donated a building. Although the public funding is earmarked for small and medium enterprises within the Yorkshire & Humberside Region, CIRCE can also carry out work for clients based across the UK. The opening of the centre marked a major milestone in offering help to Britain's chemicals industry which has an annual trade surplus of £4 bn. In Yorkshire & Humberside it employs more than 30,000 people, about 11% of the UK total. CIRCE offers an independent testing and analysis service to businesses throughout the UK. This includes chemical analysis including method development, process safety testing and environmental impact testing. A broad range of training courses focused towards the chemical industry is also being offered. In addition, the centre has available specialist business incubation units for small chemical companies, including startup and spinoff companies. Competition from developing countries has increased the need to modify, develop and manufacture high quality products faster and more cheaply. CIRCE will concentrate on enhancing the technical skills of those already in the industry, help attract new business and retain graduates by providing unparalleled opportunities for training, research and development (E-mail: keith.crane@yorkshire-forward.com).

Sustainable chemistry in Europe

The European Chemical Industry Federation, CEFIC, organised a symposium on Sustainable Chemistry as part of its 10th Sustech meeting in Brussels in December 1999 (http://www.cefic.be/sustech/sustech10/programme.htm). The symposium included presentations about the sustainable and green chemistry activities in the US and Japan (given by Nhan

Nguyen and Masao Kitajima respectively) as well as an overview of green chemistry and its importance to chemistry and the chemical industry (James Clark). It was interesting to note the similarities in the various initiatives around the globe and common goals that were shared, notably the drive towards more environmentally friendly products and processes and the recognition of the need to improve the image of chemistry and to attract more able young people into the area. The meeting also included a poster session largely designed to promote technology transfer.

The Japanese initiative is relatively new. Their "New Sunshine Project" will focus on key areas including carbon dioxide fixation, catalysis, biodegradation and supercritical fluids. It is based on an alliance between industry, government and academe.

The plans for a European Green and Sustainable Chemistry award scheme were described by Allan Astrup. Plans are at an advanced stage and involve the Green Chemistry Network who are likely to be involved in administering the awards.

David Bricknell highlighted the concerns of the European industry. These included the word "green" and ill-defined labelling which can promote one product as being greener than others. He also stated the view that the industry was already heading down the road towards sustainability and did not need outside intervention to drive this.

Further information on the Sustech programme can be found on http://www.cefic.org/sustech.

Non-food crops

…the new Food Chain and Crops for Industry Foresight panel has set up 6 task forces, including "Unlocking the potential of industrial crops". For more information contact David Rawlins on (0171) 215 6703.

…the House of Lords Select Committee Report on Non-Food Crops (NFCs) was published on 9 December 1999. The main points in the report were:

- NFCs have significant potential to make an impact both on sustainable land use and economic activity, particularly those intended for use in energy production or as sources for fibres in biocomposites.
- NFCs used for the production of speciality chemicals, notably pharmaceuticals, are also likely to become increasingly economically viable, although this will depend greatly on quality and the development of new processing techniques.
- The use of genetic modification techniques increases the number of potential applications for non-food crops. However, it is important to continue to address potential environmental concerns during the development of such crops.
- Few incentives, either from taxation or subsidies, promote long-term development of potentially important non-food crops.

The Committee recommended increased co-ordination and availability of research funding in order to take advantage of a rapidly developing area.

…ACTIN is organising a seminar 'Industrial uses of wheat' on 22 March 2000 at Chilford Halls near Cambridge, UK. The subjects to be discussed include:

- thermo-mechanical pulping of wheat straw
- packaging materials from wheat flour
- wheat straw in construction materials

On the preceding day, 21 March 2000, ACTIN is also organising a workshop for all those interested in the LINK Programme 'Competitive Industrial Materials from Non-Food Crops' (CIMNFC); this workshop will comprise a number of papers followed by discussion on the topic of Extraction Technologies.

For further information contact Ms. Saija Nakari at the ACTIN Help Desk (Tel. +44 (0)1372 802054; email info@actin.co.uk)

"The UK a long way from sustainability"

An environmental think tank, Forum for the Future (founded by three prominent environmental activists Paul Ekins, Sara Parkin and Jonathon Porritt) has published a report entitled "Estimating Sustainability Gaps in the UK." The gaps identified include:

- air pollution—where the report says emissions of CO_2, SO_2 and NO_x continue at unsustainable levels. It estimates that on current trends it will take 126 years for the UK's emissions to reach sustainability.
- water pollution—where abstraction is a number of areas is above sustainable levels, and, for a number of pollutants, quality standards for surface waters are still being exceeded.
- generation and disposal of waste—where the gap between the current situation and the various policy targets that have been adopted is substantial, and in some cases growing.

The report, written by Paul Ekins and Sandrine Simon from the Department of Environmental Social Sciences at Keele University, criticises the UK Government's own sustainable development indicators which, although welcome in themselves, fail to identify sustainability standards and UK environmental performance in relation to them. For more information see http://www.forumforthefuture.org.uk/

UK Government's Chemicals Strategy paper

On 16 December 1999 the Department of Environment, Transport & the Regions (DETR) published its Chemicals Strategy paper following its consultation document "Sustainable Production and Use of Chemicals" (*Green Chemistry*, **1**, G47). The main goals of the strategy are to:

- make full information publicly available about the environmental risks of chemicals
- continue reduction of risks presented by chemicals to the environment and human health—while maintaining the competitiveness of industry
- phase out early those chemicals identified as representing an unacceptable risk to the environment

The Strategy proposes measures to speed up assessment of the environmental risks posed by chemicals. The Strategy also proposes that a Stakeholder Forum with representatives of all those groups with an interest in chemicals should be set up to help build consensus on future policy on chemicals and the environment. For more information on the Strategy consult http://www.environment.detr.gov.uk/chemistrat/

The UK Chemical Industries Association (CIA) has welcomed the publication of the strategy paper by the DETR, endorsing the goal of sustainable development and welcoming the manner in which the industry's Confidence in Chemicals initiative has been recognised. However, the CIA states that the targets set out in the paper are challenging and it intends to work with its member companies and government to ensure it delivers its commitments on a voluntary basis.

Appeal for pesticide reduction

In an open letter addressed to European Environment Commissioner Margot Wallstrom on 28 October 1999, the Pesticide Action Network Europe (PAN Europe) criticises the EU for failing in its commitment to substantially reduce chemical pesticide use throughout Europe by the year 2000, despite heightened consumer anxiety over food production methods. Around 300,000 tonnes of pesticide active ingredients are released into the European environment each year. The EU's Fifth Environmental Action Programme had promised a significant shift from pesticide dependence towards sustainable pest control methods. Two months before the programme expires, nothing at all has been achieved. Some EU countries, such as the Netherlands, Sweden, Denmark and Finland, have recognised the urgency of the situation by adopting their own successful pesticide reduction programmes. PAN Europe is asking the rest of the EU to follow their lead.

CIA welcomes Government paper on chemicals management

The UK Chemical Industries Association (CIA) has welcomed the UK Government's strategy paper on chemicals management issued on December 16, 1999 by the Department of the Environment, Transport and the Regions (DETR); it is entitled "Sustainable Production and Use of Chemicals. A Strategic Approach. The Government's Chemical Strategy". The paper's goal is sustainable development which is welcomed by the CIA, although it is also seen as being challenging. The CIA intends to work with member companies and the government to ensure it delivers its commitments on a voluntary basis. The paper represents a new approach from the UK Government which recognises stakeholder involvement, and can be viewed at http://www.environment.detr.gov.uk/sustainable/chemicals/strategy/

New Green Chemistry Newsletter in the US

The first newsletter from the newly formed Green Chemistry and Engineering Subdivision of the ACS I&EC Division recently appeared (http://green.chem.umb.edu/greenchem/). This results from the meeting of interested professionals at the ACS National meeting in New Orleans in the summer of 1999. The meeting concerned the future of the Practical Pollution Prevention subdivision and led to the proposal for its replacement by the new subdivision. This was approved and a number of volunteers have agreed to assist with programming with the first session from the new subdivision scheduled for the San Francisco ACS meeting in the spring of 2000 (*Green Chemistry for the Reduction of Greenhouse Gases)*. At the Washington meeting in August 2000 there will be sessions on *Clean Solvents* and *Green Chemistry: Applications in Academia and Industry*. The draft mission statement for the subdivision is:

"The Green Chemistry and Engineering Subdivision focusses on activities related to waste minimization, the development of green manufacturing processes, and the minimization of environmental and manufacturing costs. Chemists and engineers involved in green manufacturing, waste minimization and chemical process optimization are encouraged to participate"

The Programming chair is Martin Abraham (University of Toledo), Membership co-Chairs are Dan Tedder (Georgia Tech: daniel.tedder@che.gatech.edu) and Michael Gonzalez (EPA: gonzalez.michael@epamail.epa.gov). The Public Relations officer is Mary Kirchoff (EPA) and the web site is being looked after by John Warner (University of Massachusetts Boston).

The future's green

Two leading chemists have highlighted the importance of green chemistry to the future of chemistry and the chemical industry. The ACS President Professor Wasserman has said that "The major concern of the chemical industry will be green chemistry." He has also stated that the greatest impact will come as a result of improvements in catalysis. Joe Blaker, former Group technical director at Glaxo-Wellcome and now Chair of the UK Government's Technology Foresight Chemicals Panel, has said that environmental concerns will transform the face of the chemical industry by 2010. He sees, for example, chemical plants the size of garages becoming commonplace and new chemical plants being more environmentally friendly. He believes that the public attitude towards the chemical industry will improve as a result of industry moving towards lower energy-consuming, less wasteful and non-environment threatening plants and processes (*Chemistry and Industry*, December 20, 1999).

Green Chemistry Network

...the Green Chemistry Network website (http://wwwchemsoc.org/gcn) is proving very popular with spot checks indicating over 900 hits per month. The site has been extensively updated and hence is well worth a visit or a re-visit. A members' area has been added which will initially contain a database of members and their areas of interest and expertise. It is hoped to extend this to include a comprehensive database on green chemistry, including who is doing what, industry examples, educational materials *etc*.

...remember that the closing date for nominations for the UK Green Chemistry Awards, to be administered by the Green Chemistry Network [with support from Salters' Company, The Jerwood Foundation, Department of Trade and Industry (DTI), Department of the Environment, Transport and the Regions (DETR) and the Royal Society of Chemistry (RSC) is now 31 May 2000; there will be an award of £10,000 for a young academic and two awards for industry. For further information on these awards see *Green Chemistry* 1999, G136-G137.

Eco-labelling: legal, decent, honest and truthful?

Becky Allen reports on the rise of eco-labelling, its scientific basis, and the operation of key national and international schemes

The phenomenon of "green consumerism" emerged during the 1980s on the back of increasing publicity and public concern about environmental issues like global warming. Manufacturers and suppliers of many consumer products saw this rising concern as an opportunity to market new and existing products on the back on environmental claims, and policy-makers viewed both developments as a chance to stimulate production and consumption of goods that were less damaging to the environment.

The 1980s and early 1990s saw the launch of dozens of national—as well as two international—eco-labelling schemes. Although some have overlapping jurisdictions, most of the schemes share similar objectives and operate in the same way. Eco-labelling is a market-based instrument with dual aims: to enable consumers to make environmentally informed purchasing decisions; and to encourage manufacturers to produce more environmentally friendly products. With the exception of the US Green Seal and Sweden's Good Environmental Choice, all major eco-labelling schemes are overseen by public bodies. Voluntarism, transparency, independence and stakeholder participation are central tenets of most eco-labelling schemes.

Most eco-labelling schemes are based on the principles of "life-cycle assessment" (LCA). A methodological heir to the global modelling studies and energy audits of the 1960s and 1970s, LCA can been seen as part of a general trend towards risk assessment in other spheres, such as health and safety.

Life-cycle assessment

LCA's primary function is to compare life cycles of alternative processes, products or services designed to achieve similar

Key eco-labelling schemes

Eco-label	*Coverage*	*Date of inception*
EU Eco-label	**EU member states plus Norway, Liechtenstein and Iceland**	**1992**
Nordic Swan	**Norway, Sweden, Iceland and Finland**	**1989**
Good Environmental Choice (Bra Miljoval)	**Sweden**	**1990**
Blue Angel	**Germany**	**1977**
NF Environnement	**France**	**1992**
Stichting Milieukeur	**Netherlands**	**1992**
Umweltzeichen Bäume	**Austria**	**1991**
AENOR Medio Ambiente	**Spain**	**1993**
Green Seal Programme	**USA**	**1989**
Environmental Choice	**Canada**	**1988**
Eco-mark	**Japan**	**1989**

Eco-labels from around the world. Clockwise from top left: Nordic Swan (Scandinavia); Green Seal (USA); Blue Angel (Germany); AENOR Medio Ambiente (Spain); EU Eco-label (EU); Eco-mark (Japan).*

*The paper for this journal has been awarded the Nordic Swan Label.

objectives, in order to discover which is the most environmentally sound.[1] As the name suggests, LCAs take a "cradle-to-grave" approach to assessing environmental impact (both positive and negative), looking at the raw materials, resources, manufacturing processes, and disposal methods of a given product, process or service. While some elements of the assessment—such as energy, water and resource consumption—are relatively straightforward to represent numerically, others—such as pollution—are more subjective and inevitably involve value judgements.

The EU eco-label

One of the two major international schemes, the European Union (EU) eco-label, examines five stages of a product in its LCA:

- pre-production
- production
- packaging and distribution
- use
- disposal

At each stage, a number of environmental effects are considered, including: waste; noise; air contamination; water contamination; ecosystem effects; energy consumption; natural resource consumption; and soil pollution. Apart from the impact of noise, most other criteria draw heavily on chemistry and the expertise of chemists in these fields.

The EU eco-label has been in operation since 1992 and aims to provide a single, authoritative and widely recognised guide to consumers on products which are less harmful to the environment than their alternatives. However, the EU eco-label has been only a qualified success. The scheme was one of the first of its kind to award labels on the basis of a serious assessment of the environmental impact of products throughout their life cycle, and although it has done much to raise the profile of LCA as a policy and product management tool, its visibility and impact on the market have been disappointingly low. By March 1999, only 250 products had been awarded the EU eco-label.

Covering all consumer goods except food, drink and medicines, the EU eco-label's criteria are adopted by qualified majority voting among member states, which had set criteria for 15 product groups—from toilet paper and light bulbs to washing machines and laundry detergents—by 1999. The following are the product groups for which the EU has already set criteria:

- footwear
- textiles
- light bulbs
- bed mattresses
- refrigerators
- dishwashing detergents
- laundry detergents
- washing machines
- dishwashers
- copying paper
- soil improvers
- personal and portable computers
- tissue paper
- paints and varnishes
- bed linen and T-shirts

The criteria are revised every three years.[2] While the criteria are set by the European Commission, eco-labels themselves are awarded by the competent national bodies.

The EU scheme has been criticised from several quarters. Small- and medium-sized enterprises (SMEs) say that obtaining an EU eco-label is prohibitively expensive (applications cost 500 ECU, plus 0.15% of annual volume sales in the EU of the eco-labelled product), and even large retailers have been far from enthusiastic. In its submission to the UK's Environment Select Committee in 1999, major UK food retailer Sainsbury's plc said: "From the beginning, Sainsbury's was supportive of the principles behind the EU eco-labelling scheme. However, we became increasingly disappointed with the lack of progress and in our opinion the following reasons contributed to its recent demise within the UK: high cost; assessment criteria [which] took far too long to be agreed; and lack of consumer interest."[3] Despite Sainsbury's views, the UK Government remains committed to the EU eco-label, even though it wound up the UK eco-labelling board in 1998.

For more information about the EU Eco-label contact the European Commission, DGXI-E.4, Rue de la Loi 200 – B1049 Brussels, Belgium. Tel: +32 (2) 295 77 55. Fax: +32 (2) 295 56 84. Email: ecolabel@dg11.cec.be

Revising the EU eco-label

The EU published a proposal to revise its eco-labelling scheme in December 1996, cautiously admitting that the scheme has suffered from "certain difficulties", not least of which have been delays in setting criteria. The proposal also concedes that the EU eco-label's visibility on the European market is still low, but says that it is still too early to judge the scheme's impact: "It is premature to assess the market effects of the Community scheme, given that the Community eco-label has not yet gained sufficient visibility in the market place because of its still relatively early stage of development. The potential of eco-labels for market influence has already been demonstrated by national and other schemes. However, the Community scheme has encountered particular obstacles to the full development of its market potential."[4]

As well as slow progress in setting criteria and poor visibility, the eco-label has also been hampered by differences in market structures and consumer expectations between member states, and the applicability of criteria to non-EU producers. As a result, the proposal suggests that a revised eco-labelling scheme should be more flexible. "It would help to introduce a graded label allowing for greater flexibility in setting the criteria and providing information to consumers on the level of 'environmental performance' of each labelled product," the proposal says. One route towards greater flexibility may be the award of between one to three eco-label flowers, instead of the current "pass or fail" regime.

The proposal also acknowledges that the scheme is too expensive for industry, and the proposed revision suggests the introduction of a ceiling on annual fees as well as reduced rates for SMEs and manufacturers from developing countries.

A measure of success

As well as the operational criticisms levelled at the EU scheme, there are more fundamental critiques of LCA and hence all eco-labelling schemes. Measuring the environmental impact of eco-labelling is extremely problematic. Most schemes have operated for too short a time to be analysed, but even for more established schemes, quantifying the environmental impact of eco-labelling—as opposed to other environmental policy tools—is difficult. Success, therefore, tends to be measured in terms of consumer awareness, manufacturers' demand for eco-labels and market information, although the latter is also difficult to measure due to commercial confidentiality.

Market share is not intrinsically indicative of an eco-label's success, as criteria are generally set (and revised) so that only around 5–30% of products in any one category can obtain an eco-label, but market power conferred on producers with eco-labels (*i.e.*, whether a product can command a higher price or market share) is an indication of success.

Manufacturers' demand for eco-labels, as with the Blue Angel in Germany (over 4100 products in 76 categories had been awarded the Blue Angel by 1996), is also an indicator of a scheme's success.

In 1997, the Organisation for Economic Co-operation and Development (OECD) produced a report on the impact of selected eco-labelling schemes.[5] The report found that consumer awareness was a key indicator of a scheme's success. Thus, the success of the Nordic Swan in Sweden—which is recognised by 95% of the population—is attributable to high levels of consumer awareness.

In contrast to Sweden, consumer awareness in Japan is relatively low, with only 47% of those questioned in a 1997 survey recognising the Japanese Eco-mark. As a result, says the OECD report: "In Japan, a wide variety of environmentally preferable products is available. However, their sales have been negligible, with the exception of recycled copy paper."

Although there are no data on the consumer awareness of the Green Seal in the USA, it might be expected to be higher than that of the Eco-mark in Japan. The OECD attributes the Green Seal's limited success to its rather different operation, in that it is privately administered by a non-profit making organisation: "The success of the Green Seal scheme has been rather limited so far, in part due to the reluctance of industry to engage in third party eco-labelling."

In Germany too, there seems to be a problematic relationship between consumer awareness and buying patterns. Historically high levels of awareness appear to have fallen, and the OECD report suggests that this may be partly due to consumers becoming confused by the proliferation of eco-labelling schemes. "Overall, eco-labelling has been, at best, moderately successful with individual consumers. The proliferation of all types of environmental labels on products has created confusion among consumers and official eco-labelling programmes have not succeeded in avoiding this problem," the OECD says.

The German experience also highlights the fact that in general, eco-labelled products have only had a significant impact on the market in certain product categories, and that green products need to be competitive on price and performance to succeed in the marketplace. Where schemes have had a greater impact, however, it has been when eco-labels become a requirement imposed by retailers and/or used for government and institutional purchasing decisions.

Although little direct evidence is available on the environmental impact of eco-labels, a Nordic Council of Ministers evaluation gives a flavour of the effect of the Nordic Swan. In detergents, for example, eco-labelling has resulted in an end to the use of optical brighteners, certain surfactants and chelates, and eco-labelling of detergents has played a major part in product development in the sector.

Green claims code

The UK Government remains committed to eco-labelling as a policy tool, although it believes the scheme should be repositioned and used primarily for key products traded across the EU. The Government was also concerned that consumers were not getting the information they needed, and launched the *Green Claims Code* in 1998 to give manufacturers guidance on making accurate environmental claims on product labels.[6] "The principles set out in this code should help create a level playing field, where good claims are able to command the credibility they deserve," the Government said. Although the code is voluntary, Environment Minister Michael Meacher warned manufacturers: "Where voluntary measures don't succeed, we are looking to crack down on the problem through the use of the Control of Misleading Advertisements (COMA) Regulations. This will be helped by a new and international standard [ISO14021] which for the first time defines good and bad practice in green claims making."

The uptake and impact of the code has been monitored since its launch by the National Consumer Council (NCC), but its report on the code's first year of operation is not encouraging.[7] According to the NCC report, the code has only been successful among a few large retailers and manufacturing sectors. The report is critical of a number of sectors, including the paper products group, saying: "The overall picture for paper products is of a plethora of conflicting and confusing claims, a wide range of logos, and several breaches of the code. Claims have changed over the first year of the code but mostly not for the better."

Overall, the NCC is not optimistic and suggests that to be effective the code must be legally enforceable. "When the code was launched we were doubtful that, as a voluntary code, it would be credible, uniform in its application and effective. Our experience in monitoring its first year of operation has reinforced this view. The code lacks a strong sanction, and this is a serious barrier to its effectiveness," says the NCC. The NCC supports Government plans to enforce the code *via* the COMA Regulations, but it says that to be effective, the Regulations must be amended to give the Director of Fair Trading greater power to act against transgressors.

Even well-policed eco-labelling, however, can only be expected to achieve so much, and there is a growing realisation that it is only one among many policy tools that can be used to secure environmental improvements. At an EU level, this realisation is taking form in the "market transformation" approach, which is using a combination of measures—including the EU energy label, negotiated sectoral agreements, incentive schemes and procurement initiatives—to achieve aims that it was probably unrealistic to believe that eco-labelling alone could achieve.

References

1. Life cycle assessment, The Royal Society of Chemistry, Environment, Health and Safety Committee, 1998.
2. http://europa.eu.int/comm/environment/ecolabel/
3. Memorandum by the Department of the Environment, Transport and the Regions (EL 14), http://www.publications.parliament.uk/pa/cm199899/cmselect/cmenvtra/149/149mem27.htm
4. Proposal for a Council Regulation establishing a revised Community eco-label award scheme, European Commission COM (96) 603 - EN, 1996, http://europa.eu.int/comm/environment/ecolabel/proprev.htm
5. Eco-labelling: actual effects of selected programmes, Organisation for Economic Cooperation and Development, 1997, http://www.oecd.org
6. The Green Claims Code, Department of Transport, Environment and the Regions, 1998 (http://www.environment.detr.gov/gcc/ and http://www.environment.detr.gov.uk/greening/greenpro/gcode.htm)
7. The Green Claims Code: is it working?, National Consumer Council, 1999.

Further reading

Swedish Society for Nature Conservation and Eco-labelling website. http://www.snf.se.hmv/hmveng/ecolabelling.htm.

Global Ecolabelling Network (http://www.gen.gr.jp/whats.html)

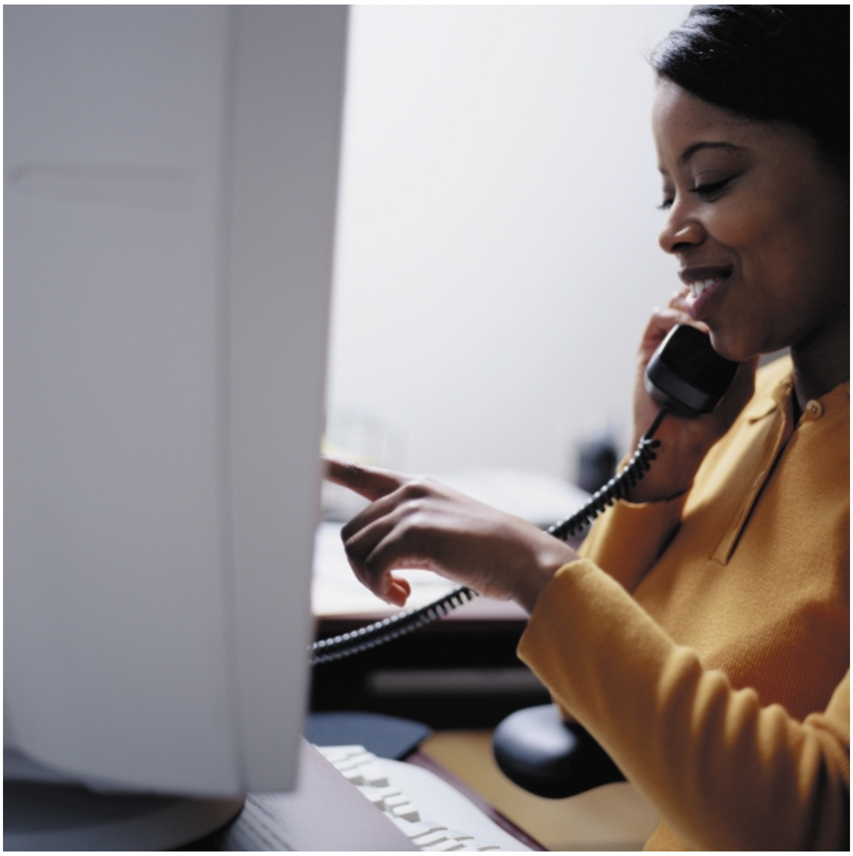
Green chemistry resources on the Internet

Hamish Kidd from the Royal Society of Chemistry reviews some the websites† which might be of interest to a 'green chemist'.

Introduction

The Internet is one of the most significant revolutions in computing and communications in recent years. The Internet was originally developed about 25 years ago to allow academic and military communities to transfer data between computers. However, the creation of the World Wide Web about 5 years ago was the driving force in moving the Internet into mainstream culture, with rapid growth in Internet users (an estimated 1 million new users go online every week). There has been a simultaneous increase in the number and diversity of Internet sites, with just about every organisation and company, as well as thousands of individuals, having their own presence in cyberspace. Data available now include text, graphics, audio and video, these being generally assembled onto a 'page', which the user can access. Internet users can not only download files, but also use the Internet to access various online publications and databases (often requiring the payment of a subscription fee). One advantage of Internet sites over more traditional publishing methods is that they can be rapidly updated and data can be easily copied and incorporated into other applications.

This short article seeks to point readers toward some of major websites which might be useful to the 'green chemist'. Experienced web users may be directed to some undiscovered sites, whereas those who haven't yet been seduced by what the web has to offer may gain an insight into the type of information that could be available to them.



The usefulness of websites varies considerably, because some organisations put up web pages merely as advertisements and image builders (often rarely updated), while other actually supply hard data or information, links to other sites of interest, photo libraries *etc.* The Internet is continually being updated, both with the arrival of new sites and an updating of existing ones—this review can provide no more than a snap-shot of sites currently available.

Searching

The Internet can be searched using a search engine which employs an index to the material on the Web. Having entered a key word or phrase, search engines compile lists of what they regard as potentially relevant sites, usually in a perceived order of relevance. There are several available search engines (Box 1), each using a different index, and hence giving different results from the same search terms. Metasearch engines give a more comprehensive search as they automatically search several of the major search engines at the same time.

One drawback of searching using search engines is that too many hits are retrieved, many of which are irrelevant, and the user finds it time consuming and unrewarding to plough through a long list of websites of possible interest. On the other hand, since less than 10% of all websites are indexed and therefore retrievable using the common search engines, many relevant sites are missed by standard searching techniques.

Research sites

UK

Centre for Clean Technology, York
(http://www.york.ac.uk/depts/chem/staff/Clark-home.html)

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† Websites are constantly changing and hence some of the websites mentioned in this article may have been discontinued.

Search engines

SINGLE SEARCH ENGINES

Excite	http://www.excite.com
Excite UK	http://www.excite.co.uk
AltaVista	http://www.altavista.com
AltaVista – Europe	http://www.altavista.telia.com
Infoseek	http://www.infoseek.com
Lycos	http://www.lycos.com
Lycos UK	http://www.lycos.co.uk
Thunderstone	http://www.thunderstone.com
Webcrawler	http://webcrawler.com
Yahoo	http://www.yahoo.com
Yahoo UK	http://www.yahoo.co.uk
Euroferret	http://www.euroferret.com
HotBot	http://www.hotbot.com
UK Index	http://www.ukindex.co.uk

METASEARCH ENGINES

Go2 (Metacrawler)	http://www.go2net.com
DogPile	http://www.dogpile.com
Metafind	http://www.metafind.com
Internet Sleuth	http://www.sleuth.com
Google	http://www.google.com

This is the group headed by Professor James Clark and is particularly interested in catalysis. Professor Clark and Dr Duncan Macquarrie are the scientific editor of this journal, and Professor Clark is also the Director of the Green Chemistry Network (http://www.chemsoc.org/gcn).

Institute for Applied Catalysis (http://www.iac.org.uk)

Centre for Alternative Technology (CAT) (http://www.cat.org.uk)

Questor
The Questor Centre was the first industry–university cooperative environmental research centre outside the USA. It was set up in May 1989 in The Queen's University of Belfast with nine founder industry members and five participating university departments (http://questor.qub.ac.uk/). From this website one can move to QUILL, the Queens University Ionic Liquids Laboratory (http://quill.qub.ac.uk/)

University of Nottingham – Clean Technology Research Group
This grouped is headed by Professor Martyn Poliakoff and is particularly interested in supercritical liquids (http://www.nottingham.ac.uk/~pczsp/clnthome.html)

University of Reading – Catalysis Research Centre (http://www.chem.rdg.ac.uk/dept/catrg/catrg.html)

Centre for Sustainable Design at the Surrey Institute of Art & Design (Farnham, Surrey, UK) (http://www.cfsd.org.uk)

Cardiff School of Biosciences – Clean Technology Group (http://www.cf.ac.uk/uwc/biosi/associates/ctgroup/)

Italy
Interuniversity Consortium of Chemistry for the Environment (http://www.unive.it/inca.html)

Italian Group of Catalysis (http://www.fci.unibo.it/gic/)

Netherlands
Netherland Institute of Catalysis Research (http://www.chem.tue.nl/niok/)

Australia
Murdoch University, Perth (http://wwwscience.murdoch.edu.au/teaching/m234/recycle32.htm)

Monash University, Clayton (http://www.monash.edu.au/).
A new Green Chemistry Centre has been established with substantial funding by the Australian Research Council. For further information contact Colin Raston (c.raston@sci.monash.edu.au)

Greece
http://www.chemeng.upatras.gr
The Department of Chemical Engineering of the University of Patras has several ongoing projects of interest to green chemists.

http://www.cperi.forth.gr
The Chemical Process Engineering Research Institute (FORTH) in Thessaloniki is particularly interested in reformulated fuels and hydrocarbons, energy conservation and renewable resources, polymer reaction engineering, solid fuels and environmental processes and aerosol and particle technology

http://www.iceht.forth.gr
The Institute of Chemical Engineering and High-Temperature Chemical Processes (FORTH) in Patras in particularly interested in surface science, catalysis and reaction engineering, materials science and technology, environment and biochemical engineering, modeling and computer-aided simulation and development of new analytical and diagnostic instruments.

http://cheng.auth.gr/cheng_uk
The Department of Chemical Engineering of the University of Thessaloniki has several on-going research activities which could be of interest to the green chemist.

USA
Centre for Clean Technology (University of California) (http://cct.seas.ucla.edu)

National Center for Environmental Research and Quality Assurance (NCERQA) (http://es.epa.gov/ncerqa/)

National Center for Clean Industrial and Treatment Technologies (CenCITT) (http://es.epa.gov/ncerqa/cencitt/cencitt.html)

Centre for Green Manufacturing—a new centre being built as part of the Alabama Institute for Manufacturing Excellence at the University of Alabama (http://bama.ua.edu/~cgm/)

Regulatory and funding sites

European Commission
A number of EU sites contain information relevant to green chemistry, both regulatory information and also

information on funding. The following are the principal websites of interest:

DG III (Environment, Nuclear Safety & Civil Protection)
http://www.europa.eu.int/comm/dg03/index_en.htm

DG IX (Industry)
http://www.europa.eu.int/comm/dg11/index_en.htm

DG XII (Science, Research and Development)
http://www.europa.eu.int/comm/dg12/index_en.htm

Fifth Framework Programme: Energy, Environment and Sustainable Development
(http://www.cordis.lu/eesd/)

European Environment Agency (EEA) – the bulk of the information available on this recently redesigned website is electronic versions of all EEA publications, including the Agency's main environmental assessment reports. (http://www.eea.eu.int)

UK

Environment Agency, England and Wales
(http://www.environment-agency.gov.uk)

Scottish Environment Agency
(http://www.sepa.org.uk)

Department of the Environment, Transport and the Regions
(http://www.detr.gov.uk)

Health & Safety Executive
(http://www.open.gov.uk/hse/)
Department of Trade and Industry
(http://www2.dti.gov.uk)

Office of Science and Technology (OST)
(http://www.dti.goc.uk/ost)

National Environment Research Council (NERC) (http://nerc.ac.uk)

Engineering & Physical Sciences Research Council (EPSRC)
(http://www.epsrc.ac.uk)

Biotechnology & Biological Sciences Research Council (BBSRC)
(http://www.bbsrc.ac.uk)

USA

EPA Green Chemistry Program
(http://www.epa.gov/opptintr/dfe/ and http://www.es.epa.gov/partners/chemistry/chemistry.html). The EPA organises the annual Presidential Green Chemistry Awards [*Green Chemistry, 1999,* **1**(4), G88; **1**(5), G124; **1**(6), G174].

Green Chemistry Institute
(http://www.lanl.gov/greenchemistry)

National Center for Clean Industrial and Treatment Technologies (CenCITT)
(http://cpas.mtu.edu/cencitt/)

Industry sites

Practically all the major (and most of the minor) chemical manufacturers have their own websites, *e.g.*, DuPont, Zeneca, Monsanto, Dow, Bayer, BASF, Novartis *etc.* Some of these sites are simply designed as image builders, but others do give news, and some information on R&D.

In addition, several trade associations have their own websites, such as the Alternative Crops Technology Interaction Network ACTIN (http://www.actin.co.uk) (*Green Chemistry*, 1999, **1**(1), G6) and the Interactive European Network for Industrial Crops and their Applications (IENICA), hosted by the UK Central Science Laboratory (http://www.csl.gov.uk/ienica) *(Green Chemistry*, 1999, **1**(2), G39)

Confederation of British Industries (CBI)
(http://www.cbi.org.uk)

The Chemical Industry Homepage
(http://www.neis.com)

SORIS
(http://www.sourcerer.co.uk/html/english/soris.htm) (*Green Chemistry* 1999, **1**(3), G63)

The Greening of Industry Network—this is an international partnership, focusing on issues of industry, environment and society, and dedicated to building a sustainable future
(http://www.greeningofindustry.org)

Learned, Professional and Charitable Societies

USA

The American Chemical Society (ACS) has a general chemistry website
(http://www.acs.org/)

American Institute of Chemical Engineers
(http://www.aiche.org/)

UK

Royal Society of Chemistry (RSC)
Green chemistry on the Royal Society of Chemistry website (http://www.rsc.org) consists mainly of the journal *Green Chemistry* (http://www.rsc.org/greenchem). The RSC also provides The Chemistry Societies Network (http://www.chemsoc.org.uk) which has a variety of information of general chemistry, including hosting the Green Chemistry Network (http://www.chemsoc.org/gcn); this network based at the Chemistry Department of the University of York, UK, was launched in 1999 (*Green Chemistry*,1999, **1**(5), G134) (http://www.chemsoc.org/gcn). The main aim of the GCN is to promote awareness and facilitate education, training and practice of green chemistry in industry, academia and schools. Its website provides a wealth of information on what is going on within green chemistry (news, events, publications, *etc.*). One useful feature on this website is a list a recent journal articles with a green chemistry theme, drawn from the published literature.

Society for Chemical Industry (SCI)— details of its meetings, several of which cover green chemistry related subjects, such as catalysis (http://sci.mond.org/)

Institution of Chemical Engineers
(http://icheme.chemeng.ed.ac.uk/)

Environmental organisations

Friends of the Earth (FoE)
FoE (http://www.foe.co.uk) in particular have a Factory Watch Website (*Green Chemistry*, 1999, **1**(3), G61) at http://www.foe.co.uk/factorywatch/

where factories are league-tabled on the basis of their pollution they cause.

Greenpeace
The Greenpeace site (http://www.greenpeace.org) is another comprehensive site which contains information, reports and press releases on all the organisation's campaigns.

WWF Global Network (http://www.panda.org)

UNEP–Cleaner Production Program (http://www.unepie.org/cp2/about/home.html)

EnviroNET Australia—Eco-efficiency and Cleaner Production (http://www.environment.gov.au/epg/environet/eecp/tools11.html)

Environmental News Network—deals with all aspects of environmental concerns to the public (http://www.enn.com)

Going for Green is a UK environmental awareness campaign funded by both the Government and the private sector which encourages people to live in a sensible way that reduces damage to the environment. The *Going for Green* website (http://www.gfg.iclnet.co.uk) contains a downloadable green calculator program called *EcoCal*, which allows the user to calculate how green their household is: *EcoCal* is fun to use and gives helpful suggestions on how to improve the environmental impact of your household.

Publications

Green Chemistry (http://www.rsc.org/greenchem)

Journal of Chemical Technology & Biotechnology (http://www.wiley.com/journals/jctb/)

Journal of Environmental Monitoring (JEM) (http://www.rsc.org/jem)

Journal of Clean Products & Processes (http://link.springer.de/link/servoce/journals/10098/index.htm)

The first newsletter from the newly formed Green Chemistry and Engineering Subdivision of the ACS I&EC Division recently appeared (http://green.chem.umb.edu/greenchem/). This results from the meeting of interested professionals at the ACS National meeting in New Orleans in the summer of 1999.

Electronic Green Journal - a journal on international environmental information (http://egj.lib.uidaho.edu)

Journal of Industrial Ecology - an international, multi-disciplinary quarterly designed to foster both understanding and practice in the emerging field of industrial ecology (http://mitpress.mit.edu/journal-home.tcl?issn=10881980)

Educational resources

Chemical Industry Education Centre, UK (http://www.york.ac.uk/org/ciec/)

Network for Chemistry Teaching (http://science.ntu.ac.uk/chph/net chemteach/)

National Pollution Prevention Center for Higher Education (http://www.umich.edu/~nppc/)

University of York Science Education Group (http://www.york.ac.uk/depts/chem/seg)

Chemical Education Foundation—an article on this US organisation, which produced a wide variety of educational resources (*Green Chemistry*, 1999, **1**(3), G60). Their website is http://www.chemed.org)

Linksites

University chemistry departments worldwide (http://chemdex.org)

ChemWeb (http://chemweb.com)

WWW Virtual Development Library – Sustainable Development (http://www.ulb.ac.be/ceese/meta/sustvl.html). This site, which is updated every 3 months and gives a vast number of useful links, is maintained by the Center for Economic and Social Studies on the Environment, located at the Université Libre de Bruxelles, Belgium.

Internet resources on Cleaner Production in Industry (http://www.marietta.edu/~spilatrs/cln_prod.html)

Links to Cleaner Production Sites (China–Canada Cooperation Project in Cleaner Production) (http://www.chinacp.com/eng/cplinks.html)
Pollution Prevention and Clean Production Europe (http://www.rec.org/poland/wpa/p2cp-eu.htm)

Solstice – an online resource from the Centre for Renewable Energy and Sustainable Technology (CREST) (http://solstice.crest.org)

Environment News Service (ENS) (http://gallery.uunet.be/internetpress/head101.htm)

The GreenWeb Guide—a Danish link site to a wide variety of green sites, *e.g.* those on sustainable development, ethical business, product life cycle design. There are also university links, related book titles, research articles and a database of educational programs and sustainable designers (http://home5.inet.tele.dk/nyboe/greenweb.htm)

The Online Fuel Cell Information Center, developed by Fuel Cells 2000 (http://www.fuelcells.org/) (available in English and Spanish) gives information on all the latest development in fuel cell development for transportation, stationary power, *etc*., together with a huge number of links to organisations involved.

Conclusion

The sites discussed here give an overview of some of the diverse resources on the Internet available to the 'green chemist'. With a subject as broad as green chemistry there are a large number of sites of potential interest, many of which are difficult to identify by keyword searching. Hence this article is only a starting point for the "green chemistry surfer".

Do you use the Internet?

This article is our first attempt to identify green chemistry resources on the Internet and we realise that it is far from comprehensive and will be quickly outdated. We would like to build on the information in this article in future issues.

Hence, if you have information on any useful green chemistry-related web sites not mentioned in this article, please send details to the editor (minhash@rsc.org), so that readers of *Green Chemistry* can be alerted.

SO_2 and NO_x emission abatement

Soghomon Boghosian of the University of Patras in Greece describes new catalytic and electrochemical processes which have earned a NATO "Science for Peace" grant

Calls for more stringent measures to ban the release of sulfur dioxide and nitrogen oxides are becoming more strident as international concern over their health hazards has grown markedly in recent years. Ultimately it seems that legislative pressures from the European Union and the United States will dictate that emission of SO_2 and NO_x must be controlled; similar control in the countries of Eastern Europe is anticipated.

Catalytic process

Researchers from the Boreskov Institute of Catalysis (Novosibirsk) have devised a method ("the reverse process") which is promising for the attainment of extremely low emission levels with significant capital and operating cost savings. The research will be carried out by Professor Bair Bal'zhinimaev and Dr. Andrey Zagoruiko and is based on non-stationary reaction kinetics, mathematical modelling and process engineering. Figure 1 shows the concept of the process in a simplified flow-sheet pertaining to the sulfur dioxide process for sulfuric acid production.

The installation (actually the second stage of a Double Contact/Double Absorption system) consists of two catalyst beds. One of the beds is fed with the reaction mixture which contains SO_2 (flow line shown solid). SO_2 is absorbed in the liquid film on the surface of the catalyst, partly oxidising to SO_3. In the beginning of the cycle, no SO_2 is detected in the outlet gas which is discharged to the SO_3 adsorber. Meanwhile, the second bed is blown by air in the counter-current direction (dotted line). Thus SO_2 and SO_3 are being desorbed and the catalyst is being oversaturated with dioxygen. When the SO_2 content in the outlet of the first bed eventually reaches 50 ppm, the gas flows are reversed and the first bed is blown by air while the second operates under catalytic reaction conditions. It should be noted that the oversaturation of the catalyst melt with dioxygen during the first step of the cycle favours the equilibrium. The following table summarises some data which are based on preliminary studies.

Number of catalysts beds	**2+2**
Loading of Catalyst/ m^3 per ton of H_2SO_4/year	**0.12**
SO_2 content at the outlet/ ppm	**<50**
Total conversion/ %	**99.995**

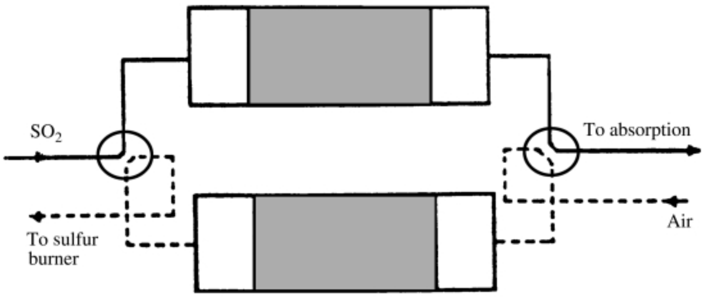


Figure 1

Electrochemical process

Furthermore, scientists at the Georgia Institute of Technology (Atlanta, USA), led by Professor Jack Winnick, have indicated the potential for a novel electrochemical membrane desulfurisation process (EMD) for efficient and economic removal of SO_2 from flue gas. The operation of EMD in a coal-burning power plant is shown in Figure 2.

The gas is fed to the cathodes at about 400 °C. While the chemical and electrochemical reactions are somewhat complex, the net effect is one of dioxygen reduction and sulfate ion production:

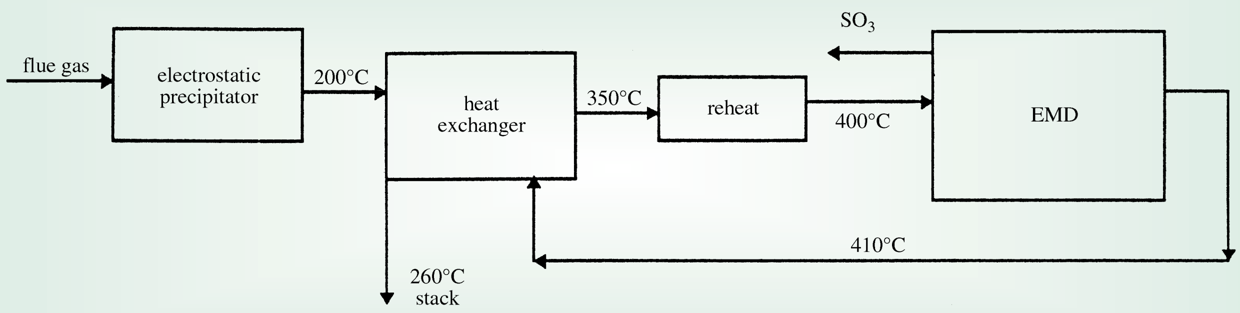


Figure 2

$$SO_3 + 1/2O_2 + 2e^- \rightarrow SO_4^{2-}$$

The sulfate ions migrate in the applied electric field across the electrolyte-filled membrane to the anodes, where the sulfate is oxidised, producing concentrated SO_3.

$$SO_4^{2-} \rightarrow SO_3 + 1/2O_2 + 2e^-$$

The net effect is one of continuous *in situ* concentration of the sulfur oxides from sub-percentage levels, in the wet flue gas, to 60% or so in the dry process stream, available for economic oleum manufacture.

A consortium (see box) under the coordination of Soghomon Boghosian, has now been awarded a substantial NATO “Science for Peace” grant ($325,000) to help develop the catalytic and electrochemical methods for SO_2 and NO_x emission abatement. The consortium is in close collaboration with Professor Kenneth R. Seddon (Queen’s University, Belfast, UK) who acts as a consultant appointed by NATO, and two expert/advisors, Professor Chris Adams of the Institute of Applied Catalysis (UK) and Dr Paul Anastas of the Environmental Protection Agency (USA).

MEMBERS OF THE CONSORTIUM

working to develop catalytic methods for SO_2 and NO_x emission abatement

FORTH/ICE-HT, Patras, Greece	**Dr Soghomon Boghosian (Coordinator)**
Technical University of Denmark, Lyngby, Denmark	**Professor Rasmus Fehrmann**
Georgia Institute of Technology, Atlanta, USA	**Professor Jack Winnick**
Boreskov Institute of Catalysis, Novosibirsk, Russia	**Professor Bair Bal’zhinimaev**
University of Bucharest, Romania	**Professor Vasile Parvulescu**
Byisk Oleum Plant, Byisk, Russia	**Dr Yurii N. Zhukov**

NATO “Science for Peace” programme

The objective of the “Science for Peace” programme is to offer support to Partner countries1 in their transition towards a market-oriented, environmentally-sound economy (http://www.nato.int/science/sfp.htm)

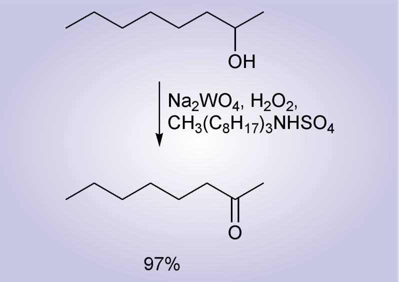
[1] Albania, Armenia, Azerbaijan, Belarus, Bulgaria, Estonia, Georgia, Kazakhstan, Kyrghyz Republic, Latvia, Lithuania, Moldova, Romania, Russian Federation, Slovak Republic, Slovenia, Tajikistan, Macedonia, Turkmenistan, Ukraine, Uzbekistan.

Coordinator

Soghomon Boghosian holds an M.Sc. (1984) and a Ph.D. (1988) in Chemical Engineering from the University of Patras, Greece. After two years as a postdoctoral fellow at the Technical university of Denmark and at the Norwegian Institute of Technology he became lecturer (1995) and assistant professor (1999) in chemical engineering at the University of Patras. His research interests include spectroscopic studies of high temperature molten salts and vapours and spectroscopic studies of systems.

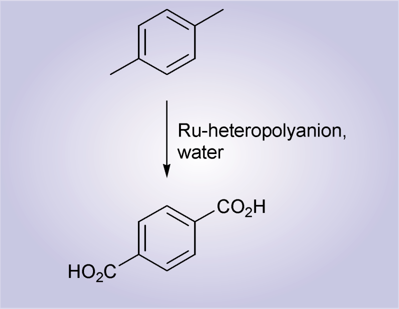
Green oxidations

A group led by Ryoji Noyori from Nagoya University in Japan has published a very detailed and thorough paper on their work on green oxidations (*Bull. Chem. Soc. Jpn.*, 1999, **72**, 2287). In this work, they have taken sodium tungstate and hydrogen peroxide, and used this to oxidise secondary alcohols to ketones, a quite difficult task to carry out in a green manner. They run the reaction without solvent. Under these conditions, the system is biphasic, and they use a phase transfer catalyst, methyl trioctyl ammonium sulfate. Yields are excellent with a range of alcohols, and competitive experiments show that a large number of functional groups (including epoxides and nitriles) are tolerated. Primary amides do interfere, probably by blocking the alcohol coordination site at the metal. A further very impressive feature is that the turnover numbers (mol product/mol catalyst) are extremely high, in the range of 79 000 to 179 000, over 100 times better than other systems. The reaction has been carried out with 100 g of bulk substrate, indicating that the reaction at this scale presented no difficulties whatsoever.



Further uses of this system include the oxidation of primary alcohols to carboxylic acids, and the oxidation of benzylic alcohols to aldehydes in good yields can also be achieved.

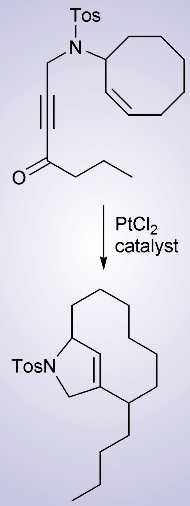
A second example of green oxidation from Japan has been published by Michio Higashijima of Mitsubishi. (*Chem. Lett.*, 1999, 1093) He reports the preparation of a ruthenium-substituted heteropolyanion $[SiW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ which is very active as a water soluble catalyst for the oxidation of *p*-xylene to terephthalic acid. One of the problems of current manufacturing processes for this important product is the corrosive medium (acetic acid, Co, Mn, and Br) in which the reaction takes place. Not only is the bromide very corrosive, but the reaction leads to the destruction of significant amounts of the solvent. The new catalyst functions in water at 200 ºC, and give a good conversion to terephthalic acid (58.8%) after five hours. Other products are partially oxidised compounds such as toluic acid, as well as a significant amount of CO_2 from over oxidation.

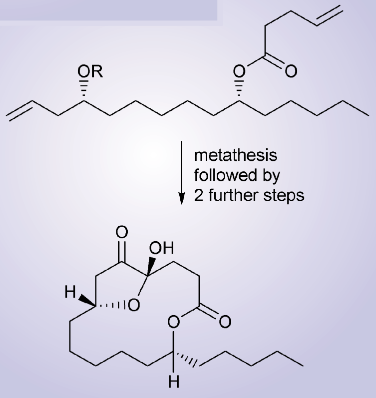


Green total synthesis

Contributions to green total synthesis from the groups led by Alois Fürstner at the Max Planck Institut für Kohlenforschung in Mannheim, have recently been summarised in a very interesting short review (A. Fürstner, *Synlett*, 1999, 1509). The concept of using catalytic alternatives to improve efficiency and reduce the length of synthetic pathways through novel transformations is well illustrated. The article illustrates how clever use of strategy and innovative methodology can be used to make the synthesis of many complex target molecules more efficient and less wasteful. In particular, novel approaches to the formation of heterocyclic rings are discussed.

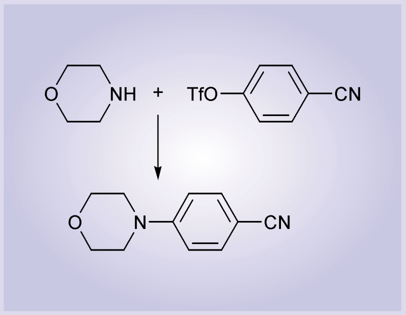
Illustrated are two examples of catalytic processes which are highly efficient and increase the complexity of the molecule significantly. Other processes include a sonochemically assisted S_N2 reaction at a sterically hindered secondary position on a mannose residue.





Green route to aromatic amines

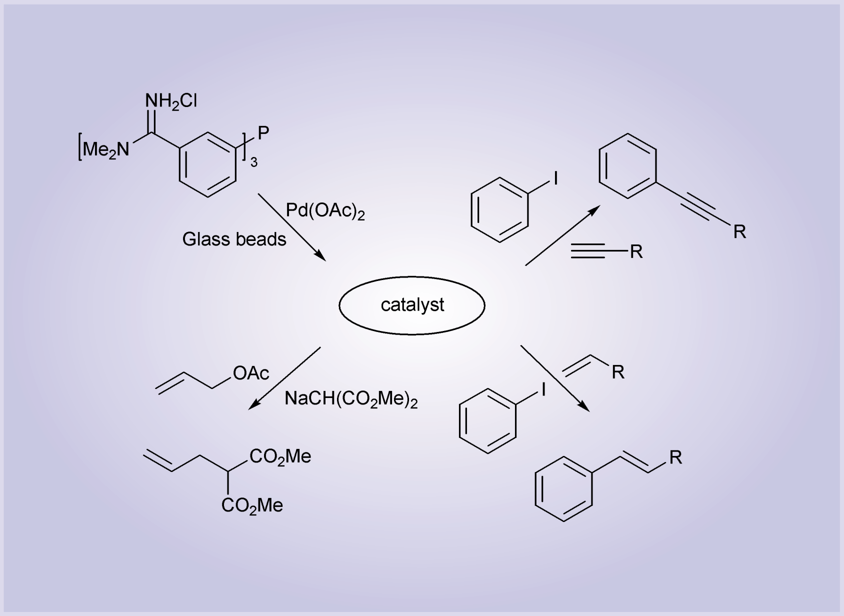
Researchers at Hoechst Marion Roussel have published a route to aromatic amine, involving the displacement of aryl triflates with piperidines (L. Schio, G. Lemoine and M. Klich, *Synlett*, 1999, 1559). This work demonstrates that efficient palladium-catalysed coupling of the two reagents takes place under relatively mild conditions (up to 110 ºC) in the absence of solvent. Good yields were obtained for a variety of triflates (themselves prepared from phenols with triflic anhydride). The activity of the triflate was correlated with its softness, with the reactants with the lowest energy LUMO being the most reactive. Very good yields could be obtained with reaction partners with reactive functional groups. Two limitations were discussed.



The hard nucleophile octylamine reacts preferentially with the harder electrophilic sulfur centre in preference to the ring carbon, leading to formation of the phenol rather than the coupling product. Bulky amines such as diisopropylamine do not react.

Supported aqueous-phase catalysts

Glass beads continue to provide interesting opportunities for supported aqueous phase catalysts. Jonathan Williams and Matthew Leese of the University of Bath (*Synlett*, 1999, 1645) have shown that guanidinium-substituted phosphines can be used as water soluble ligands for Pd complexes. They claim that the synthesis of these ligands is much easier and more reliable than the synthesis of the more usual water soluble phosphine (TPPTS, containing aryl sulfonates as solubilising groups). The resultant catalysts were found to be very active for Heck reactions, Sonogashira couplings, and allylic substitutions (see scheme below). Very little Pd leaching was noted, and reuse was possible.

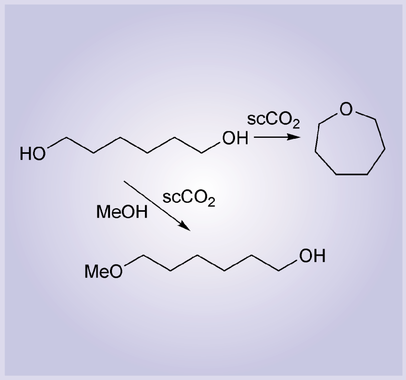


Organometallic catalysis in aqueous biphasic media

Roger Sheldon and co-workers have published a very accessible review on “Organometallic Catalysis in Aqueous Biphasic Media”, which details recent work on a range of catalytic systems such as organometallics with water soluble ligands (*e.g.* sulfonated triphenylphosphines). The review (*Chemtracts – Organic Chemistry*, 1999, **12,** 777) discusses applications of these systems in a wide variety of reactions including hydroformylation, hydrocarboxylation, copolymerisation, ring opening metathesis polymerisation (ROMP), hydrogenation and oxidation and Heck coupling reactions.

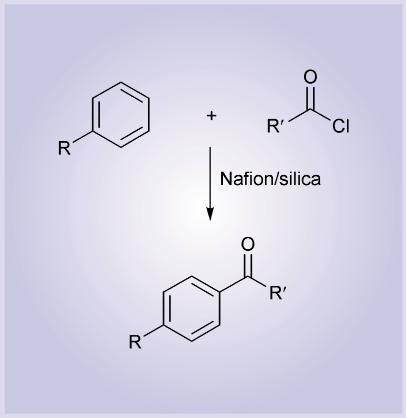
Heterogeneous catalysis in scCO2

Groups led by Martyn Poliakoff at the University of Nottingham and Thomas Swan Ltd. have published details of their work using heterogeneous catalysts in a supercritical CO_2 ($scCO_2$) flow reactor (*J. Am. Chem. Soc.*, 1999, **121**, 10711). Deloxan ASP and Amberlyst were used as the solid catalysts, and the reactions studied were dehydration of alcohols to ethers, and acetal/ketal formation. Generally, results were impressive, but some unusual effects were also noted. For example, large ring ethers can be made in very good selectivity, which is in contrast to what is found in the conventional systems, where rearrangement to smaller rings predominates. Similarly, excellent selectivity towards *mono*methyl ether formation is seen even with diols which otherwise cyclise, and with a threefold excess of methanol.



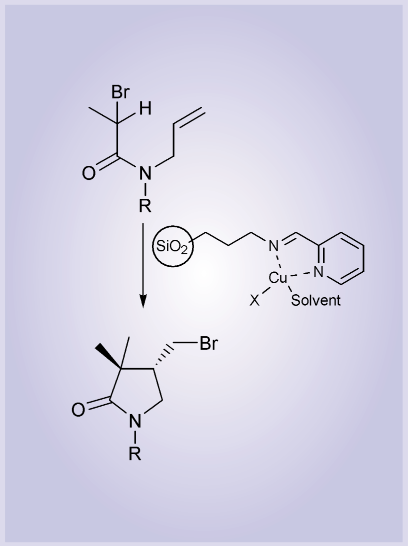
Acylation of aromatics

The acylation of aromatics remains a formidable challenge for chemists trying to replace aluminium chloride. New research carried out by Wolfgang Hölderich and Alfred Heidekum at the RWTH in Aachen, and by Mark Harmer at DuPont, Wilmington, Delaware, has shown that Nafion/silica composites are very promising systems for such chemistry (*J. Catal*., 1999, **188**, 230). The acylation of anisole with acid chlorides was shown to proceed much more readily with the composites than with the simple Nafion resins themselves. Conversions up to 100% and selectivities up to 97% have been obtained using this system.



Formation of 5-membered heterocyclic systems

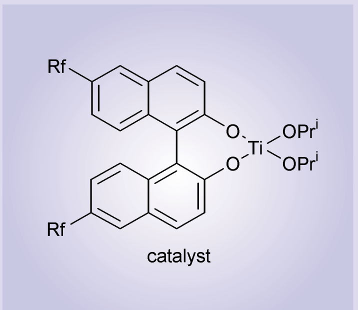
Atom transfer radical cyclisation is an atom efficient method for the formation of 5-membered heterocyclic systems. A group led by Andrew Clark at the University of Warwick has described supported Cu^I catalysts which are efficient at carrying out this reaction cleanly and in high yields (*J. Org. Chem*., 1999, **64**, 8954)

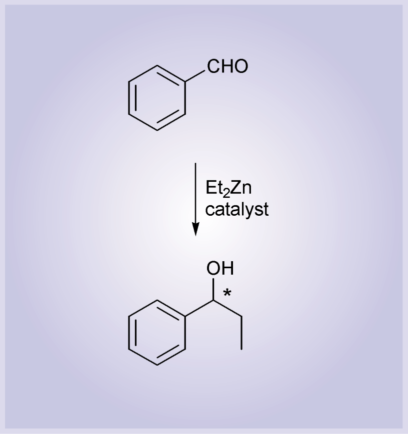


The catalyst could be used twice, without leaching of the Cu, but with a reduction in rate on the last reuse indicating some deactivation. Yields were still high and only slightly lower than the first use.

Fluorous BINOL-Ti complex

Groups led by Dennis Curran and Seiji Takeuchi have prepared a fluorous soluble BINOL-Ti complex (*Tetrahedron Lett*., 2000, **41**, 57) and demonstrated that it is a very active and reusable catalyst for the addition of diethylzinc to benzaldehyde. The fluorous phase could be recovered and reused five times without loss in either activity or enantioselectivity. The preparation of the fluorous BINOL was achieved in four steps from the dibromo derivative in high yield.





Green chemistry reviews in RSC journals

Useful reviews on broad areas of green chemistry can be found in recent issues of other RSC journals:

The latest issue of *Dalton (J. Chem. Soc., Dalton Trans.* 2000, 101–110) Professor James Clark, along with his colleagues at York (Peter Price and Duncan Macquarrie) has written a perspective entitled “Modified silicas for clean technology”. A wide variety of novel materials can be prepared through the chemical modification of silica gels with organic and inorganic functionalities. In addition to their use in chromatographic separations, they have been increasingly used as catalysts in liquid phase organic reactions. It is the application of these materials as viable, more environmentally friendly, alternatives to traditional homogeneous catalysts that forms the main body of the perspective. Their use as efficient materials for the selective pre-concentration of trace metals from aqueous systems is also discussed.

If you read the recent article in *Green Chemistry* (*Green Chem.* 1999, G167–G168) on clean polymer synthesis and processing using supercritical carbon dioxide (scCO$_2$) by Andrew Cooper you may be interested to know that Dr Cooper has recently written a much more extensive review of this topic in *Journal of Materials Chemistry* (*J. Mater. Chem.* 2000, **10**, 207–234). This 28-page review highlights the wide range of opportunities available to the materials chemist through the use of scCO$_2$. The synthetic techniques discussed include homogeneous solution polymerisation, precipitation polymerisation, dispersion and emulsion polymerisation, and bulk polycondensation. The use of scCO$_2$ in polymer processing is fully discussed with examples, such formation of microcellular polymer foams, polymer particle formation, spray coating and microlithography.

Read any green chemistry papers?

If you have any items from your literature reading which could be included in the PERSPECTIVES section of Green Chemistry, please send them to James Clark or Duncan Macquarrie [email: greenchem@york.ac.uk; FAX: +44 (0)1904 434533 or +44 (0)1904 423559]

Conference Diary

March 2000

Process Design and Operation for Sustainable Development **March 5–9**
The Hilton Hotel, Atlanta
(http://www.cpe.surrey.ac.uk/staff/aa.htm)

Renewable Raw Materials - Chemicals from Agricultural Crops **March 9**
University of Wales, Aberystwyth, UK
(http://www.rsc.org/lap/rsccom/locsecs/localsec77.htm)

Green Chemistry **March 15**
University of York, UK
(http://www.chemsoc.org/events/_events/00002021.htm)

Biocatalysis as a tool for organic synthesis **March 20–22**
Crowne Plaza Hotel, Amsterdam, The Netherlands
(http://www.scientificupdate.co.uk/pages/biocatalysis/biocat.html)

Industrial Uses of Wheat **March 22**
Cambridge, UK
(http://www.actin.co.uk/newsletter/index.htm#anchor.events)

INBIO Europe 2000: Biocatalysis - New Science and Applications **March 23–24**
Crowne Plaza Hotel, Amsterdam, The Netherlands
(http://www.scientificupdate.co.uk/pages/inbio/inbio.html)

Teaching the Environmental Sciences in the Millennium **March 25**
Including a session on Green Chemistry
Scientific Lecture Theatre, Burlington Place,
London, UK
(greennet@york.ac.uk)

ACS National Meeting Including Green Chemistry for Reduction of Greenhouse Gas Emissions **March 26–31**
San Francisco, California, USA
(http://www.lanl.gov/greenchemistry/conf.html)

April 2000

GreenTech® 2000 - Sustainable Raw Materials **April 3–5**
Royal Dutch Jaarbeurs, Utrecht, The Netherlands
(http://www.europoint-bv.com/)

Hazards XV. The process, its safety, and the environment—getting it right **April 4–6**
UMIST, Manchester, UK
(http://www.chemsafety.gov/info/IchemE1.pdf)
(mikeadams@valrichardson.com)

5th International Symposium on Supercritical Fluids: "Supercritical Fluids for Sustainable Technology" **April 8–12**
Westin Atlanta North Hotel, Atlanta, Georgia, USA
(http://www.issf2000.org)

Wood and Cellulose: Building Blocks for Chemicals, Fuels and Advanced Materials **April 9–12**
SUNY-EST, Syracuse, New York, USA
(http://www.epa.gov/opptintr/greenchemistry/calendar.htm)

Rapid Process Development and Safe Process Scale-Up **April 12**
North London, UK
(http://www.helgroup.co.uk/index.cfm/page,news)

CAPoC5 – 5th International Congress on Catalysis and Automotive Pollution Control **April 12–14**
Université Libre de Bruxelles, Belgium
(http://www.ulb.ac.be/sciences/surfcat/CAPoC5/)

9th International (and 4th European) Symposium on Supercritical Fluid Chromatography and Extraction. **April 13–14**
In cooperation with Analytica Conference 2000
Munich, Germany
(sfc2000@mx.uni-saarland.de)

RSC Annual Congress including Symposium "Towards Sustainability" **April 16–20**
UMIST, Manchester, UK
(http://www.rsc.org/lap/confs/sciprog.htm)

InLCA: The International Conference and Exhibition on Life Cycle Assessment **April 25–27**
Cincinnati, USA
(InLCA.CI@epamail.epa.gov)

May 2000

Synthetic Methodology and Total Synthesis: New Horizons in NaturalProduct Chemistry **May 16**
University of Glasgow, UK
(http://www.rsc.org/lap/rsccom/dab/perkidiv.htm)

3rd International Workshop on Green Chemistry in China **May 16–20**
Guangzhou, China
(jhf@mail.gic.ac..cn)

16th Canadian Symposium on Catalysis **May 23–26**
Banff, Alberta, Canada
(http://www.gch.ulaval.ca/~sayari/16csc/)

Green Chemistry Symposium **May 24**
University of Leicester, UK
(greennet@york.ac.uk)

DIARY

June 2000

R’2000 Recovery, Recycling, Re-integration. 5th World Congress with Trade Show **June 5–9**
Toronto, Ontario, Canada
(barrage@peak.ch)

Gordon Conference on Industrial Ecology **June 11–16**
New London, New Hampshire, USA
(ballenby@att.com)

4th Annual Green Chemistry and Engineering Conference **June 26–29**
“Sustainable Technologies: From Research to Industrial Implementation”
National Academy of Sciences, Washington DC, USA
(http://www.epa.gov/opptintr/greenchemistry/calendar.htm#4thGC&EC)

July 2000

World Renewable Energy Congress **July 1–7**
Brighton, UK
(asayigh@netcomuk.co.uk)

4th International Symposium - Supported Reagents and Catalysts in Chemistry **July 2–6**
St Andrews University, UK
(http://ch-www.st-andrews.ac.uk/conferences/)

12th International Congress on Catalysis **July 9–14**
Granada, Spain
(http://lcpb00.lc.ehu.es/12icc/index.html)

5th Gordon Conference on Green Chemistry **July 16–21**
Connecticut College, New London, CT
(http://www.grc.uri.edu/00sched.htm)

IEX 2000: Ion exchange at the Millennium **July 16–21**
Organised by the SCI.
Churchill College, University of Cambridge, UK
(http://sci.mond.org/conference/meetings/IEX.HTM)

August 2000

ACS 220th National Meeting including Green Chemistry - Applications in Academia and Industry Symposium **August 20–25**
Washington DC, USA
(williamson.tracy@epa.gov)

September 2000

The 4th International Conference on the Scale-Up of Chemical Processes Including Safety and Environmental Issues **September 25–28**
Hotel de France, St Helier, Jersey, Channel Islands
(http://www.scientificupdate.co.uk)

Chemsource: Clean Technology for Manufacture of Speciality Chemicals **September 26–27**
New Century House, Manchester, UK
(http://www.chemsoc.org/events/_events/00002188.htm)

December 2000

Pacifichem 2000 including Symposium on Environmental Chemistry **December 14–19**
Honolulu, Hawaii
(http://www.acs.org/meetings/pacific2000/)

April 2001

Green Chemistry Sustainable Products and Processes **April 3–6**
University of Wales, Swansea, UK
(greennet@york.ac.uk)

July 2001

CHEMRAWN XIV World Conference on Green Chemistry: Toward Environmentally Benign Chemical Products and Processes **July 9–13**
University of Colorado-Boulder, USA
(http://www.lanl.gov/greenchemistry/chemrawn.html)

New processes

…niacinamide
Alusuisse Lonza has commissioned a niacinamide plant in Guangzhou, China, which will use a new technology that combines traditional chemical processes with an enzymic step and is said to be environmentally friendly and low-energy. The continuous process converts methylpentane diamine to 3-cyano-pyridine which is then subjected to a highly selective bio-hydrolysis with immobilized enzymes to yield niacinamide. This is the water-soluble form of the B-vitamin niacin.

…trimethylolpropane (TMP)
BASF AG is to erect a 20,000 tonne per year plant for TMP, for commissioning in 2001. The plant will use a patented BASF process that produces no by-products. The first step is the base-catalysed aldol addition of formaldehyde to *n*-butyraldehyde, and then hydrogenation of the product to TMP. The current process produces around 50 kg of sodium or calcium formate byproduct per 100 kg of TMP.

…key polyester ingredient from glucose
Genencor International (Genencor) and DuPont on 22 Nov 1999 announced the achievement of another important milestone on the path to manufacturing a critical component for a high performance polyester from glucose, a renewable raw material; Genencor and DuPont scientists have successfully combined enzymes from two different micro-organisms into one production strain and, in so doing achieved greater than a five-hundred-fold improvement in productivity. The final goal of using fermentation technology to manufacture this ingredient for performance polyester is now in sight. The companies celebrated the first milestone only 20 months ago. Once commercialized by DuPont in the next few years, the patented technology will represent a breakthrough in “green chemistry”. The well documented technology is a bioprocess to 1,3-propanediol (3G or PDO), a monomer precursor to the 3GT polyester (http://www.genencor.com).

…palm oil separation
Concept Engineering, Malaysia, in collaboration with the Palm Oil Research Institute of Malaysia, has developed a cleaner, more efficient method of separating palm oil. The membrane-filter press separates oil, water and solid waste. The system is known as Zero Effluent Discharge Technology. It recycles 95% of the waste into fertilizers or animal feed. Malaysia produced 8.3 M tonnes of palm oil in 1998, mainly using steel presses and centrifuges.

…from NO_x to fertilizer
A recent technology developed at NASA’s John F Kennedy Space Centre and available for licensing, is the Nitrogen Oxides (NO_x) Waste Conversion to Fertilizer. This converts NO_x into potassium nitrate. Prior to the development of this new technology, the NO_x gas stream was absorbed by sodium hydroxide, with produced sodium nitrate, sodium nitrite, and nitric oxide. The disposal cost for this waste stream was about 23 c/lb or $700,000/year. Benefits of the new technology include: the elimination of hazardous waste disposal expenses; reduction of facility fertilizer expenses; and improved scrubbing efficiency.

…coatings
In spring 2000, a production facility for three monomers is due to be completed by Nippon Kasei Chemical in Onahama. The monomers are used in the production of environmentally friendly coatings. The development of the monomers has been undertaken in conjunction with Nippon Kasei Chemical’s parent company, Mitsubishi Chemical. This is the first commercial application of dimethylol butyric acid (DBC) which is being used in production of water-based polyurethanes. The other two monomers are dimethylol propionic acid, also used for water-based polyurethanes, and diacetone acrylamide.

…continuous processing
Kvaerner Process Technology of Stockton-on-Tees, UK, has developed a continuous process for chemical transformations that are traditionally carried out on a batch basis.. The process is economically and environmentally beneficial, and can achieve clean and efficient esterification. The process uses a novel counter-current reactor for undertaking diphasic and triphasic reactions. The process should be of interest to all sectors of the industry, *e.g.* butanediol from maleic anhydride.

Green moves at Unique Images

Unique Images, part of Hallmark, Europe's largest suppliers of gift wrapping paper (120 million metres per year) is now using water-based inks instead of inks based on organic solvents as part of company policy to reduce or even eliminate VOCs (volatile organic compounds). The problem of paper dampening from use of such water-based ink has been overcome by incorporation of a steam heat drying unit. In fact Unique Images are getting 6–10% faster printing with the new ink.

Unique Images has also installed Salter Weigh-Tronix electronic weighing equipment to monitor waste in its greetings card business (again Europe's largest producer at 1.2 billion cards per year); the company is targeting a reduction in waste to a 1% level.

Mattel turns from traditional plastics

Mattel Inc. is bringing together a consortium of the world's most innovative materials developers and consultants to formally begin investigating newly developed, environmentally friendly, and organically based materials for its products and packaging. Mattel's mandate to these firms is to identify materials that are derived from organic and renewable sources while maintaining the safety and structural integrity of the company's products. The company intends to begin the introduction of products produced from organically derived materials as early as the year 2001, based on extensive research in the year 2000. As the viability of these new technologies is confirmed, their use will be expanded into all brand categories and product lines. Mattel says its decision is based more on the use of environmentally friendly materials than current pressure throughout the industry to phase out the use of phthalates in toys, which Mattel has already stopped using in its teething toy products. Headquartered in El Segundo, California, USA, Mattel has offices and facilities in 36 countries (http://www.mattel.com).

Catalysts

…for alkylbenzene synthesis

Fushun Petrochemical Corporation, Dalian Institute of Chemistry and Physics, and the Chinese Academy of Sciences have developed a new catalyst for the production of linear alkylbenzene (LAB), which they have developed. This is a solid catalyst, which is not corrosive, to replace hydrofluoric acid. This means that savings can be made in plant costs, such as acid generators, re-generators and pipelines. The new catalyst is environmentally friendly and its record for reuse is good.

…chiroporphyrins

A CNRS-CEA research team at a university in Grenoble has discovered a new family of chiral molecules, chiroporphyrins. The user would be able to make either chiral form by changing the metal (iron or manganese).

Alternative uses of tobacco

India produces about 600 M kg of cured tobacco and the entire production is used for conventional smoking and chewing applications. The Central Tobacco Research Institute (CTRI), Rajahmundry, is trying to find alternative uses of tobacco. Proteins can be extracted from the green tobacco leaves and these proteins can be used to manufacture various animal feeds. About 381 kg of protein/hectare crop can be extracted. The resulting residue in the process can be used for solvent extraction of solanesol, which is a high value alcohol used in the synthesis of products like the cardiac drug co-enzyme Q9, and vitamins K and E. India exports crude solanesol worth Rup 20 M/y to Japan. The scientists at CTRI are aiming to extract 95% pure solanesol, which is valued at $500/kg in the global markets. It is possible to extract about 18.3 kg of solanesol/hectare of tobacco crop. Also from tobacco waste, the scientists have developed technology to extract nicotine sulfate of 40% purity an environmentally friendly insecticide effective against a wide range of insect pests.

Biodegradable fire-fighting foam

French company Bio-Ex has developed a new range of environmentally friendly fire-fighting foams. These foams are biodegradable, and are resistant to variations in external temperatures. Their low viscosity means that Bio-Ex foams put out fires quickly and can function at low pressure and low temperatures. These foams create a film on hydrocarbon matter, and a thin gel on polar and special products preventing any risk of re-ignition or the release of gases or toxic fumes. The high performance of Bio-Ex foams exceeds current European standards. Bio Filmopol 3 and Bio Newpol 3S are multipurpose foams for fighting hydrocarbon and polar solvent fires. Their single concentration application rate of 3% means they are long-lasting and easy to store. Bio For C, on the other hand, an additive for class A fires (forests, towns, homes, cars, gas, paper mills) is a foaming/wetting agent for use at very low concentrations: from 0.1% to 0.6%. So, as well as providing significant cost savings and water self-sufficiency, which enables a higher number of turnarounds, Bio For C also limits water damage in urban environments, so reducing the clearing time by firemen. Bio-Ex is the leading supplier to prestige chemical industries. It is an ISO 9001 certified European leader, thanks to services like centralised 24 h emergency services, and its product development. Bio-Ex is looking for distribution for its products in the UK.

Green burial

Green chemists can now take the "cradle to grave" approach a little further. Green Burials (http://www.green-burial.co.uk) offers corrugated cardboard flatpack biodegradable coffins, which can be assembled in less than 10 minutes. The coffins are suitable for burial or cremation are available in plain or woodgrain effect finishes. A variety of other eco-coffins are available, *e.g.* a British store called Green Undertakings sells biodegradable body bags and wicker burial stretchers, and in California, Biofab offers coffins made of 99% biodegradable straw, available in a range of colours. For further information on green burial see http://www.worldtrans.org/naturaldeath.html or http://www.funeral.com/casket.

Recycling

…polyester bottles

Eastman Chemical Co. have developed and patented a new polyester bottle recycling technology in which the depolymerization process is independent of dyes, coatings or barrier plastics and is energy-efficient. The resulting polyester is admissable for food contact. The depolymerization involves glycolysis, methanolysis and 'supercleaning', each of which is patented. The attributes of the methanolysis, glycolysis and hydrolysis processes are tabulated. Eastman expect the new process to deal with all colours of beverage bottles and with regulated compositional variants, and to tolerate some PVC contamination, but does not expect it to compete economically with mechanical recycling for clean, clear monolayer bottles for general use.

…nylon carpets
A joint venture between AlliedSignal Inc. and DSM Engineering Plastics has been set up to recycle old carpets into high quality grade caprolactam. The joint venture Evergreen Nylon Recycling is located in Augusta, Georgia, will produce 100 M lbs/y of caprolactam and 100 M lbs/y of virgin nylon 6. To generate this quantity the Evergreen facility will have to process 200 M lbs/y of nylon carpet. The joint venture uses patented technology, the Infinity nylon process, developed jointly by AlliedSignal and DSM Engineering Plastics. The recycling process will have energy savings of 4.4 M BTUs/y. DSM will launch its new nylon 6 products Akulon Renew early in 2000. The products contain 25% caprolactam and the range includes standard unreinforced, glass reinforced and glass/mineral compounds.

Solvents

...corn-derived green solvent
NTEC Inc and Archer Daniels Midland, USA, have signed an agreement to jointly develop and commercialize new markets for ethyl lactate, a biodegradable solvent made from corn. Under the auspices of this arrangement, all North American sales of ethyl lactate manufactured by Archer Daniels Midland will be handled under the umbrella of a strategic relationship between NTEC and Archer Daniels Midland. This product, already being shipped to several customers in the US, is sold under the "Versol" brand name. Ethyl lactate is a high performance, environmentally friendly green solvent that can successfully replace hundreds of millions of pounds of toxic petroleum based chemical compounds used in the world today. Ethyl lactate is 100% biodegradable: it simply decomposes into carbon dioxide and water. Archer Daniels Midland, based in Decatur, Illinois, is engaged in the business of procuring, transporting, storing, processing and merchandising agricultural commodities and products (http://www.admworld.com).

...“Solvents for Green Chemistry” report
US industry uses more than 3.8 M tons/y of solvents, most of them designated as toxic. A new Futuretech report from Technical Insights, a unit of John Wiley & Sons Inc., "Solvents for Green Chemistry" shows how industry can replace toxic solvents with safer, more efficient materials, how to minimize solvent use, recycle solvents and optimize design of processes to use solvents more efficiently. Demand for chemical solvents is expected to reach 12.4 bn lb, valued at $4 bn, by the year 2003. Several polychlorinated solvents have already been eliminated, while coatings, inks, and adhesives have undergone reformulation to reflect new regulations. Green solvents are poised to grab market share, with demand for ether solvents, alcohol solvents, ester solvents, and other solvents growing modestly over the next five years. The market for ether solvents is expected to grow 1.6% between the years 1998 and 2003 as will the market for alcohol solvents. Ester solvents will see growth projected at 3.7% and demand for other solvents will grow by 4.7%. However, market projections based on conventional technologies do not factor in such advances as ethyl lactate, near critical water, room temperature ionic liquids, and phytosols, all promising new technologies that are just now edging their way into commercialization.

New emission limits from power stations

The UK Environment Agency has announced new limits to protect the environment from excessive emissions of sulfur dioxide, nitrogen oxides and particulate matter from coal- and oil-fired power stations. The Agency will require that by September 2005 the total amount of sulfur dioxide to be released from the stations in England and Wales is less than 398,000 tons – a reduction of about 60% over 1996/7 rates. For further information see http://www.environment-agency.gov.uk.

Resolving pollution

David Lewis, a microbiologist who has worked at the US EPA for 30 years, has warned regulators that world-wide data on pollution are flawed because they do not account for the effect of chirality on toxicity. It has been shown through laboratory and field tests that environmental changes in soil can alter the risk posed by chemicals in pollutants because of chirability. Lewis points out that the pharmaceutical industry has been aware of the chirality– toxicity link for many years and that the same could be done in the manufacture of plastics, pesticides and herbicides.

Environmentally friendly credit cards

The world's first plant-based biodegradable credit card has been launched by the UK's Co-operative bank. The card is made from biopol which was first made by Zeneca using a carbohydrate-based fermentation process. Subsequently Monsanto acquired the technology and have subsequently produced a thermoplastic copolymer in plants. The Co-operative Bank is committed to replacing all of its existing 2 million credit cards with the new ones before the end of the year 2000.

Insecticide-treated mosquito bed nets

The Academy for Educational Development (AED) will utilize its experience in social marketing to lead an ambitious alliance of public and private organizations aimed at reducing the risk of malaria deaths among children and pregnant women in Africa. NetMark, a five year Africa regional project funded by the US Agency for International Development, seeks to create a commercially sustainable market for insecticide treated materials such as bed nets. The $15.4 M NetMark project will be managed by AED, a non-profit organization that has implemented development projects in more than 100 countries. AED has formed a collaborative relationship with private and public partners. Technical expertise on malaria and insecticide treated materials research will be provided by Johns Hopkins University's Department of International

Health and The Malaria Consortium, a joint venture of the London School of Hygiene and Tropical Medicine and the Liverpool School of Medicine. The sales promotion effort will be supported by Group Africa and other African consumer product promotion groups (http://www.aed.org).

Tin as an environmentally friendly alternative to lead

...The UK Department of Trade and Industry (DTI) has announced a collaborative project between the National Physical Laboratory and ITRI (the tin research organisation) on replacement of lead in solders used in the assembly of printed circuit boards. Lead-based solders are the subject of legislation around the world. Japan has already banned lead-based solders by the end of 2001óMatsushita has announced that four of its home electronic products will be lead-free by 2001. Hitachi will stop using lead solder by 2001. In October 1999 ITRI launched SOLDERTEC, the Lead-Free Soldering Technology Centre to meet the rising demand for lead-free soldering information and research. All lead-free solders can now be found on the SOLDERTEC website at http://www.lead-free.org along with much other information on lead-free soldering.

...Several major US police departments now use tin bullets on their practice shooting ranges as an answer to the lead fumes generated by firing large numbers of lead bullets in such confined spaces. There is also an increasing concern over hazards to wildlife resulting from deposition of toxic lead shot on wetlands. Voluntary and regulatory bans on lead shot are being introduced worldwide and various non-toxic alternatives are proposed.

...A new technological development from the Advanced Lead Acid Battery Consortium (ALABC) has highlighted the benefits of increasing the tin content of alloy grids used in lead-acid batteries. Originally applied to Electric Vehicle technology, manufacturers worldwide are applying this technology in the SLI battery sector.

...Other applications are tin wine capsules (the traditional lead, and more recently plastic, covers over corks), tin-zinc based flame-retardants as replacements for antimony/bromine based compounds, and tin weights to replace lead weights to balance car wheels. For further information on tin see http://www.itri.co.uk/home.htm.

Green glue

...USA

The “feet” of mussels produce an epoxy with adhesive-like properties that rivals any “super” glue on the market. Unfortunately, it takes about 10,000 mussels or molluscs to produce just one gram of adhesive, resulting in a prohibitive cost.

So molecular biologists at the DOE’s Idaho National Engineering and Environmental Laboratory (INEEL) are developing methods to clone the mussel’s genes, through DNA technology, that will allow them to economically produce large quantities of the adhesive protein for use as a strong cementing element for manufacturing plywood, oriented strand and other building materials. The dental industry is also looking for a better, safer adhesive for dentures.

The INEEL, in collaboration with scientists at the University of California, Santa Barbara, is identifying five proteins that go into the thread makeup that constitutes the “glue.” Cloning the mussel proteins is expected to be the crucial step in opening doors for developing this amazing epoxy. The ability to remain intact in sea water is only one advantage the “mussel glue” offers. It doesn’t require high temperatures to activate its cementing qualities as do other conventional waterproof glues, and, it’s also environmentally safe (http://www.home.doe.gov/mussels.htm).

...UK

Simon McQueen-Mason from the Biology Department at York, UK, is leading a team developing ìgreen glueî from genetically engineered tobacco plants. McQueen-Mason is exploiting the strong glues produced by mussels to anchor themselves to rocks by transferring the gene for the mussel protein into tobacco plants where they are expressed in plant cell wall proteins (extensins) with similar properties to the mussel glues. The advantage of the tobacco extensins, similarly crosslinked oxidatively through a key tyrosine residue, is that easily extracted from the plants in high yield.

Snippets

…India will encourage the use of secondary lead and zinc provided they are recycled using environmentally safe processes. There is growing use of lead and zinc in railway electrification, road transport and agriculture and this is leading to a national shortage.

…CK Witco is to allocate $70 M to the expansion of its green tyre activities and to its trimethoxysilane process to produce organofunctional silanes. $50 M is to be spent doubling sulfur silane capacity at Termoli, Italy by mid-2001. The remaining $20 M will be used to develop the TMS process in North America, with particular emphasis on intermediates. Full production is scheduled for mid-2001.

Moves towards greener cars

Mike Lancaster reports on several recent developments around the world towards making cars both more energy efficient and less polluting

All the major car companies are researching cleaner cars

Introduction

Pick up any journal from the popular scientific press or even any quality daily newspaper and you are likely to come across at least one article on cars and pollution. In the UK the topic is a current political 'hot potato' with the Government trying to introduce policies to reduce traffic congestion and pollution without alienating the motorist. Elsewhere, particularly in developing countries, governments are starting to introduce legislation which will help control pollution as the growth in car ownership continues to rise. Industry, particularly in the US and Europe, is meanwhile putting more and more research efforts into finding alternative cleaner technologies whilst at the same time pushing existing technology to the limits of energy efficiency.

In this article some of the recent developments which have made the headlines throughout the world are pulled together to give an overview of the area.

USA

Effect of changes in US rules on emission levels

In order to reduce the effects cars have on the environment the Clinton administration has announced sweeping new rules to cut car emissions and sulfur levels in gasoline, a twin effort aimed at keeping 2 million tons of smog-forming pollution out of the air.

The new rules from the Environmental Protection Agency will for the first time address not just pollution from automobiles but also from the gasoline used to fuel them. "This is a big deal, taking 2 million tons of air pollution from the air," said Rebecca Stanfield of the US Public Interest Research Group. The rules will become part of "the lasting White House legacy on the environment," she said.

The cleaner gasoline and tougher tailpipe emissions standards would be phased in over five years, beginning in 2004. The current level of sulfur in gasoline, which nationally now averages 330 parts per million, would be reduced by 90% over 5 years to 30 ppm under the new rules. High sulfur levels in gasoline are blamed for clogging vehicles' catalytic converters, which control tailpipe emissions and reduce pollution.

At the same time, minivans, trucks and sport utility vehicles (SUVs) would have to reduce their emissions of nitrogen oxides, which cause smog. Bigger SUVs would have until 2009 to comply.

EPA and White House officials have stressed the health benefits of cutting smog-forming pollution, notably stopping what the administration says is an explosion in child asthma cases around the country.

ARB bans MTBE and modifies rules for cleaner burning gasoline

The California Air Resources Board (ARB) approved a new set of gasoline rules that will ban the additive methyl tert-butyl ether (MTBE) while preserving all the air-quality benefits obtained from the state's cleaner-burning gasoline programme. The new rules, known officially as the Phase 3 gasoline regulation, prohibit the formulation of gasoline with MTBE after 31 December 2002. To better enable refiners to cost-effectively produce non-MTBE gasoline, the new regulation changes several ARB cleaner-burning gasoline specifications that have been in effect since 1996. The regulation establishes more stringent standards for two major gasoline pollutants, sulfur and benzene, while relaxing two standards for distillation temperatures. The new standards will improve the ability of refiners to make non-MTBE gasoline while ensuring motor vehicle emissions do not increase. These new standards will also take effect on 31 December 2002 (http://www.arb.ca.gov).

Powerball Technology

A report prepared by Energetics Inc. for the Department of Energy (DOE) Office of Power Technologies Hydrogen Programme shows that Powerball Technology can be competitive as a future infrastructure fuel. The report predicts that the future cost of powerballs may be $1.56/gallon of gasoline equivalent, and perhaps much lower when produced in high volume using efficient conversion technologies. Additionally, the DOE funded report points out that "the application of the Powerball Technology in the chemical industry represents an attractive option". The estimated plant gate manufacturing cost of sodium metal via Powerball Industries' thermochemical process could be as much as ten times less than the current commodity price for sodium produced via electrolysis. Powerballs can be produced from plentiful and clean natural gas energy. The fuel pellets are easy to transport, store, and use and are ideal as an energy carrier since they produce zero point-of-use emissions. Each gallon of powerball fuel pellets stores an impressive 17.8 kWh of energy in the form of clean, environmentally friendly hydrogen. Powerball Technologies LLC is a joint venture between Powerball Industries and Natex Corp., focused on innovative hydrogen distribution. At the heart of their technology is the proprietary hydride pellets which dramatically increase the storage density and distribution efficiency for hydrogen through incremental and on-demand production to portable fuel cell systems (http://www.powerball.net).

Ford Motor Co.

Ford Motor Co. has received the single largest electric-vehicle order in US history. The world's no. 2 carmaker said the US Postal Service is purchasing an initial order of 500 electric mail-delivery vehicles based on the Ford Ranger EV pickup truck. The postal service also has the option to order a total of 6000 vehicles.

Ford Postal EV

Ford Ranger EV

Photo credits: Ford Motor Co.

Production of the 500 vehicles will begin in the autumn and continue through next year, said Ford, which is working in partnership with Baker Electromotive of Rome, NY Ford said the bulk of the electric pickups will be used for mail delivery in California with the rest being used in the Washington DC metro area.

The Ranger EV is the national leader in electric vehicle sales, with 561 sold in North America during the 1999 model year. There are now over 1000 Ranger EVs in use in the United States and Canada. Electric vehicles have failed to catch on with consumers because of limited driving ranges, frequent required recharges and a weak infrastructure that offers limited locations for recharging. They have proven more popular for fleets like that of the postal service

Ford's other alternative fuel vehicles include the Prodigy, a diesel-electric hybrid family saloon capable of 80 mpg ; this vehicle was previewed at the North American International Auto Show in Detroit in January 2000.

DaimlerChrysler

Hundreds of thousands of air travellers will experience electric vehicle technology in traveling to and from Los Angeles World Airport as the first 10 DaimlerChrysler Electric Powered Interurban Commuter (EPIC) minivans join the fleet of Xpress Shuttle.

The five-passenger minivans, which represent DaimlerChrysler's state-of-the-art electric vehicle presence in California, are being added to the shuttle company's fleet, each expected to log up to 100,000 miles of service per year, an unprecedented workout for an electric vehicle. The breakthrough comes thanks to EPIC's unique fast-charging capabilities that allow the minivans to quickly refuel with electricity and return to the road.

The EPIC can carry a payload of 925 lbs—about five passengers and 175 lbs of cargo. The current model is powered by twenty-eight 12-volt advanced nickel-metal-hydride batteries that deliver up to 80–90 miles per charge. AeroVironment Inc. of Monrovia, California, is providing the fast-chargers for this project. Where a traditional charger delivers six-to-seven kilowatts and recharges an electric vehicle in 5–7 hours, the EPIC fast-charger operates at much higher power (60–150 kilowatts) and has the minivan back at close to full charge within a half-hour.

General Motors Corp.

Meanwhile General Motors Corp. have taken strides to make the more conventional combustion engine more energy efficient when it recently unveiled the Precept, an experimental, teardrop-shaped sedan capable of 80 miles per gallon.

The car was developed under the federally sponsored Partnership for a New Generation of Vehicles (PNGV). Members of the industry–government collaboration,launched in 1994, are committed to building by 2004 production-ready prototypes that can offer triple the fuel economy of a typical family sedan without sacrificing performance.

Company officials say the Precept will probably never go into mass production because of their high costs. But some of the advanced fuel-economy technology could wind up in consumer-ready cars and trucks.

The hybrid-electric Precept is driven by a battery-powered electric traction system that moves the front wheels, and a lightweight, 1.3 litre, 3 cylinder diesel engine in the rear. The direct-injection engine, featuring turbocharged compression ignition, was developed by Isuzu Motor Co. Ltd., one of GM's Asian affiliates.

GM has developed the electric motor to run off either a nickel metal hydride battery, like the kind used in the new version of its EV1 electric car, or a lithium polymer battery. The electric traction system also captures energy from braking and sends it back to the battery. Designers of the Precept took their overall design cues from the EV1 and constructed the car to be as aerodynamic as possible. Exterior door handles have been eliminated, and outside mirrors were replaced by a camera system. Because front-facing grills create wind drag, the Precept has special air openings behind the rear wheels (http://www.gm.com/).

Honda

Honda has introduced their new gasoline-electric hybrid car, the two-door Insight, into the California auto market. It has a 65 mpg fuel efficiency which will substantially reduce emissions that contribute to global warming. However, the vehicle will certify to a level of smog-forming pollution ten times greater than the standard set by California for Super Ultra Low Emissions Vehicles. Some of Honda's model year 2000 Accords and Toyota's forthcoming Prius hybrid will meet this higher standard.

The FCX concept vehicle, unveiled at the Detroit International Auto Show in January 2000, features Honda's innovative fuel cell unit powertrain. Honda has announced its intentions to put fuel cell-powered vehicles on the road in 2000 and is researching both methanol and hydrogen fuel cell prototypes. In the FCX concept vehicle, the fuel cell unit, located below the floor of the passenger cabin, employs a methanol-type fuel cell. Power is achieved when a methanol and water mixture moves from a storage tank, located in the rear of the unit, through a "fuel processor" where hydrogen is extracted. The hydrogen is then mixed with oxygen within the cell stack (part of the fuel cell system) to produce electricity. This in turn powers the electric drive motor.

Buyer's Guide to Cleaner Cars

The California Air Resources Board (ARB) has a buyer's guide to cleaner cars on its web site at http://www.arb.ca.gov/msprog/ccbg/ccbg.htm. This site gives a lot of information on the models of cars fit into the various categories of cleaner cars as defined in California [transitional low-emission vehicles (TLEVs), low-emission vehicles (LEVs), ultra-low-emission vehicle (ULEVs), super-ultra-low-emission vehicles (SULEVs) and zero-emission vehicles (ZEV)] to help the environmentally conscious purchaser to choose.

The Environmental Health Center (part of the National Safety Council) has a very useful Cleaner Cars Module on its website (http://www.nsc.org/EHC/mobile/intro.htm).

Sections include :

- background to air pollution
- buying a cleaner car
- alternatively fueled vehicles
- cleaner refueling and energy-efficient driving
- responsible recycling of motor vehicle fluids

Europe

European Automobile Manufacturers' Association (ACEA)

At the same time, European car manufacturers have called on the European Commission to support German moves to introduce sulfur-free diesel and petrol.

The European Automobile Manufacturers' Association (ACEA) said the Commission should encourage European Union states to introduce tax incentives similar to those planned in Germany to bring the sulfur content of fuels down to 10 ppm.

"We've written to the Commission to ask it to support the German government," said Giovanni Margaria, emissions and fuels director of ACEA. "Lower-sulfur fuels would improve environmental conditions and help European carmakers catch up technologically with their Japanese counterparts", Margari said. The average sulfur content of petrol sold in Japan is already below 10 ppm.

ACEA said it would be wrong to renegotiate recently agreed laws under which the sulfur content of petrol and diesel will fall to 50 ppm by 2005. But it said the EU should back countries which introduce tax incentives to encourage reductions in sulfur, which causes pollution by dangerous particulates as well as nitrous oxides which produce harmful ground-level ozone.

Germany introduced tax incentives in August last year for the introduction of so-called "sulfur-free fuels"—containing no more than 10 ppm—which will be effective from January 2003.

Meanwhile, as a ban on leaded petrol in Europe comes into force, the European Commission said it had given Italy, Spain and Greece until January 1, 2002 to enact the new laws, two years later than the rest of the European Union.

"The main justification for this is to ensure that they have adequate time both to time the transition to unleaded petrol and to ensure a good public information campaign," said an EU official. In making the decision, the Commission said it rejected the governments' claims that the move to unleaded petrol would force older cars to be scrapped and bring severe socio-economic problems for the countries involved (http://www.acea.be/).

Germany

Sales of biodiesel, a renewable fuel from oilseed rape, have doubled in Germany since 1996 to 100,000 tonnes in 1998. 800 German petrol stations now sell the green fuel. A study by the International Economic Platform for Renewable Energies (IWR) at the University of Munster indicates that the area dedicated to the growth of the rapeseed used in the fuel's manufacture is also increasing. However, the fuel still remains a niche market, amounting to less than 1% of total German diesel sales.

Saudi Arabia

The move towards unleaded petrol is also gaining momentum in other parts of the world. Saudi Arabia, the world's biggest oil producer, will introduce unleaded gasoline in 2001. Arab News daily quoted Essam Tawfiq, manager of Saudi Aramco's public relations department, as saying the cleaner fuel would hit the domestic market on January 1, 2001.

Like other Gulf Arab states which sit on nearly half of the world's oil reserves, Saudi Arabia is struggling to introduce unleaded gasoline to a population unfamiliar with the cleaner burning fuel. Gulf Arab states will need to perform major upgrades on refineries across the region to produce unleaded gasoline.

Vietnam

Vietnam have announced that they will develop an action plan to phase out leaded petrol as the first step to completely stopping the use of such fuel. At present, only leaded petrol is currently used in the country.

India

The Union Ministers for Petroleum & Gas and Environment & Forests met to discuss a long-term plan to supply cleaner and better quality fuel to the auto sector that will reduce the levels of pollution. The aim is to achieve compliance norms more stringent than Euro II in the auto sector. There is a proposal to supply low-sulfur diesel not only in the National Capital Region but also in other metros. The Supreme Court has directed the Government of India to ensure supply of high-speed diesel with sulfur content of less than 0.05% by 1 April 2000. Efforts are being made to achieve this by commissioning nine diesel hydro-desulfurisation plants that would bring down the sulfur content in high-speed diesel to 0.25%.

Brazil

The government in Brazil has abandoned subsidies for fuel alcohol distilled from sugarcane. They argue that this is no longer appropriate when alcohol is now much cheaper than gasoline. Hydrous alcohol, which has been subsidised by the State, is used by less than 1% of new cars in Brazil. Anhydrous alcohol, which has also been State-subsidised, is added to all gasoline sold in Brazil at a rate of 24%. The combined annual savings to the government will be $175M.

Developments in fuel cell technology

Fuel cell project at Houston Advanced Research Center (HARC)

Two utility companies, a major energy company, and a major supplier of engine components and automotive products have joined forces to power up a fuel cell demonstration and evaluation project at HARC. The three-year, $7 M project seeks to test and determine the various conditions under which fuel cells can be put to use as a clean, reliable, and affordable energy source. The four companies participating in this initial project of HARC's newly created Center for Fuel Cell Research and Applications are Dana Corp., Texaco, Southern Co. and Salt River Project. The project's objective is to demonstrate the value of stationary, near-zero emission proton exchange membrane fuel cell units in both small and large-scale applications. HARC plans to operate fuel cells from multiple US and foreign-based manufacturers, first looking at a large 250 kW fuel cell system. Based in Toledo, Ohio, Dana Corp. is one of the world's largest independent suppliers to vehicle manufacturers. Salt River Project is the third largest public power utility in the US. Southern Co., based in Atlanta, is an international energy company. Texaco Energy Systems Inc. is exploring business opportunities in fuel cells, hydrocarbons-to-liquids, and alternative fuels (http://www.harc.edu).

Record 3 M hours of 'green' power

A fleet of PC25 commercial fuel cell power plant systems, developed by International Fuel Cells Inc., and manufactured and serviced by ONSI Corp., has accumulated more than 3 M hours of in-service operation, breaking its own world record. ONSI has produced more than 200 of the power plant systems which are operating in 84 cities throughout the US as well as 11 countries in Europe, Asia and North America. The fleet's previous record, 2 M hours of operation, was set in June 1998. Each PC25 power plant provides 200 kilowatts of power, operating on a variety of fuels. While most use natural gas, some use methane from anaerobic digesters at waste water treatment plants or landfills, others use propane, butane, pure hydrogen or methane. The PC25 system contains the fuel cell itself and the components to make it commercially viable, including the fuel processing equipment and the devices needed to convert the direct current from the fuel cell into the alternating current normally used in homes and businesses. International Fuel Cells and its manufacturing arm, ONSI, both of South Windsor, Connecticut, are world leaders in fuel cell production (http://www.internationalfuelcells.com).

New US hydrogen fuel cell station

Energy and motor companies are to set up a dedicated hydrogen filling station and fuel-cell vehicle centre in 2000 at Sacramento, California, at the headquarters of the California Fuel Cell Partnership—a group including the state government, energy firms and vehicle manufacturers. The fuelling facility, jointly funded by Shell International, Arco (Atlantic Richfield Co.) and Texaco Inc., will dispense liquid and compressed hydrogen fuel for 16 fuel-cell powered passenger vehicles. "Refuelling is one of the key issues for enabling fuel-cell vehicles to reach the mass market," said Don Huberts, chief executive of Shell Hydrogen.

Automobile companies involved in the venture include DaimlerBenz AG, Ford Motor Co., Honda Motor Co. Ltd. and Volkswagen AG, and each will have garage bays at the centre for servicing, repairs and diagnostics (http://www.drivingthefuture.org).

Ballard Power Systems

Ballard have produced a new fuel cell, the Mark 900, which was included in the new Ford prototype fuel-cell vehicle, the TH!NK FC5, presented at the North American International Auto Show in Detroit in January 2000 (http://www.ballard.com and http://www.thinkmobility.com).

DaimlerChrysler

DaimlerChrysler have stated that they believe it will take another 10 years to produce fuel-cell-powered vehicles that are truly competitive with conventional cars. Despite this, the company plan to start selling such cars by 2004 and they believe that the market for them will reach 25% of the global market for vehicles in 2020. Popular Science magazine, in its 1999 "Best of What's New" issue, awarded the DaimlerChrysler NECAR 4 the Grand Prize as the year's best achievement in science and technology.

For more information on developments in the application of fuel cells to transportation see the Online Fuel Cell Information Centre developed by Fuel Cells 2000 at http://www.fuelcells.org/, the Fuel Cells Network (http://www.keele.ac.uk/deps/ch/fuelcell/network/board/htm) and http://evworld.com.

Future outlook

Most people involved in the industry now agree that fuel cell technology will play an important role in the future of transport. The only real question is over how long this will take before a significant impact is made: 10, 20 or 30 years? There are still several key technical and economic questions to be answered, but with the sheer volume of high quality research going on it is surely only a question of a few years before we start to see fuel cell powered cars on the forecourt.

In the meantime, as the article on the Ford EV pick-up highlights, existing clean technology solutions will continue to find niche markets but even the most ardent enthusiast does not believe the electric battery powered car will become widely used. Whilst the world waits for the new clean technologies to come on stream, small but valuable incremental improvements can still be made. Leaded gasoline will soon be phased out in many parts of the world and more stringent control of levels of sulfur in both diesel and gasoline are being introduced. Designers are still striving for the perfect aerodynamic shape but for all practical purposes we must surely be near the limit of where this area of research can have a significant impact on fuel efficiency.

pH-Dependent partitioning in room temperature ionic liquids

provides a link to traditional solvent extraction behavior

Ann E. Visser, Richard P. Swatloski and Robin D. Rogers*

Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA. E-mail: RDRogers@bama.ua.edu

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Summary

Room Temperature Ionic Liquids (RTILs) are emerging as novel solvent replacements for Volatile Organic Compounds (VOCs) traditionally used in liquid/liquid separations, however, the basic science involved with fully characterizing these systems (physical properties, solubilities, partitioning of solutes, water miscibilities, *etc.*) may be artificially holding back utilization of these green solvents. By demonstrating the compatibility of RTILs with fundamental principles used in solvent extraction (SX), separation scientists may use the considerable expertise developed in SX techniques for novel separations with RTILs. Here, using a simple indicator dye, thymol blue, the following are demonstrated: (*a*) reversible pH-dependent liquid/liquid partitioning, (*b*) the use of CO_2(g) and NH_3(g) to activate the 'proton switching' of phase preference, (*c*) that structural variation within the RTIL ions may be utilized to fine-tune partitioning behavior, and (*d*) solid/liquid separations are possible with low melting ionic liquids.

Introduction

Over 90% of hazardous waste is aqueous,[1] and thus much of the industrial reliance on VOCs is based on the need for efficient separations from liquid media. Traditional solvent extraction employs partitioning of a solute between two immiscible phases, typically an organic solvent and aqueous solution.[2,3] One area of opportunity for new chemical science and engineering technology which will help meet the goals of sustainable industrial technology is the development of new separations technologies that eliminate the use of flammable, toxic VOCs as solvents.[4] Used in conjunction with, or instead of appropriate current manufacturing processes, such technologies would help to prevent pollution and increase safety.

Room temperature ionic liquids[5] are gaining worldwide academic and industrial attention[6–9] as replacements for organic solvents in catalysis,[10] synthesis[11–15] and separations,[16–19] in addition to their established use in electrochemistry.[20–22] This interest is understandable given the major industrial reliance on VOCs as solvents and the ever increasing regulation of toxic release of these solvents.[23,24] The unique properties of several RTILs enable their use as solvent alternatives and may speed the introduction of these potentially 'green' solvents into sustainable industrial processes.

Three key communications have appeared involving the utility of RTILs in separations. The partitioning of a series of substituted aromatic solutes in RTIL/aqueous systems has been correlated to their hydrophobicity, partitioning to the RTIL increasing with 1-octanol/water partition coefficient (log *P*),[18] but charged solutes studied tended to stay in the aqueous phase. Stripping of nonvolatile aromatic solutes from a RTIL-loaded phase was demonstrated using supercritical CO_2.[16] (Although this technology may be too exotic for immediate industrial application, sc-CO_2 technologies are gaining wider acceptance.) In a third paper, a crown ether extractant was used to enhance metal ion partitioning to a RTIL phase from water, however, stripping was not demonstrated and the reported behavior appeared to be opposite to accepted trends in organic solvents.[17]

Despite these interesting developments and growing interest in the field, the workhorse of solvent extraction, pH-dependent reversible partitioning,[25] has not been addressed for these ionic fluids. In these techniques, the receiving phase is loaded at one pH and stripped at another. Such systems may involve uptake of ionizable organic solutes or extraction of metal ions using a lipophilic ligand which complexes the metal ion and transfers it to the organic phase at one pH and releases the metal ion to an aqueous phase at another pH. Adaptation of these principles of traditional liquid/liquid separation are also often made to solid/liquid and liquid membrane separations.

Results and discussion

In order to qualitatively and quantitatively study reversible pH-dependent separations in RTILs, we have investigated the

Green Context

Room temperature ionic liquids are among the most promising new "greener" solvent systems since their lack of vapour pressure removes vapour loss and atmospheric pollution. While there is an expanding interest in their use, there remains little knowledge about their physical properties and this is holding back their exploitation and application in areas such as separation science. In particular the workhorse of solvent extraction, pH dependent reversible switching, has not been addressed for these liquids. Here for the first time, reversible pH-dependent liquid/liquid partitioning for such systems is proven. Furthermore, it is shown how this partitioning can be fine-tuned through structural variations in the ionic liquids. This new knowledge should greatly facilitate the use of room temperature ionic liquids in separations and indeed facilitate their development in other application areas.

JHC

partitioning of an indicator dye, thymol blue, as a function of aqueous phase pH for a series of 1-alkyl-3-methylimidazolium hexafluorophosphates ([$C_n$mim][PF_6]) RTIL[18] (Fig. 1). The butyl, hexyl and octyl derivatives are liquid at room temperature,[26] stable to moisture, and form a two phase system upon contact with water. The decyl derivative is a solid at room temperature and its cyrstal structure[19] indicates solid-state behavior similar to analogous higher order alkyl derivatives.[26,27]

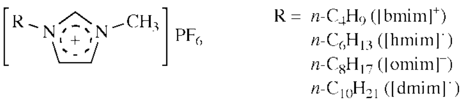

Fig. 1 Structural variation in the 1-alkyl-3-methylimidazolium hexafluorophosphate salts used in this study.

Fig. 2 illustrates the qualitative partitioning of thymol blue in its three forms between aqueous (top) and [bmim][PF_6] (bottom) phases as aqueous phase pH is changed from very acidic to very basic. The behavior of this molecule can be explained in terms of its ionization constants; 1.65 and 8.9.[28] At low pH thymol blue exists in its red form as a neutral zwitterion which prefers the RTIL phase. As the pH is increased *via* the addition of NaOH, the yellow monoanion forms with some detectable increase in concentration in the aqueous phase. The blue dianion, above pH = 10, partitions quantitatively to the aqueous phase.

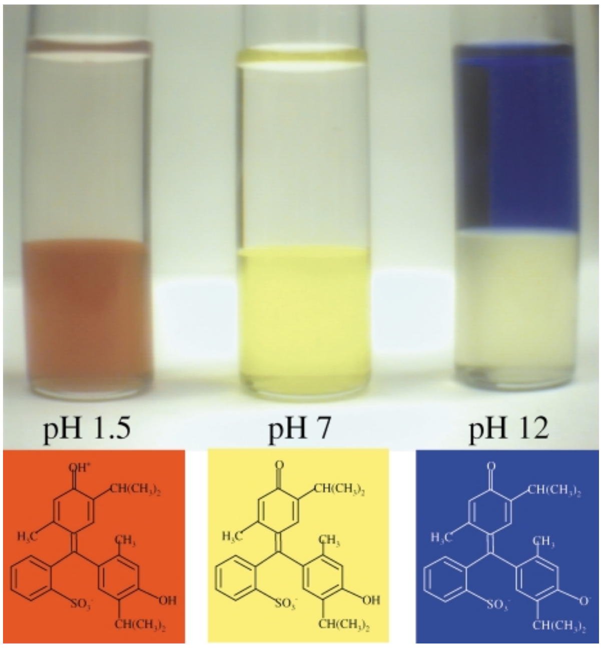

Fig. 2 The phase preference of the three forms of thymol blue in [bmim][PF_6].

Adjustment of system pH, and thus phase preference of the solute, can be accomplished using mineral acids, and in this study both H_2SO_4 and HPF_6 were utilized with no observable differences based on the acid used.[29] A more environmentally-benign approach to pH adjustment may be accomplished using recyclable gases which can modify aqueous phase pH [*e.g.* CO_2(g) for acidic adjustments and NH_3(g) for basic adjustments].[30] To test this latter approach, a bubbler was loaded with 3 mL each of [bmim][PF_6] and a 10 mM aqueous thymol blue solution at pH = 13 [Fig. 3(*a*)] where the dye in the blue form remains in the upper aqueous phase. Bubbling CO_2 through the system lowered the pH of the aqueous phase to 8.3 observable by the change in dye color from blue to yellow [Fig. 3(*b*)]. Agitation of the system by the bubbles resulted in thorough mixing and transport of the yellow form of the dye to the RTIL phase [Fig. 3(*c*)]. The yellow form can be converted back to the blue dianion and stripped from the RTIL phase by bubbling NH_3 through the system [Fig. 3(*d,e*)]. (Further control of the pH, and thus extraction efficiency, can be accomplished by operating at increased pressure, where, for example, bubbling CO_2 through the system could lower the pH enough to observe the red zwitterionic form of the dye and further enhance distribution to the RTIL phase.)

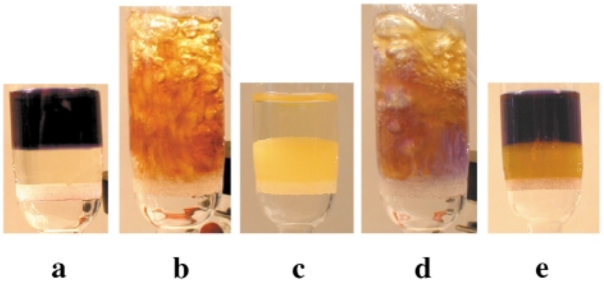

Fig. 3 Utilizing recyclable gases to activate the proton switch: (*a*) Thymol blue in the upper aqueous phase at pH = 13; (*b*) Bubbling CO_2 through the RTIL/aqueous system, note the change in dye color; (*c*) The yellow form of thymol blue in the RTIL phase; (*d*) Bubbling NH_3 through the RTIL/aqueous system, note the darker color of the dye; (*e*) The blue form of thymol blue settling into the top aqueous phase.

The overall properties of an RTIL are a result of the composite cations and anions and can range from superacidic in, for example, the moisture sensitive [$C_n$mim][$AlCl_4$] salts,[31] to water miscible (*e.g.* [$C_n$mim][BF_4] salts),[32] to water immiscible and hydrophobic.[32,33] The anion is currently used to control the water miscibility, but the cation can also influence the hydrophobicity or hydrogen bonding ability. The properties of both ions are useful tools for fine-tuning an RTIL for particular 'solvent' properties.

To demonstrate the ability to fine-tune extraction properties, quantitative analysis of the partitioning of thymol blue was carried out using [bmim][PF_6], [hmim][PF_6], and [omim][PF_6] (Fig. 1). The subtle differences in the distribution of the solute in the three ionic liquids is shown in Fig. 4. Although the general trend is the same in each RTIL, distribution ratios increase with increasing length of the alkyl substituent on the cation, with differences in distribution ratios of over an order of magnitude.

Interestingly, at pH 12 the phase preference for the blue form is reversed as R is increased from C4, to C6, to C8. Distribution ratios show a distinct preference for the aqueous phase when using [bmim][PF_6], essentially no phase preference using [hmim][PF_6], and a preference for the RTIL phase when [omim][PF_6] is utilized. Thus, phase preference for specific solutes can be engineered into these designer solvents.

The decyl derivative of the RTIL used in this study, [dmim][PF_6], is a solid at room temperature, melting at 38 °C and illustrates yet another potential separation strategy. (The crystal structure of this compound was determined[19] and it exhibits similar packing properties to its C12[26] and C14[35] analogs; forming bilayers with interdigitated alkyl chains.) A 10 mM solution of thymol blue at pH = 1.8 (red form) was added to a test tube containing crystalline [dmim][PF_6] [Fig. 5(*a*)]. When heated just above its melting temperature, the solute immediately

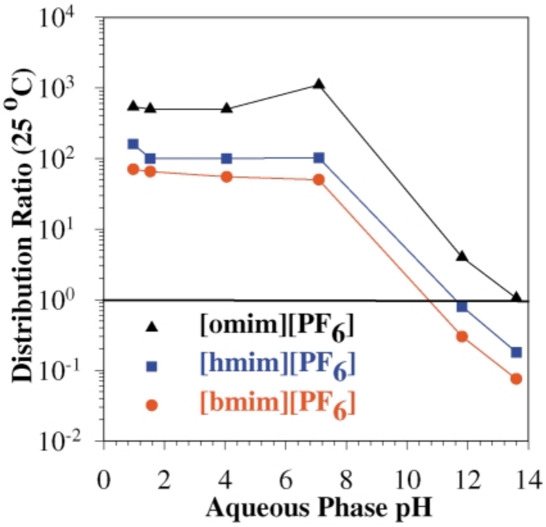

Fig. 4 Distribution ratios of thymol blue in [$C_n$mim][PF_6]/ aqueous systems as a function of aqueous phase pH.

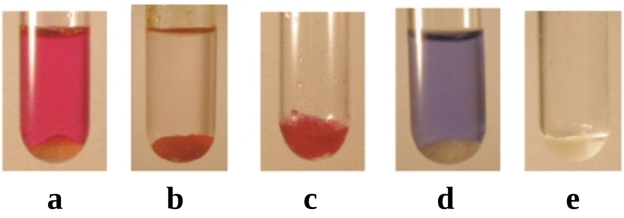

Fig. 5 Solid/liquid separations utilizing the low melting [dmim][PF_6]: (*a*) An acidic thymol blue solution residing over solid [dmim][PF_6] prior to melting; (*b*) After melting the salt, thymol blue partitioned to the [dmim][PF_6]; (*c*) Recrystallization of [dmim][PF_6] leaves behind a red residue; (*d*) An alkaline wash is added to remove the dye from the solid surfaces; (*e*) The colorless crystalline [dmim][PF_6] solid after washing.

partitions to the RTIL phase [Fig. 5(*b*)]. Separation of the RTIL phase, followed by crystallization at reduced temperature leads to pure [dmim][PF_6] crystals and deposits of the dye [Fig. 5(*c*)]. This material can be easily removed by washing with pH = 13 NaOH [Fig. 5(*d*)] and decanting to obtain the pure crystalline solid [Fig. 5(*e*)]. (The crystal structure of [dmim][PF_6] was determined both before and after melting, contact with an acidic thymol blue solution, and recrystallization, indicating no incorporation of thymol blue or water into the crystalline lattice and no change in the structural properties of the solid.)

Conclusions

The results reported in this work if derived from organic/aqueous extraction data, are not surprising yet they dramatically illustrate the similarities of specific RTILs to organic diluents in traditional SX. Given the ever increasing regulatory demands on the use of VOCs, RTILs offer a potentially green alternative worthy of additional study. If the use of RTILs can be put into the general context of previous work in SX, RTILs may offer drop-in replacements of current VOC-based technologies. Such efforts, coupled with the development of RTIL libraries and physical properties databases (such as those under development at the Queen's University Ionic Liquid Laboratory[36]) will lead to new sustainable industrial technologies which help to eliminate the health and safety concerns which arise from the pervasive use of VOCs.

Experimental

All reagents were at least 99% pure and used as received from Aldrich (Milwaukee, WI, USA). The preparation of any aqueous solutions used 18.3 Ω cm deionized water (Nanopure). Thymol blue was used as the disodium salt. Adjustments in pH were carried out using NaOH, H_2SO_4, or HPF_6.

Partitioning of thymol blue in the three ionic liquids was monitored *via* UV–VIS with a Cary 3 spectrophotometer. A calibration curve for the absorbance of thymol blue in each phase was constructed over a region of concentrations that corresponded to a linear response and obeyed Beer's Law. The partitioning of thymol blue was carried out by contacting equal volumes of ionic liquid and aqueous phase, thoroughly mixing them with two repetitions of vortexing (2 min) and centrifugation (2 min, 2000 g) followed by separation of the two phases. The absorbance was measured in each phase. The concentrations of thymol blue were determined from the calibration curve for each phase and the partitioning of the solute was calculated as a distribution ratio (*D*), as follows:

$$D = \frac{\text{Concentration in the Lower Ionic Liquid Phase}}{\text{Concentration in the Upper Aqueous Phase}}$$

The solid/liquid partitioning in [dmim][PF_6] was performed by adding 3 mL of thymol blue in H_2SO_4 (pH 1.07) to solid [dmim][PF_6] (1.56 g) which was then heated to 50 °C to melt the solid. After thorough mixing, the dye partitioned to the ionic liquid phase, the aqueous phase was removed and the RTIL crystallized by cooling in a freezer (−5 °C). The red dye appeared to coat the colorless [dmim][PF_6] crystals and 3 mL of NaOH (pH 13.6) was added to remove the dye. The resulting crystalline material was colorless and determined by crystallographic analysis to be [dmim][PF_6].

The partitioning of several organic solutes was measured in a [bmim][PF_6]/water system to determine whether using H_2SO_4 or HPF_6 to adjust the pH of the aqueous solution would have an effect on their affinity for the RTIL phase. Using an aqueous phase pH of 3.3, the behavior of acetophenone, *p*-toluic acid, dichlorobenzene, salicylic acid, and phthalic acid were examined and indicated no observable difference in distribution ratios. (The partitioning of these organic solutes was determined radiometrically according to a method detailed in a previous report.[19])

The experiments using CO_2 and NH_3 to adjust the pH were carried out in a glass tube with a frit at the bottom to allow the gases to permeate the solution. Rubber tubing was connected to the bottom of the tube and CO_2 (from an Erlenmeyer flask containing dry ice) or NH_3 (produced by passing air over concentrated aqueous ammonia) was bubbled through the biphasic system. The reported pH values are those for the aqueous phase and were measured using a Corning 220 pH meter.

Synthesis of [1-alkyl-3-methylimidazolium][PF_6]

The ionic liquids used in these experiments were synthesized according to the method outlined in a previous report.[18] For the synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate, equal molar amounts of methylimidazole and 1-chlorobutane in a round-bottomed flask fitted with a reflux condenser were refluxed for 24–72 h at 70 °C with stirring until two phases formed. The top phase (unreacted starting material) was decanted and ethyl acetate added (a volume approximately equal to half that of the bottom phase) followed by thorough mixing. The ethyl acetate was decanted and the procedure repeated twice using fresh ethyl acetate to ensure that any unreacted starting material was removed from the bottom phase. After the third was decanted, any remaining ethyl acetate was removed by heating the liquid bottom phase to 70 °C under vacuum with stirring.

The resulting liquid, [bmim]Cl, was poured from the reaction vessel to a 2 L plastic container lined with a perfluorinated material followed by addition of 500 mL of deionized water. HPF_6 (60% aqueous solution; 1.1 : 1 stoichiometry) was added. (This addition must be made slowly to prevent the reaction temperature from rising too high.) As the addition proceeds, two phases form: the [1-butyl-3-methylimidazolium][PF_6] forms the lower phase and the upper phase is acidic. Repeated washings of the ionic liquid was carried out until the upper aqueous phase was no longer acidic.

The hexyl, octyl and decyl derivatives were prepared in a similar fashion, although the yield from the first step dropped to *ca.* 85–95%. All other parameters remained as described.

Acknowledgements

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Construction of bicyclo[2.2.2]octanone systems

by microwave-assisted solid phase Michael addition followed by Al_2O_3-mediated intramolecular aldolisation. An eco-friendly approach

Brindaban C. Ranu,*[a] Sankar K. Guchhait,[a] Keya Ghosh[a] and Amarendra Patra[b]

[a] *Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India*

[b] *Department of Chemistry, University College of Science, Calcutta-700 032, India*

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Summary

Microwave irradiation of a mixture of cyclohexenones and ethyl acetoacetate adsorbed on the surface of solid lithium *S*-(−)-prolinate which is then placed on a column of basic alumina leads to the stereoselective construction of bicyclo[2.2.2]octanone systems through Michael addition and subsequent intramolecular aldolisation.

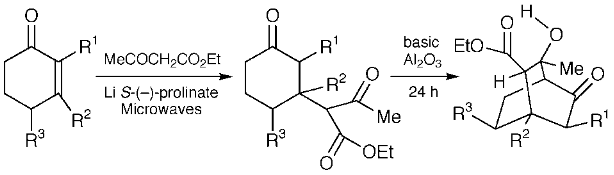
Introduction

Bicyclo[2.2.2]octane derivatives constitute an important class of synthons for natural product synthesis[1] as well as other synthetic applications.[2] Although there are a number of approaches for the construction of this system,[3] a simpler and environment friendly approach is still required. During the course of our investigations on the surface-mediated solid phase Michael reaction,[4] a mixture of cyclohexenone and ethyl acetoacetate adsorbed on the solid surface of lithium *S*-(−)-prolinate was microwave irradiated.[5] During purification of the crude reaction mixture through a column of alumina, very interestingly a small amount of a crystalline compound which was eventually found to be the bicyclo[2.2.2]octanone derivative **3a**, was isolated together with the usual Michael addition product. The importance of the bicyclo[2.2.2]octane system[1,2] prompted us to study the synthesis of this compound in a useful yield.

Results and discussion

In a typical procedure, a mixture of cyclohexenone and ethyl acetoacetate adsorbed on the solid surface of lithium *S*-(−)-prolinate was irradiated in a domestic microwave oven for 6 minutes and the reaction mixture (as a semisolid mass) was kept in a basic alumina column for 24 hours. Elution of the column (ethyl acetate) furnished the bicyclo[2.2.2]octanone derivative **3a** in 75% yield (Scheme 1).

The Michael adduct **2** undergoes intramolecular aldolisation[6] in the alumina column to form the bicyclo[2.2.2]octanone system. The reaction is found to be effective for substituted cyclohexenones also, although the yields of **3** from 2-methyl- and 3-methylcyclohexenones are relatively low. This is possibly due to the fact that these Michael additions are never complete leaving a considerable amount (20–25%) of unreacted cyclohexenones. Microwave irradiation with higher power or longer duration also did not help. However, in general, for all Michael additions microwave irradiation is essential as conventional heating in dry media (100 °C) leads to marginal addition products with



1 **2** **3**

1		Period of microwave irradiation/min	Yield of 3(%)^a
a	$R^1 = R^2 = R^3 = H$	6	75
b	$R^1 = Me$, $R^2 = R^3 = H$	14	60
c	$R^1 = R^3 = H$, $R^2 = Me$	15	55
d	$R^1 = R^2 = H$, $R^3 = Me$	15	72

^{a} yields refer to pure isolated products starting from 1

Scheme 1

Green Context

While the search for new more efficient catalytic systems including the substitution of catalysts for reagents, and the development of more environmentally friendly reagents are important aspects of clean synthesis, an equally important goal is the discovery of alternative greener routes. This article builds on the observation that during investigations on a Michael reaction under dry conditions, an unexpected product was also observed in small quantities. By-products are commonly observed in organic synthesis and are not usually welcome but in this case it turned out to be a valuable product. Progress in Green Chemistry will require the exploitation of such serendipitous observations. Here we can read how through observation, awareness of an opportunity and subsequent studies to maximise the by-product a new cleaner synthesis route to valuable products can be developed. ***JHC***

considerable amounts of polymeric material. Refluxing in THF also failed to produce more than 20% of the desired adduct. The aldolisation step is also best carried out in a column of basic alumina. Irradiation in the microwave oven beyond the Michael addition period does not induce aldolisation considerably. This process of Michael addition and subsequent aldolisation is stereoselective producing the bicyclo[2.2.2]octanone derivatives as crystalline compounds and single stereoisomers as revealed from ^{1}H and ^{13}C NMR data. To conclude, this protocol of Michael addition and subsequent intramolecular aldolisation on the solid surface for the stereoselective synthesis of functionalised bicyclo[2.2.2]octanone derivatives is novel, simple and has high potential for useful applications in organic synthesis. In addition, this reaction has been carried out in dry media under microwave irradiation avoiding any toxic reagent and solvent and the inorganic supports used can be recycled.

Although the use of lithium *S*-(−)-prolinate as a reactive surface in the Michael addition step was to induce optical activity, under the present reaction conditions this was not successful. However, further attempts to broaden the scope of this strategy and induce asymmetry in the Michael addition step will be our next goal.

Experimental

Typical general procedure for the synthesis of bicyclo[2.2.2]octanones. Synthesis of 3a.

A mixture of cyclohexenone (288 mg, 3 mmol) and ethyl acetoacetate (390 mg, 3 mmol) was absorbed uniformly on the surface of lithium *S*-(−)-prolinate powder (454 mg, 3.75 mmol), prepared by adding an equivalent amount of an ethanolic solution of lithium ethoxide to a solution of *S*-(−)-proline in ethanol followed by evaporation of solvent and drying under vacuum, and was then irradiated in a domestic microwave oven (BPL-Sanyo, India) at 240 W in an open round-bottomed flask fitted with a CaCl$_2$ guard tube for 6 min (irradiation for longer duration was made with a break after every 6 min). The remaining semisolid mass was then confined in a basic alumina column for 24 h. Elution of the column (ethyl acetate) furnished the bicyclo[2.2.2]octanone **3a** (508 mg, 75%), mp 80 °C; ν_{max}(KBr)/cm^{-1} 1720–1730(broad); δ_H (300 MHz, CDCl$_3$) 1.26 (3 H, t, *J* 7 Hz), 1.52 (3 H, s), 1.56–1.8 (4 H, m), 1.92–2.14 (1 H, m), 2.25 (1 H, t, *J* 3 Hz), 2.52 (2 H, br), 2.8 (1 H, dt, *J* 18 and 1.09 Hz), 3.2 (1 H, s) and 4.19 (2 H, q, *J* 7 Hz); δ_C (75 MHz, CDCl$_3$) 14.16 (CH$_3$), 19.59 (CH$_2$), 25.30 (CH$_2$), 27.47 (CH$_3$), 30.40 (CH), 40.37 (CH$_2$), 52.22 (CH), 55.72 (CH), 60.65 (CH$_2$), 72.83 (C), 171.90 (C) and 214.32 (C).

3b: mp 68 °C; ν_{max}(KBr)/cm^{-1} 1720–1730 (br); δ_H (300 MHz, CDCl$_3$) 1.13 (3 H, d, *J* 7.5 Hz), 1.29 (3 H, t, *J* 7.2 Hz), 1.46–1.56 (2 H, m), 1.56 (3 H, s), 1.76–1.77 (2 H, m), 2.36 (1 H, dt, *J* 18 and 1.1 Hz), 2.66 (1 H, br), 2.69 (1 H, s), 2.83–2.84 (2 H, m) and 4.24 (2 H, q, *J* 7.2 Hz); δ_C (75 MHz, CDCl$_3$) 12.11 (CH$_3$), 14.18 (CH$_2$), 20.18 (CH$_2$), 20.62 (CH$_2$), 27.85 (CH$_3$), 36.90 (CH), 41.78 (CH$_2$), 53.47 (CH), 55.49 (CH), 60.83 (CH$_2$), 72.79 (C), 172.30 (C) and 216.65 (C).

3c: mp 75 °C; ν_{max}(KBr)/cm^{-1} 1720–1735 (br); δ_H (300 MHz, CDCl$_3$), 1.04 (3 H, s), 1.30 (3 H, t, *J* 7.2 Hz), 1.35–1.42 (1 H, m), 1.48 (3 H, s), 1.76–1.93 (3 H, m), 2.32 (1 H, t, *J* 1.1 Hz), 2.49 (1 H, d, *J* 2.1 Hz), 2.94–3.08 (2 H, m) and 4.21 (2 H, q, *J* 7.2 Hz); δ_C (75 MHz, CDCl$_3$) 14.22 (CH$_3$), 19.49 (CH$_2$), 23.15 (CH$_3$), 27.69 (CH$_3$), 34.04 (CH$_2$), 35.72 (C), 45.32 (CH$_2$), 55.90 (CH), 57.30 (CH), 60.55 (CH$_2$), 72.55 (C), 171.64 (C) and 213.97 (C).

3d: mp 73 °C; ν_{max}(KBr)/cm^{-1} 1720–1730 (br); δ_H (300 MHz, CDCl$_3$) 1.01 (3 H, d, *J* 7.2 Hz), 1.30 (3 H, t, *J* 7.2 Hz), 1.30–1.32 (1 H, m), 1.55 (3 H, s), 1.92–1.95 (1 H, br), 2.02–2.15 (1 H, m), 2.2–2.32 (3 H, m), 2.50 (1 H, br), 2.54–2.79 (1 H, m), 2.90 (1 H, br) and 4.23 (2 H, q, *J* 7.2 Hz); δ_C (75 MHz, CDCl$_3$) 14.21 (CH$_3$), 20.37 (CH$_3$), 28.30 (CH$_3$), 29.23 (CH$_2$), 30.07 (CH), 34.82 (CH$_2$), 36.31 (CH), 54.34 (CH), 56.41 (CH), 60.88 (CH$_2$), 72.36 (C), 171.82 (C) and 213.65 (C).

Alternatively, the initial Michael adduct can be isolated by extraction of the lithium *S*-(−)-prolinate solid support with ethyl acetate followed by evaporation of solvent and then alumina column to obtain the same final product. The lithium *S*-(−)-prolinate can be recycled after being dried.

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Nafion resin–silica nanocomposite solid acid catalysts.

Microstructure–processing–property correlations

Mark A. Harmer,*[a] Qun Sun,[a] Alexander J. Vega,[a] William E. Farneth,[a] Alfred Heidekum[b] and Wolfgang F. Hoelderich[b]

[a] *DuPont Central Research and Development, Experimental Station, Wilmington DE 19880-0356, USA. E-mail: Mark.A.Harmer@usa.dupont.com*

[b] *Department of Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Germany*

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Summary

We have developed a new class of solid acid catalyst, a Nafion resin/silica nanocomposite, which effectively catalyzes a wide range of industrially important reactions. These include olefin isomerizations, alkylations, acylations, oligomerizations, the Fries reaction, esterifications and benzylations. We have found that the catalytic activity of these materials is dependent upon the synthetic conditions. The catalytic activity is related to the extent of dispersion of the Nafion resin acid groups within the porous silica framework. The use of an *in situ* sol-gel technique is preferred over infiltration of a pre-formed support with a Nafion solution. Here we show how we can use solid state NMR, electron microscopy and temperature programmed desorption to elucidate the chemical environment and dispersion of the acid sites. We also show how the microstructure may be tailored depending upon the synthetic conditions. This is a rare example of tuning catalyst activity for particular reactions. In the case of alkylations (such as formation of linear alkyl benzenes), transalkylation and acylation chemistry, the activities are increased several fold using a catalyst in which the Nafion resin is slightly aggregated. A highly dispersed form of the Nafion resin within the silica is preferred for dimerization chemistry. In the case of olefin isomerization chemistry, variations in the Nafion resin dispersion have little effect upon catalytic activity. A correlation of microstructure–processing–properties is described.

Introduction

Because of environmental concerns, there has been a strong interest in the use of solid acid catalysts as a replacement to homogeneous catalysts such as HF, $AlCl_3$ and H_2SO_4.[1–10] Although these latter catalysts are very effective, they produce highly corrosive media with chemically reactive waste streams. Purification can be both difficult and hazardous. The major challenge in this area is in the development of cost effective, highly active, selective and stable solid acid replacements. By contrast, the solid acid counterparts are easier to handle, purification is simpler and cheaper, and the general operation of a large chemical process is safer.

Over the years, a number of different types of solid catalysts have been developed ranging from sulfated zirconias,[1] heteropolyacids,[2] zeolites,[3,4,11–13] and perfluorinated resinsulfonic acids.[5,6] The exact nature of the acid site in these materials and a comprehensive approach to the acid strength remains an area of controversy.[7] In the case of sulfated zirconia, long term stability can be a problem due to loss of the active sites whereas in some applications zeolites have high initial activity. Stability however decreases due to the blocking of the small pores by larger product molecules and coke formation. There appears to be a need to fine tune catalyst properties for particular applications. No one single catalyst will be optimal for all acid catalyzed reactions.

Perhaps one of the better characterized solid acid catalysts can be represented by the perfluorinated resinsulfonic acids[5,6] which have been reported to have an acidity close to that of 100% sulfuric acid. In particular, Nafion resin which was developed about thirty years ago, is known to catalyze a wide variety of reactions.[5,6] Nafion is a copolymer derived from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether, which after hydrolysis of the sulfonyl fluoride, yields the strongly acidic terminal $CF_2CF_2SO_3H$ group. The equivalent weight of the polymer is typically about 1070 with an acid content of about 0.95 meq g^{-1}. This material is both chemically stable (as expected due to the fluorocarbon nature of the backbone) and thermally stable. Recent reports indicate that Nafion is thermally

Green Context

Nafion is a good example of a solid acid which through structural modification has been made more suitable for organic reaction chemistry. The composites with silica seem particularly promising as replacements for hazardous conventional acids such as hydrogen fluoride. However, like many solid acids, the nature of their activity is poorly understood—especially in terms of distribution of active sites and their local environments. Without this information catalyst optimisation is largely a serendipitous exercise. In this article by one of the pioneers of this type of material, we see how analytical techniques can inform us about the nature of the solid acids and how this information can help to improve catalytic performance.

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stable up to 280 °C, at which temperature the sulfonic acid groups begin to decompose.[14] One major drawback of the commercially available material (Nafion NR50 resin beads) is the very low surface area (0.02 m^2 g^{-1}). The activity of this material either in non-swelling solvents or in the gas phase is very low which in turn has limited the utility of these materials. In order to increase the acid site accessibility of this material we have recently described a new class of solid acid catalyst based upon a high surface area Nafion resin–silica nanocomposite[15] where nanometer sized Nafion resin particles are entrapped within a highly porous silica network. This significantly increases the effective surface area of the Nafion particles (within the porous silica) by orders of magnitude and as a result the catalytic activity of this material per unit weight of Nafion resin has been found to be increased up to 1000 times higher than in the pure polymer. A number of very promising applications of this composite material has been described in the literature, ranging from olefin isomerization,[16] Freidel–Crafts benzylation,[17] dimerization type chemistry,[18,19] the Fries rearrangement,[20,21] esterifications,[22] acylations[23] and a number of alkylation reactions.[15]

We have found that the catalytic activity of these new materials is dependent upon the processing variables, in particular, the source of the silica used. By altering the silica source, we can, in turn, alter the extent of dispersion of the Nafion resin within the porous silica framework. This change of the Nafion–silica microstructure in turn effects the catalytic activity. In the dimerization of α-methylstyrene a highly dispersed form of the Nafion gives the optimum activity. However, in the case of acylation or alkylation chemistry, a slightly aggregated form of the Nafion is preferred. Controlling and understanding the microstructure of these solid acid containing nanocomposites may allow one to fine-tune the characteristics of these materials to optimize both activity and selectivity.

Experimental

Materials. The Nafion resin solution (5 wt% Nafion in a mixed water–alcohol solution) is available from Aldrich. Sodium silicate solutions (20 wt% in silica) and tetramethylorthosilicate [$Si(OMe)_4$] are available from DuPont and Fluka and were used as received. Reagents used in catalysis studies were all of the highest grade available and the liquids were distilled and stored over molecular sieves before use.

Catalyst synthesis

The high surface area Nafion resin–silica nanocomposites were prepared according to previously published procedures.[15,24] A brief description of the two synthetic methods used is as follows. Both of these methods are based upon an *in situ* sol-gel technique. In one approach silicon alkoxides were used as the silica source and will be known as the Type 1 catalyst.[24] Typically 204 g of $Si(OMe)_4$ were stirred with 33 g of deionized water and 3 g of 0.04 M HCl for 30 mins. In a separate flask, 150 g of 0.4 M NaOH was added to 300 g of the 5 wt% Nafion containing solution. The silica containing solution was added to the basic Nafion containing solution and the whole system gelled to a solid mass in a few seconds. The gel was dried (90 °C, overnight) and re-acidified by repeated washing with 25 wt% nitric acid. Another approach was to use sodium silicate as the silica source. The resulting catalyst will be referred to as Type 2 catalysts. In a typical procedure, 200 g of a 10 wt% silica containing solution (*via* diluting down a sodium silicate solution) was added to 100 g of a 3 wt% Nafion containing solution and the pH adjusted to 7. Using this approach, the system gelled in about 10–15 s. In all of the catalyst testing, both Type 1 and Type 2 catalysts were fractionated in order to obtain particles of approximately the same size. We were able to alter the pore diameter for the Type 1 materials by adjusting the pH prior to gelation.[15] For Type 2, the silicate route, this was achieved by aging the wet gel at temperatures between room temperature and 90 °C, prior to drying. Using this approach, the pore diameter could be varied from about 100 to 200 Å, although these variations did not have a large effect upon the catalytic activity. The Nafion content of both catalysts was verified using both thermogravimetric analysis (using a TGA V5.1 from DuPont) and measuring the acid capacity. Typical Nafion loadings using the above procedure was about 13–14 wt% of Nafion.

Catalysis studies

Catalytic reactions were carried out using a batch reactor. In all catalysis experiments, the reactants and solvents were dried for at least 24 h over 4 Å molecular sieves, and the catalysts were dried for 18 h at 150 °C under vacuum. All of the reactions were performed under an atmosphere of nitrogen and the glassware was dried prior to use. The reaction rate was determined from the reactant conversion using only the linear section of the rate curves which essentially represents initial reaction rates. Liquid samples were taken at certain time intervals and separated from the solid catalyst by filtering. All the samples were analyzed by a Hewlett Packard 5890 Series II GC equipped with FID detectors. The product identification was carried out with a GC/MS analysis.

For comparative purposes an Amberlyst-15 resin was also used in some experiments. The Amberlyst-15 resin catalyst was washed with an acetone and water mixture several times until a neutral solution was obtained. The washed catalyst has an acid capacity of 4.3 meqH g^{-1}. Amberlyst-15 resin was dried at 110 °C. Benzene and 1-dodecene were purchased from Aldrich. Both reagents were distilled and 3 Å molecular sieves were added to keep the reagents dry. The purity of the 1-dodecene was 95%, which contained *ca.* 4% branched olefins.

Characterization

BET surface area, pore diameter, and BJH cumulative pore volume were obtained using a Micromeritics instrument. Scanning electron microscopy (SEM) was performed using a Hitachi S-5000SP scanning electron microscope.

Results and discussion

(I) Alkoxide based *in situ* Nafion–silica composites

We have developed Nafion resin–silica nanocomposites, made by an *in situ* sol-gel technique.[15] A detailed description of the silica chemistry can be found in the literature.[25] Soluble silica precursors, such as silicates or alkoxy silanes, were mixed with a nanometer-sized colloidal dispersion of Nafion in a polar solvent. As the gel was dried, the Nafion based particles became entrapped within the network as it was formed. Fig. 1 shows a schematic of how the composite was formed. The silica network forms *via* the aggregation of nanometer sized silica particles. The gel shrinks during this condensation stage. During the final drying, shrinkage is accelerated due to capillary forces which results in further condensation. A porous continuous network results with a very high surface area. The Nafion particles become entrapped within this porous network. The Nafion is readily accessible due to the pores in the silica network which are in the range of 10–25 nm. The final Nafion resin–silica nanocomposite is shown in Fig. 2.

The surface area of these new nanocomposites is approximately 20 000 times greater than that of the starting polymer, with surface area typically 150–500 m^2 g^{-1}. Variations of the synthesis can be used to alter pore structure, surface area and acid loading in order to optimize activity. The Nafion resin is dispersed throughout the porous silica network. As shown previously using energy dispersive X-ray analysis for elemental F (from the Nafion) and Si (from the silica) we have shown the two materials are intimately mixed at the nanometer level.[15]

(II) Dispersed Nafion catalysts on pre-formed supports

The *in situ* approach has many advantages compared to attempts to disperse the Nafion resin upon a pre-formed support. One alternative to the *in situ* method is to take a pre-formed high surface area silica support and deposit the Nafion over the entire support. We have found however, this approach has several drawbacks. Firstly, the Nafion resin solutions are not really true solutions, but a fine colloidal dispersion and the polymer does not significantly penetrate within the internal pores of the support, but sits as larger micron sized lumps on the outer surface of the support. Fig. 3 shows SEMs (including X-ray image analysis) resulting from the two synthetic approaches. We have used a number of pre-formed silica supports and the results were essentially the same for all of these. The support surface area was typically in the range of about 200–400 $m^2 g^{-1}$, with a pore diameter around 15 nm (for example using a Grace Davison 62 and Grace Davison 653 silica support). The highly dispersed and entrapped Nafion resin–silica nanocomposite *via* the *in situ* approach is unattainable using the pre-formed support. In this latter case the Nafion resin does not coat the bulk on the internal surface but rather coats the very low external surface area resulting in a film in the micron sized range (the coating is also non-uniform and some regions have no Nafion). Using this latter approach, a much poorer dispersion is obtained.

In addition to giving a much improved polymer dispersion the *in situ* approach leads to a more stable material with respect to solvent leaching. The nanocomposite can be stirred in refluxing ethanol for 48 h with no leaching of the Nafion (from TGA analysis and by measuring the number of acid equivalents), whereas using the pre-formed support, in excess of 40 wt% is washed off over the same period. The catalytic activity is also higher for the *in situ* nanocomposite versus using a pre-formed support. For the nanocomposite, the heptene alkylation of toluene and the 1-dodecene alkylation of benzene over a period of about 2 h gives conversons in the range of 90–95%. This is compared to about 25–50% for the pre-formed support. A number of other supports were also investigated (a range of low and high surface area silicas, some low surface area aluminas, some high porosity PTFE based supports such as Chromosorb T). In all cases, lower activities were found compared to the *in situ* method sol-gel method. In summary, the *in situ* approach appears to have the advantages of improved dispersion, higher effective surface area of the Nafion and improved stability, all of which lead to major improvements in catalytic performance.

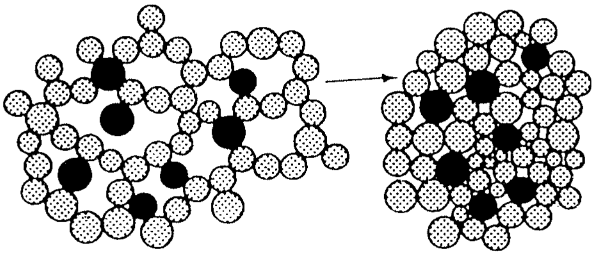


Fig. 1 The Nafion resin particles (●) become entrapped within the structure as the silica particles condense to form a network of porous silica gel.

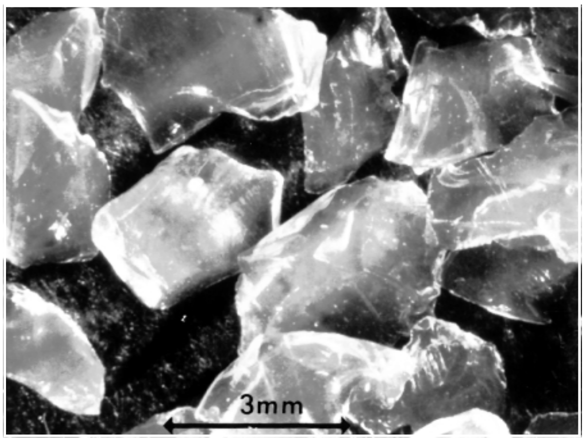


Fig. 2 Nafion resin–silica nanocomposite.

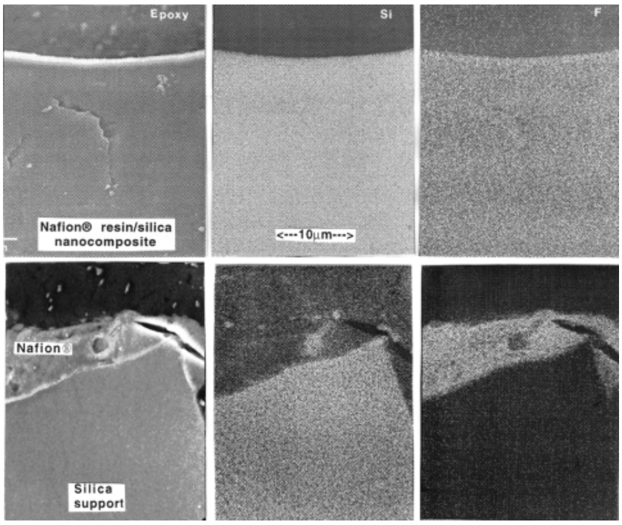


Fig. 3 SEM of an *in situ* developed Nafion resin–silica nanocomposite showing the Si map (top, center) and F map (top, right). Below shows an SEM of a material prepared using a pre-formed support (same scale), showing the Si map (center) and F map (right); the Nafion does not penetrate into the support but simply sits on the very outer surface.

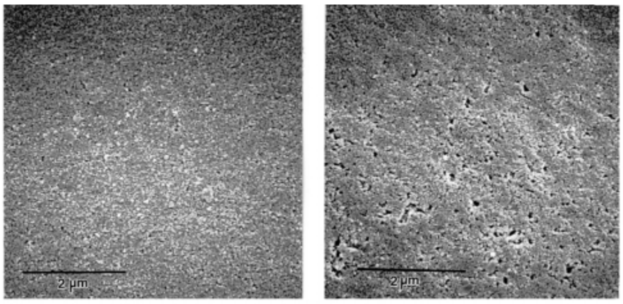
(III) Tailored Nafion–silica composites based upon *in situ* sol-gel techniques: characterization

We have also recently found that we can tailor the microstructure of the *in situ* prepared Nafion resin–silica nanocomposites. An initial report of this has appeared in the literature.[24] Small variations within the synthesis (mainly the nature of the silica network precursor) leads to pronounced changes in the catalytic activity. In going from an silicon alkoxide precursor (Type 1) to a silicate type precursor (Type 2), has in general led to an increase in catalytic activity compared to results reported earlier.[15]

Possible differences between the Type 1 and Type 2 catalysts can be elucidated using pore structure analysis, microscopy and temperature programmed desorption. In an earlier study, we suggested the Nafion particle size was in the range of 20–60 nm for the alkoxide source material. We examined the surface area, pore size, pore size distribution and pore volume of calcined composites (600 °C at which temperature the polymer is completely removed) and compared the before (polymer present) and after (polymer absent) microstructures. In the case of the Type 1 material the major changes in the pore structure occur in the 50 to 300 Å range. For Type 1, the nitrogen adsorption isotherms indicated that upon calcination the average pore diameter had increased to about 216 from 146 Å (the pore volume also went up to about 0.95 from about 0.75 cm^3 g^{-1}). Careful examination of the data indicates the Nafion particle size is in the range of about 5–30 nm (a bit lower than previously reported) with the majority in the range of about 10–20 nm. Before calcination, the porosity had an envelope in the range of about 80–250 Å with an average pore size of 146 Å. Upon calcination, the general envelope of pore size distribution (pore diameter for a particular pore volume) shifted to higher values. Control experiments with silica itself did not show any appreciable change after calcination to 600 °C. The increase in pore size and pore volume is consistent with the model that the Nafion is distributed throughout the silica at the 10–20 nm level.

In contrast, for the Type 2 material, only a small change (5%) occurred in the pore structure in 0–600 Å pore diameter range. The average pore diameter before calcination was about 138 Å and this shifted slightly to 149 Å (measured using nitrogen, BJH). The major change for the type 2 materials however occurred in the sub-micron range with a new collection of pores found in the 0.1 to 0.25 micron range using mercury intrusion data. The change over this region was not observed for the Type 1 materials. In this case, the data is consistent with the Nafion being dispersed throughout the silica at the 0.1 to 0.25 micron level with a much smaller population at the 10–20 nm level.

The difference between the two materials can also be seen in Fig. 4, using scanning electron microscopy. Fig. 4(*a*) shows the SEM (polished cross section) of the Type 1 Nafion resin–silica catalyst material, where the Nafion has been removed at 600 °C *via* calcination. We have used this approach before to highlight where the Nafion resided within the silica microstructure. As can be seen in Fig. 4(*a*), only small pores (consistent with our estimate above of < 30 nm sized particles) are evident. In Fig. 4(*b*) (for the Type 2 material) a new collection of pores on a larger scale (in the 0.1 to 0.2 μm range) is found. This is consistent with at least some of the Nafion particles aggregating into larger particles within the porous silica network. In all of these experiments several areas were investigated with similar findings.



(*a*) (*b*)

Fig. 4 SEM micrographs of Nafion resin–silica composites [Type 1(*a*) and Type 2(*b*)] after calcination to 600 °C.

The microscopy and pore size data are consistent with the Nafion resin in the Type 2 catalyst being more aggregated than in Type 1. This data is also consistent with some of the experimental observations during synthesis of these material. It was noticed that upon mixing the Nafion solution with sodium silicate (without the addition of acid to induce gelation) that the solution became slightly cloudy within a few seconds. When the solution was left overnight then the Nafion polymer settled out, above which was a clear silica containing layer. Such a settling was not observed upon mixing hydrolyzed alkoxide pre-cursors with the Nafion solution. It appears that the sodium silicate solution (with its very high ionic strength at pH 12–13) induces some slight aggregation of the Nafion polymer in which case it may be better to describe the Type 1 catalysts as 'dispersed' compared to the Type 2 catalysts.

Supporting evidence for this more aggregated Nafion resin dispersion comes from TGA/TPD experiments (adsorption/temperature programmed desorption) using isopropanol as the reactant. Essentially complete conversion to propylene and other hydrocarbons (secondary products) occurs on all three materials. The high temperature peak in the desorption from NR50 (and to a lesser extent the Type 2 composite) is mostly fragments of higher hydrocarbons, not propylene. Only on the Type 2 catalysts is there a very small amount of propanol evolved. At the same Nafion loading, the rate of adsorption of isopropanol within the sodium silicate derived composites, occurs at a much lower rate than using the alkoxide based materials. This is consistent with a larger Nafion domain size in the former case where the isopropanol uptake rates are more like that of pure Nafion. The desorption characteristics of the Type 2 catalysts are also more 'Nafion-like.' This is reflected in the broader desorption traces for primary products (propylene and water) and the appearance of a significant amount of secondary product formed for these materials, Fig. 5. The product desorption peaks for the Type 1 composite is complete at 150 °C. The desorption behavior of the pure polymer is not clean and extensive desorption still takes place at 200 °C due to the poor diffusion. The Type 2 material behavior is somewhat in between the two, which is consistent with a larger domain size of the Nafion within the Type 2 materials.

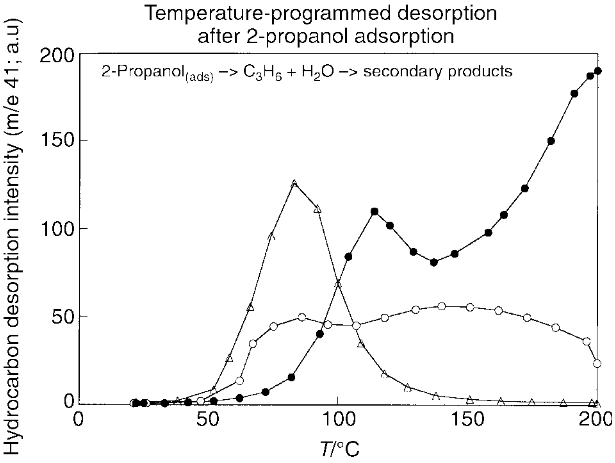


Fig. 5 Temperature-programmed desorption after 2-propanol adsorption on Nafion NR50 (●), Type 2 composite (○) and Type 1 (△). The ramp rate was 5 °C min^{-1}.

The microstructure of the two respective catalysts has been investigated using solid state NMR. For comparison the NMR of the pure polymer Nafion NR50 was also studied. Fig. 6 shows the proton MAS spectra of the 13 wt% Nafion–silica composites (both Type 1 and Type 2) upon gradual exposure to water vapor.

The interaction of the Nafion with water using MAS NMR at room temperature has been reported by Fraissard *et al.*[26] The chemical shift of the unsolvated hydronium ion in Nafion with one water molecule per acid site, determined by ^{1}H MAS NMR at room temperature, was reported to be 10.4 ppm relative to

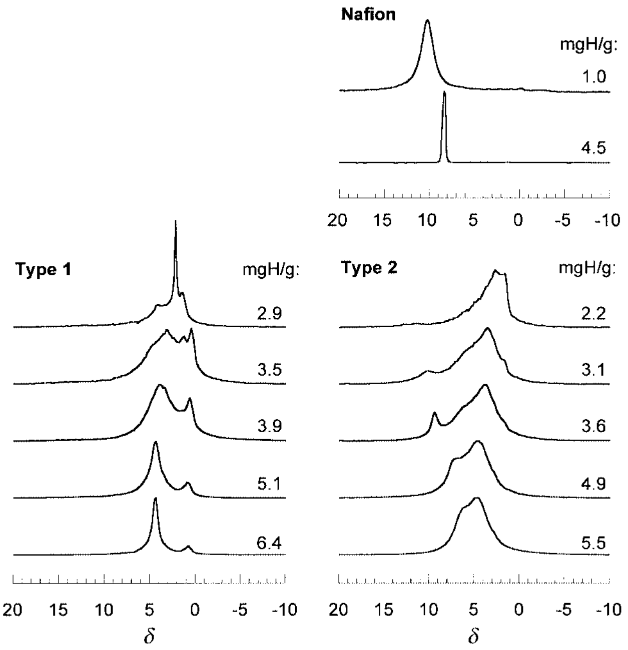


Fig. 6 Proton MAS spectra of 13% Nafion–resin silica composites shown for the Type 1 and Type 2 material as a function of gradual exposure to water vapor. The proton MAS NMR of Nafion is shown for comparison (top right).

external TMS. Upon increasing the water content (up to 2.1 water molecules per acid site), the chemical shift was found to decrease to 8.5 ppm. This is also in agreement with earlier studies where it has been found that the proton NMR of the Nafion decreases continuously with increasing water content. The peaks around 5 ppm and below are due to the silica network (silanols for example) and shall not be discussed further. These peaks are obtained when the synthesis is carried out in the absence of the Nafion. There is a clear difference between the Type 1 and Type 2 microstructure. In the case of the silicate derived material (Type 2) the proton NMR is characteristic of a composite of Nafion and silica. The chemical shift of the unsolvated hydronium ion in Nafion is present as a broad band around 10.4 ppm (in agreement with Nafion, ref. 26). As the water level increases, this peak becomes sharper and shifts to a smaller chemical shift (a value of 8.5 ppm at 5 H per sulfonate group). The peak position was in agreement with the proton NMR of bulk Nafion which shows a sharp peak at 8.6 ppm. In contrast, no peaks due to the hydronium ion of the Nafion, could be detected in the Type 1 material. The only signals observed correspond to shifts in the silicate spectrum. Although the exact reason for the apparent absence of the Nafion peak is not known, one possible explanation is that the acid sites are well dispersed on and within the silica surface. This may, in turn, lead to considerable line broadening. Consistent with the TPD data above the microstructure in the Type 2 composite is more ‘Nafion like’ than in the Type 1 composite.

(IV) Tailored Nafion–silica composites based upon *in situ* sol-gel techniques: catalysis

Table 1 shows a comparison of a number of catalytic reactions investigated using the Nafion resin–silica nanocomposites prepared from the two alternative silica precursors. In general, using sodium silicate as the silicate source (Type 2), leads to a Nafion resin–silica microstructure which is about 10 times more active in the industrially important area of alkylations than previously reported using the alkoxide route (Type 1),[15] specifically in the formation of cumene and linear alkyl benzenes, Table 1. Using the synthetic conditions as described above leads to materials with very similar pore structures. Typical values of surface area, pore volume and pore size for the Type 1 and Type 2 catalysts are 201 (m^2 g^{-1}), 0.77 (cm^3 g^{-1}), 146 Å and 165 (m^2 g^{-1}), 0.65 (cm^3 g^{-1}), 127 Å respectively. The Nafion content of both of these materials was in the range of 13–14 wt% (determined using TGA) and the number of acid sites *ca.* 0.15 meq g^{-1} as described previously.[15]

Table 1 shows the catalytic activity using the Type 1 and Type 2 catalyst for seven different reactions including alkylations, acylation, olefin isomerization, the dimerization of α-methylstyrene and hydroperoxide decomposition. Although both catalysts have a similar pore structure and Nafion loading the activity

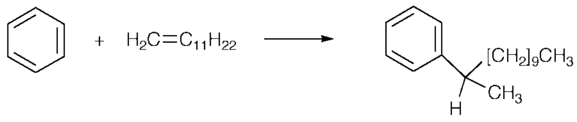
Table 1 Initial reaction rates for Nafion resin–silica catalyzed reactions in the liquid phase

	Rate [mM/(meqH+ h)]		
Reaction	Type 1 (*via* alkoxide route)	Type 2 (*via* silicate route)	Conversion[a] (%)
Benzene/dodecene alkylation (a)	32	430	99
Transalkylation (d)	1100	3086	98
Benzene propylation (c)	46	289	30
Freidel–Crafts acylation (b)	200	900	80
1-Dodecene isomerization (e)	1280	1580	99
AMS dimerization (f)	6500	1980	98
Hydroperoxide decomposition (g)	1750	1040	99

[a] Conversions shown are found using the optimum amount of catalyst (typically 5 wt% loading) according to the following conditions: (a) At 80 °C from benzene (21.5 g) alkylation with 1-dodecene (10 g) using 2 g of catalyst, 2 h, (b) acylation of *m*-xylene (21 g) with benzoyl chloride (10 g) at 140 °C, 2 h, 1 g of catalyst; (c) benzene alkylation with propene at 70 °C (using a 20 g solution of benzene saturated in bubbling propene) with 1 g catalyst, 1 h; (d) *tert*-butyl-*p*-cresol (10 g) with toluene (30 g) with 1 g of catalyst at 115 °C, 1 h; (e) 1-dodecene (25 g) at 80 °C with 1 g of catalyst, 1 h; (f) α-methylstyrene dimerization (6 g of AMS in 54 g of cumene as solvent, 0.5 g of catalyst added) at 50 °C, 20 min; (g) decomposition of cumene hydroperoxide (35 g) with 0.1 g catalyst at 50 °C to form phenol and acetone, 1 h.

varies quite dramatically. What is particularly interesting is whereas catalyst Type 2 is very effective for alkylation chemistry, the reverse is true in the case of the AMS dimerization and hydroperoxide decomposition. In the case of olefin isomerization, there appears to be only a small difference between the two materials investigated. For each reaction, the catalyst and conditions have been optimized to give very high conversions with good selectivity. The selectivity did not vary appreciably for the two different types of catalysts. As shown below, for example, the two catalysts gave about 28% of 2-dodecyl-substituted benzene. In the acylation type chemistry, the main acylated product (*ca.* 85%) occurs at the 4-ring position using 1,3-xylene, with minor amounts of the 5-ring (*meta* to the CH_3, *ca.* 1%) and about 13% in the 2-ring position. In the case of α-methylstryrene chemistry, the only three products observed were 2,4-diphenyl-4-methyl-1-pentene (**I**), 2,4-diphenyl-4-methyl-2-pentene (**II**) and the saturated dimer 1,1,3-trimethyl-3-phenylindan (**III**).[18] No higher oligomers were found. As shown in reference 18, typical selectivities were about 72% (**I**), 16% (**II**) and 12% (**III**). Similar values were obtained using either the Type 1 or Type 2 materials.

As shown above, we have been able to tune the catalytic activity of a number of industrially important reactions by tailoring the microstructure. A more detailed account of two of these reactions is described below. Improvements in catalytic activity have been found in a number of areas, for example in the area of alkylations and transalkylations. A good example of this was observed in the use of these catalysts in the formation of linear alkylbenzenes. Linear alkylbenzenes (LAB) are used in the production of linear alkylbenzene sulfonates (LAS), which are extensively used as surfactants. Over 2 million metric tons of LAB are produced each year. The total market for LAS exceeds \$30 billion. Currently, it has primarily been produced by the HF catalyzed alkylation of benzene with C_{10}–C_{16} olefins and the $AlCl_3$ catalyzed alkylation of benzene with chloroparaffins.[27] The products of these reactions contain a mixture of alkylbenzenes with the phenyl group attached to different C-atoms in the linear hydrocarbon chain. The 2-phenyl isomer is the most preferred product.



Branched isomers, which are a result of skeletal isomerization of the linear hydrocarbon chain, are very undesirable due to lower biodegradability. This leads to extensive environmental problems.[28]

Owing to the corrosive nature of mineral acids, solid acid catalysts have been sought for the production of LAB. Various solid acids including zeolites,[29,30] heteropolyacids[31] and clays[32,33] have been investigated for LAB formation *via* alkylation of benzene with linear olefins. Recently, UOP has developed a new process using a fluorided silica-alumina catalyst.[28] It was indicated that this process has two advantages over the HF process. It produces LAB with higher 2-phenyl isomer content (28% *vs.* 17% from HF in average) and higher linearity (94.5% *vs.* 93% from HF in average).

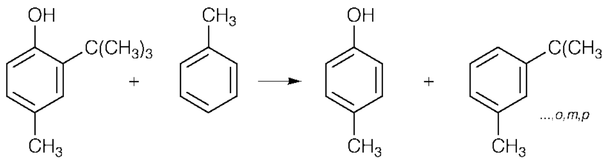
In this work we have studied LAB formation by using the alkylation of benzene with 1-dodecene. Both composite catalysts were tested. The composite catalysts not only show very high activity but also produced LAB with very high linearity ($>99\%$). The formations of linear alkyl benzenes (LAB) *via* the alkylation of benzene with 1-dodecene are listed in Table 1 for the Type 1 and 2 catalysts. With 2 g of the composite catalyst (Type 2), 99% dodecene conversion was obtained after 2 h at 80 °C, with an activity based upon initial reaction rates about 10× that of the Type 1 composites. At 99% dodecene conversion, the products contain $>95\%$ LAB and the remainder ($<5\%$) are the *ca.* 4% branched alkylates from the *ca.* 4% branched olefins (impurity in the feed), dimers of 1-dodecene and disubstituted benzene. The linearity of the alkylation using 1-dodecene is $>99\%$. The alkylation product distribution (among the LAB) changes with the benzene conversion. In general, at low conversion more 2-phenyldodecane is obtained. Values for the LAB product distribution are as follows: 2-Ø(28%), 3-Ø(19%), 4-Ø(16%), 5-Ø(17%) and 6-Ø(20%) where Ø denotes phenyl and the number refers to the substitution on the dodecene.

The LAB product distribution is quite typical from solid acid catalysts[34,35] including a mechanistic study by Beck *et al.*[35] who have shown the influence of transition state selectivity and/or pore diffusion on the isomer distribution. The 28% 2-phenyldodecane selectivity is significantly higher than that obtained from the HF process (15–18%). In addition to the high activity (high conversion) the major advantage of the Type 2 catalyst is the very low production of the undesirable branched alkylbenzenes, of which even in the UOP process *ca.* 5–7% are produced. This is primarily due to the fact that, unlike HF and $AlCl_3$, the Nafion–silica catalyst does not readily catalyze the skeletal isomerizations of linear olefins.

Interestingly, we have also found that the activity of the Type 2 catalysts was approximately 400× greater than an Amberlyst-15 and pure Nafion (Nafion NR50) catalyst (same weight of catalyst). Typical values of conversion (%) and initial reaction rate (mM/meqH^+ h) for the composite, Amberyst-15 and Nafion NR50 are 90(430), 4(1) and 1(1) respectively. In comparison to the pure polymer these results illustrate the greater accessibility to the strong acid sites within the high surface area composite (compared to the non-porous, non-swollen pure Nafion polymer) in this reaction medium. In the case of the Amberlyst catalyst these results presumable reflect the inherent higher acid strength of the perfluorosulfonic acids sites as compared to the phenyl sulfonic acids.

In conclusion, sodium silicate derived 13 wt% Nafion resin–silica composite is very active for catalyzing LAB formation *via* the alkylation of benzene with linear olefins. Very high linearity ($>99\%$) and higher 2-phenyldodecane selectivity are obtained compared to the current homogeneous acid catalyzed processes.

We have also found higher activities using the Type 2 catalysts in acylation and transalkylation chemistry. The transalkylation between 2-*tert*-butyl-*p*-cresol and toluene was studied.



Substituted phenols and derivatives are widely used in polymer resins, agricultural products, and antioxidants in fuels and fragrances. Transalkylation is a significantly more demanding chemistry than the alkylation of phenol with olefins, typically requiring strong acid catalysts and elevated temperatures. The reaction rate from the Nafion resin–silica (Type 2) was around 3 times higher than that from Type 1, with conversions of 99.6%. It appears that more aggregated Nafion resin particles in the composite may lead to higher activity for these more demanding chemistries in general. Comparisons of the Type 2 catalysts with Nafion and Amberlyst-15 also revealed higher activities. Typical values of conversion (%) and initial reaction rate (mM/meqH^+ h) for the composite, Amberyst-15 and Nafion NR50 are 99.6 (463), 87 (79) and 55 (27). Some swelling of the pure Nafion polymer does occur in these types of phenolic resins giving rise to modest activity although the improved dispersion within the composite leads to almost quantitative conversion. In both of the above reactions the use of an highly active solid acid catalyst will have a number of processing advantages over the homogeneous analogues. We have also found that these catalysts can be regenerated in most cases. As we have reported previously[24] for some reactions such as the isomerization of olefins, these materials exhibit excellent lifetime stability with greater than 10 000 turnovers. After this period the catalyst begins to loose activity and darkens in colour (brown). The catalysts can be regenerated using nitric acid (using 25 wt% HNO_3 at 50 °C for 4 h). We have restricted these studies to non-aromatic based reactants due to potential reactions of the aromatics with the nitric acid.

It is interesting to rationalize the microstructural causes for the activity patterns shown in Table 1. However, each one of these reactions has a unique structure–activity profile that ultimately derives from the combined effect of microstructure and a complex sequence of elementary kinetic steps that is different for each reaction type. We know very little about these mechanisms, so our observations about the underlying effect of microstructure is speculation, at best. With that disclaimer, here are some observations. The reactions that are faster for the Type 1 catalyst are those that are the most likely to be rate-limited by the initial proton transfer. We have demonstrated that proton transfer is rate-limiting for the AMS dimerization.[18] This is probably the case for the peroxide decomposition as well, where the protonated hydroperoxide–sulfonate anion pair should not be unstable. It seems logical that the reaction rates are optimized for the catalysts that have the better dispersed, more accessible acid site distribution when proton transfer is rate-limiting. On the other hand, reactions (a)–(e) probably all involve discrete intermediates in the rate limiting step. Reactions (a), (c) and (e) presumably proceed through protonated olefin intermediates, which are likely present under the reaction conditions, primarily as covalently bound sulfonate esters. We have evidence that the chemical rate limiting step in the 1-dodecene isomerization, (e), is ester decomposition. Similarly (a) and (c) are likely to proceed through sulfonate esters, and a key feature of the ester reactivity as an electrophile for aromatic substitution may be the energetic difference between its neutral and ion pair forms. The relative stabilities of neutral and ion pair structures will be sensitive to the microenvironment, a higher effective dielectric constant, for example, or a more fluid local ‘solvation sphere’, favoring ion pair stabilization. We speculate that the more ‘Nafion-like’ acid site environments of the Type 2 catalysts can enhance the rates of reactions like (a)–(e) through these types of medium effects on intermediate and transition state stabilities. In the case of the Type 1 materials we have modified the silanol groups (controlled reaction of these composites with HF vapor using an HF/pyridine mixture) to convert some of the Si–OH groups to Si–F groups. Treating materials prepared using the alkoxides leads to a five fold increase in alkylation activity. Again this reflects the importance of micro environments upon activity.

Two interesting reports by Palinko *et al.* [36] and Botella *et al.*[37] appear consistent with some of our findings. Palinko *et al.*[36] have reported on the surface characterization of both Nafion and a Nafion–silica composite catalyst by infrared microscopy. The composite was made using silicon alkoxide and would correspond in our study to a Type 1 catalyst. One conclusion reached was that of an interaction of the highly dispersed sulfonate groups SO_3H containing pockets of the Nafion and the hydroxyl groups of the silica within the composite. It was also suggested that this may lead to some decrease in acidity. The influence of the composition within the Nafion–silica composites on the isobutane/2-butene alkylation has also been reported.[37] A similar conclusion was also observed. In the highly dispersed Nafion in silica systems (made from silicon alkoxides), the sulfonic groups of the polymer interact to a greater extent with the silanol groups of the silica, resulting in a decrease in the activity of the sulfonic acid groups. In the Type 2 materials, where the Nafion is more aggregated, one would expect the interaction of the sulfonate groups (SO_3H) and the hydroxy groups (SiOH) of the silica to be considerably reduced, leading to a material with an acidity which is more ‘Nafion-like’. A more detailed study is required to fully understand all of these effects. Overall, then, we are inclined to think of the ratio of rates for Type 1 and Type 2 catalysts as the result of a trade-off between acid site accessibility, more favorable for Type 1 catalysts, and acid site ion pair micro-solvation effects, which may have a higher inherent acidity, more favorable for Type 2 catalysts. The observed activity is a complex function of the reaction mechanism and reaction conditions.

Summary

We have described a number of industrially important reactions that can be catalyzed by Nafion resin–silica nanocomposites. The activity of the catalyst is very dependent upon the processing. An *in situ* sol-gel method gives a catalyst with the highest activity. The sol-gel method can also be adapted to alter the dispersion of the Nafion within the porous silica network. This in turn has allowed fine tuning of catalyst activity. This kind of material may represent a very attractive alternative for the more hazardous homogeneous acids such as triflic acid, HF, BF_3 and aluminium trichloride.

Acknowledgements

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Dynamic behaviour of 1,1,2-trichlorotrifluorethane

on aluminium(III) chloride and related surfaces

David G. McBeth,[a] Margaret M. McGeough,[a] Geoffrey Webb,*[a] John M. Winfield,*[a] Archie McCulloch[b] and Neil Winterton[b]†

[a] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ.*
E-mail: J.Winfield@chem.gla.ac.uk
[b] *Research and Technology Department, ICI, The Heath, Runcorn, UK WA7 4QD*

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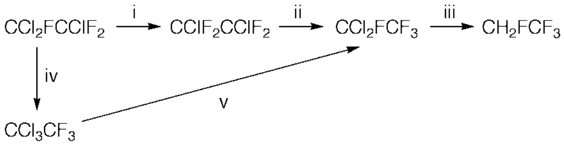
Summary

The isomerization of CCl_2FCClF_2 to CCl_3CF_3 is one of the steps in a possible scheme of reactions to convert CCl_2FCClF_2 to the more environmentally-acceptable refrigerant CF_3CH_2F. A reinvestigation of the isomerization in the presence of solid aluminium(III) chloride at ambient temperature indicates that the catalytically active sites for isomerization are generated *in situ* by the behaviour of aluminium(III) chloride as a chlorinating reagent towards CCl_2FCClF_2. Aluminium(III) chloride pretreated with CH_3CCl_3 exhibits very similar behaviour but γ-alumina chlorinated with CCl_4 shows little or no isomerization activity.

Introduction

One of the imperatives that underlie current research in the halocarbon field is the need to devise suitable methods for the destruction or conversion of compounds such as chloro- and bromo-fluorocarbons (CFCs and Halons) whose production and consumption may be prohibited by legislation following the Montreal Protocol and its successors. The methods selected should be capable of being operated on a reasonably large scale and are required urgently, not least as a discouragement to the illegal traffic in CFCs that has developed.[1] It is important that conversion processes do not result in the risk of toxic or ozone-depleting emissions and, ideally, they should lead to useful products. The literature relating to catalytic[2] or non-catalytic[3] methods for the oxygenation of CFCs is now extensive, the products being CO_2 and hydrogen halides. Catalytic hydrogenolysis, for example the conversion of CCl_2F_2 to the useful, low-temperature refrigerant CH_2F_2, is also attractive and this reaction is receiving considerable attention.[4,5]

Existing stocks of 1,1,2-trichlorotrifluoroethane held worldwide may be considerable, in view of its former use in a wide variety of industrial applications. In principle, the hydrogenolysis route is applicable here, Scheme 1. Steps i–iii of this scheme form part of the route used in a large scale process for the preparation of CFC-alternative refrigerant CF_3CH_2F (HFC-134a) from HF + C_2Cl_4/Cl_2[6] and aspects of the catalytic fluorination[7] and hydrogenolysis[8] reactions have received fundamental study. As an alternative, CCl_2FCClF_2 could be converted to CCl_2FCF_3 and hence to CH_2FCF_3, *via* the isomerization CCl_2FCClF_2 → CCl_3CF_3 followed by fluorination of CCl_3CF_3 to CCl_2FCF_3, steps iv and v of Scheme 1.



Scheme 1 Possible routes from CCl_2FCClF_2 to CH_2FCF_3. (i) Fluorination with HF, fluorinated chromia catalyst, refs. 6 and 7. (ii) Isomerization, fluorinated chromia catalyst, refs. 6 and 7. (iii) Hydrogenolysis, Pd/C catalyst, ref. 8. (iv) Isomerization, see text. (v) Fluorination, see text.

Here, attention is focused on the conditions required to achieve facile isomerization of CCl_2FCClF_2. Mechanistically, this is an interesting reaction. We have previously shown that on heavily fluorinated chromia at 700 K the reaction occurs *via* an intramolecular process in contrast to other transformations, chlorination or fluorination, that are intermolecular.[7]

It has been known for many years that CCl_2FCClF_2 is isomerized extensively to CCl_3CF_3 when it is refluxed in the presence of aluminium(III) chloride[9] and this has been the basis for a large scale batch process to prepare CCl_3CF_3 as a synthetic

Green Context

The safe destruction of CFCs is one of the major current issues in halocarbon chemistry. It seems likely that their production and consumption will be prohibited by the Montreal Protocol and related agreements. The remarkable volume of illegal traffic in these substances adds to the urgency to devise effective methods of destruction. Ideally their destruction should lead to other useful products and among the more likely are the more environmentally acceptable hydrofluorocarbons. This paper is concerned with one of the more important reactions that can be utilised in trying to achieve these goals—the isomerisation of 1,1,2-trichlorotrifluoroethane. *JHC*

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† *Present address*: The Leverhulme Centre for Innovative Catalysis, Dept. of Chemistry, The University of Liverpool, Liverpool L69 3BX, UK.

intermediate. Extensive chlorination of CCl_2FCClF_2 also occurs, the stated composition obtained from the reaction under laboratory conditions being CCl_3CF_3 (50%), CCl_3CClF_2 (40%), C_2Cl_6 (5%) and unchanged CCl_2FCClF_2 (5%). When [^{36}Cl]-labelled aluminium(III) chloride was used, the radiolabel was detected only in CCl_3CClF_2 and C_2Cl_6, suggesting that in this case the isomerization is also intramolecular.[9] This observation was the starting point for the investigation reported here, undertaken at room temperature under vapour–solid heterogeneous conditions. The original observations have been confirmed but, although isomerization and chlorination are nominally separate processes, the latter is required to produce the catalytically active sites for isomerization. These are believed to be related closely to the recently reported strong Lewis acid aluminium chlorofluoride.[10]

Results

The behaviour of CCl_2FCClF_2 vapour over resublimed solid aluminium(III) chloride, aluminium chloride sublimed directly onto calcined γ-alumina and γ-aluminina previously chlorinated with carbon tetrachloride has been studied at room temperature under static, anhydrous conditions. In some instances solids were pretreated with 1,1,1-trichloroethane to determine the effect of a supported organic layer[11,12] on the subsequent behaviour of CCl_2FCClF_2. The components of product mixtures were identified by ^{19}F NMR spectroscopy, GC and GCMS and, although the isomerization of CCl_2FCClF_2 under the conditions used was slow, its progress could be followed conveniently by quantitative IR spectroscopic measurements made over 24 h periods. Uptakes of CCl_2FCClF_2 and related CFCs by the solids were determined by mass balance measurements and changes occurring at the surface during series of catalytic reactions by direct Geiger-Müller monitoring[13] in experiments where [^{36}Cl]-labelled CCl_2FCClF_2 or aluminium(III) chloride were used. The key observations made, which must be taken into account in formulating a model to explain the dynamic behaviour of CCl_2FCClF_2, are summarised below.

Mass balance and spectroscopic studies

Solid aluminium(III) chloride and aluminium(III) chloride sublimed directly onto calcined γ-alumina are active catalysts for CCl_2FCClF_2 isomerization at room temperature, although their activity is reduced markedly by the presence of even trace quantities of water vapour. In contrast, γ-alumina chlorinated with CCl_4 shows little or no catalytic ability even though it, like solid aluminium(III) chloride, is a strong Lewis acid capable of room temperature dehydrochlorination of CH_3CCl_3 and subsequent oligomerization of the $CH_2{=}CCl_2$ produced.[11,12] Exposure of solid aluminium(III) chloride to CCl_2FCClF_2 vapour results in an immediate change in colour, colourless → pale yellow, and the retention of a substantial fraction of organic material which is removed only with difficulty by pumping at room temperature. After 24 h exposure, the major volatile product is CCl_3CF_3; minor products are the chlorinated species CCl_3CClF_2, CCl_3CCl_2F and C_2Cl_6 and traces of the fluorinated product, CCl_2FCF_3, are also present. However the symmetric isomers, CCl_2FCCl_2F and $CClF_2CClF_2$, were never observed in product mixtures. Analysis of the retained organic material indicated that C_2Cl_6 and CCl_3CClF_2 were present. Both compounds have very small vapour pressures at room temperature (C_2Cl_6, mp 463–468 K; CCl_3CClF_2, mp 314, bp 364 K) and their incomplete removal by static sublimation *in vacuo* does not necessarily indicate any significant interaction involving surface Al^{III} centres.

A similar pattern of behaviour was observed when samples of aluminium(III) chloride, were repeatedly exposed to aliquots of CCl_2FCClF_2 vapour (up to five) for 24 h periods. The results of two such experiments, including the experimental conditions used, are given in Table 1. In the first experiment complete consumption of CCl_2FCClF_2 was not achieved, although formation of its isomer, CCl_3CF_3, was always significant. In the second experiment, the highest conversions to CCl_3CF_3 were associated with prior addition of a CCl_2FCClF_2 aliquot from which the formation of highly chlorinated organics had been significant. Most importantly, there was no indication of a chlorine-to-fluorine mass balance, among the organic products, hence a dismutation of CCl_2FCClF_2 was unlikely. Analogous experiments using aluminium(III) chloride pretreated with CH_3CCl_3 led to very similar results (Table 2). There is no evidence that the highly unsaturated hydrochlorocarbon oligomers that are the result of the pretreatment,[11] inhibit the isomerization of CCl_2FCClF_2. The purple colour of the oligomer–aluminium(III) chloride surface was discharged during the course of an experiment, the solid becoming grey, and the proportion of highly chlorinated C_2 species in the volatile product mixture was somewhat higher (Table 2) than was the case using aluminium(III) chloride (Table 1). Interestingly, pretreatment of aluminium(III) chloride with aliquots of CCl_2FCClF_2, had no effect on its ability to catalyse CH_3CCl_3 dehydrochlorination.

Table 1 Mass balance data from multiple additions of CCl_2FCClF_2 to freshly sublimed aluminium(III) chloride[a]

	Addition number	Retained material[b] (w/w%)	Volatile material[c] (w/w%)	
			CCl_3CF_3	CCl_2FCClF_2
Expt. 1	1	25	69	trace
	2	0	35	62
	3	5	32	62
	4	3	57	37
Expt. 2	1	70	29	0
	2	85	13	trace
	3	10	84	0
	4	6	89	1
	5	48	48	2

[a] *Reaction conditions*: room temperature, 24 h, aluminium(III) chloride (expt. 1, 7.3 mmol, 0.976 g) or (expt. 2, 12.8 mmol, 1.710 g) sublimed directly into the reaction flask *in vacuo*, CCl_2FCClF_2, aliquots in the range 4–7 mmol. [b] Defined as (CCl_2FCClF_2 − volatile products) g × 100/(CCl_2FCClF_2) g [c] Defined as (product) g × 100/(CCl_2FCClF_2) g, individual components being determined using ^{19}F NMR. Other products observed after each addition were (w/w%): $CCl_2FCF_3 \leqslant 1$, $CCl_3CClF_2 \leqslant 3$, CCl_3CCl_2F trace; a build-up of C_2Cl_6 (identified by GCMS) on the solid was observed in each expt.

The decrease in CCl_2FCClF_2 in the vapour phase above solid aluminium(III) chloride, aluminium(III) chloride pretreated with one or more aliquots of CCl_2FCClF_2 or CH_3CCl_3 or γ-alumina-supported aluminium(III) chloride pretreated with CCl_2FCClF_2, were inversely related to the formation of CCl_3CF_3 in the vapour phase as demonstrated by IR spectroscopic measurements over 24 h periods. In all cases three isosbestic points were observed,

Table 2 Mass balance data from multiple additions of CCl_2FCClF_2 to freshly sublimed aluminium(III) chloride pretreated with CH_3CCl_3[a]

	Addition number	Retained material[b] (w/w%)	Volatile material[c] (w/w%)		
			CCl_3CF_3	Cl_2FCClF_2	CCl_3CClF_2
Expt. 1	1	45	24	6	6
	2	4	37	53	1
	3	3	36	54	3
	4	82	15	trace	trace
	5	95	0	0	0
	6	56	43	0	0
	7	98	0	0	0
Expt. 2	1	73	1	0	25
	2	25	67	trace	3
	3	38	59	trace	1
	4	30	55	0	9
Expt. 3	1	25	72	0	trace
	2	38	57	trace	3
	3	37	55	1	2
	4	75	17	trace	5

[a] *Reaction conditions*: room temperature, 24 h, aluminium(III) chloride (sublimed directly into the reaction flask *in vacuo* then pretreated with CH_3CCl_3 vapour for 1 h at room temperature; quantities of aluminium(III) chloride and CH_3CCl_3 were respectively: 0.01 and 0.03 mol (expt. 1), 0.49 and 0.06 mmol (expt. 2) and 8.7 and 3.9 mmol (expt. 3). [b] See note *b* in Table 1. [c] Defined as in Table 1. Product analyses by ^{19}F NMR (expts.1 and 3) or GC/GCMS (expt. 2). Other products observed after each addition were $CCl_2FCF_3 \leqslant 2$, $CCl_3CCl_2F \leqslant 1$, C_2Cl_6 and C_2Cl_4 (both trace).

indicating a direct relationship between consumption of CCl_2FCClF_2 and formation of CCl_3CF_3. However, neither of these processes followed simple first or second order kinetics under the conditions used.

The isomerizations of both CCl_2FCClF_2 and $CClF_2CClF_2$ are catalysed by fluorinated chromia at *ca.* 700 K under flow conditions,[7] but there was no evidence that isomerization of $CClF_2CClF_2$ occurred at room temperature in the presence of aluminium(III) chloride. No interaction was observed between solid aluminium chloride and $CClF_2CClF_2$ or n-C_6F_{14} (which has physical properties similar to CCl_2FCClF_2) but a mixture of solid CCl_3CClF_2 and aluminium(III) chloride did react slowly to give a mixture of CCl_3CF_3, CCl_3CCl_2F, CCl_2FCF_3 and CCl_2FCClF_2. It appears therefore that only chlorofluoroethanes containing CCl_xF_{3-x}, $x = 2$ or 3, groups interact with aluminium(III) chloride.

[^{36}Cl]-Radiotracer studies

The extent to which chemical reactions occurred at the surface of aluminium(III) chloride was highly dependent on the degree of hydration/hydroxylation of the surface. For example, the effect of trace H_2O, adventitious or deliberately added, on [^{36}Cl] exchange between $H^{36}Cl$ vapour and resublimed aluminium(III) chloride samples is shown in Table 3. The extent to which exchange was observed increased markedly when H_2O vapour was deliberately added to the surface prior to $H^{36}Cl$ and was usually measurable when the reagents had been manipulated in a Pyrex vacuum system. It was demonstrated many years ago that no observable [^{36}Cl] exchange occurred between $H^{36}Cl$ and solid aluminium(III) chloride when the materials were rigourously purified.[14]

In contrast, exposure of solid aluminium(III) chloride to [^{36}Cl]-CCl_2FCClF_2 led to the immediate observation of [^{36}C]-activity on the solid, the count rate due to [^{36}Cl]-CCl_2FCClF_2 vapour decreasing by 41% over 25 min in agreement with mass balance measurements that indicated 42% retention by the solid. Subsequent addition of aliquots of non-radioactive CCl_2FCClF_2 had little effect on the surface [^{36}Cl] count rate. [^{36}Cl]-Activity in the vapour phase was too small to quantify precisely but IR spectroscopy showed that CCl_3CF_3 was the major component. A very slow desorption process occurred over a period of weeks in the counting vessel resulting in a small increase in surface count rate, attributable to a reduction in the β^- self absorption effect from the [^{36}Cl]-species on the solid. This was accompanied by the observation of C_2Cl_6 on the walls of the vessel.

Table 3 [^{36}Cl] Exchange between solid resublimed aluminium(III) chloride and $H^{36}Cl$ at room temperature

Pretreatment of reagents	Fraction of [^{36}Cl] activity exchanged[a]
$H^{36}Cl$ distilled directly from P_4O_{10}	0.27, 0.24, 0
None	0.13, 0.36, 0.55, 0.59
$AlCl_3$ exposed to H_2O vapour	0.60, 0.78, 0.83

[a] Defined as $S_o - S_t/S_o - S_\infty$, where S_o and S_t are the [^{36}Cl] specific count rates [counts s^{-1} (mg AgCl)$^{-1}$] of $H^{36}Cl$ before and after exposure to aluminium(III) chloride; S_∞ is the specific count rate calculated on the basis of complete exchange.

Consistent with these observations, exposure of [^{36}Cl]-labelled solid aluminium(III) chloride to CCl_2FCClF_2 did not result in the incorporation of [^{36}Cl] into CCl_3CF_3, formed as a result of isomerization. It is possible that [^{36}Cl] was incorporated to a small extent into the minor, volatile components of the reaction mixture, CF_3CCl_2F and CCl_2FCClF_2, but this could not be established definitively.

Exposure of solid aluminium(III) chloride to [^{36}Cl]-CH_3CCl_3 at room temperature led to a rapid build-up of [^{36}Cl]-activity on the surface of the solid as the purple colour developed. The surface count rate was unaffected by removal of volatile products and fractionation of the latter indicated that $H^{36}Cl$ was formed. Addition of inactive CH_3CCl_3 to the [^{36}Cl]-labelled purple solid had no effect on the surface count rate, although a small quantity of $H^{36}Cl$ was detected in the vapour. The incorporation of [^{36}Cl] onto the surface when [^{36}Cl]-CH_3CCl_3 vapour was admitted to an unlabelled purple solid was minimal, indicating that the reaction depends on the availability of aluminium(III) chloride surface sites. Consistent with this view, no [^{36}Cl]-surface count rate and no colour change were observed when aluminium(III) chloride which had been pretreated with H_2O vapour was exposed to [^{36}Cl]-CH_3CCl_3. The reaction was not inhibited if H_2O vapour and [^{36}Cl]-CH_3CCl_3 were added concurrently. These observations, taken together, suggest that H_2O can block the adsorption of CH_3CCl_3 on aluminium(III) chloride but that it does not compete effectively with CH_3CCl_3, providing the latter is in large excess. The purple layer was hydrolytically unstable. Admission of H_2O vapour to the [^{36}Cl]-labelled purple solid resulted in a steady decrease in the surface count rate together with the colour changes, purple → brown → off-white. Some [^{36}Cl] was still retained however.

Admitting successive aliquots of CCl_2FCClF_2 to aluminium(III) chloride pretreated with [^{36}Cl]-CH_3CCl_3 as described above, resulted in behaviour which was similar to that observed for aluminium(III) chloride pretreated with [^{36}Cl]-CCl_2FCClF_2. Significant retention was normally observed and the major components in the vapour above the solid were CCl_2FCClF_2 and CCl_3CF_3, although the extent of conversion to the latter was generally less than observed with unlabelled CH_3CCl_3 (Table 2). [^{36}Cl]-Activity in the vapour was too small to quantify but admission of a CCl_2FCClF_2 aliquot did have an affect on the [^{36}Cl] surface count rate. An immediate change was observed when CCl_2FCClF_2 was admitted (increase or decrease observed in different experiments) but thereafter, the surface count rate remained constant over 24 h at its new value. The behaviour indicated that although there was no evidence for [^{36}Cl] incorporation during the isomerization, $CCl_2FCClF_2 \rightarrow CCl_3CF_3$, changes to the nature of the organic material coating aluminium(III) chloride did occur but in an unpredictable fashion.

The behaviour of CCl_4-chlorinated γ-alumina

γ-Alumina chlorinated with CCl_4 is a solid Lewis acid which like aluminium(III) chloride is capable of catalysing the room temperature dehydrochlorination of CH_3CCl_3 and the oligomerization of $CH_2{=}CCl_2$ so formed.[12] However mass balance and spectroscopic data obtained under identical conditions to those in Table 1 indicated that its activity for room temperature isomerization of CCl_2FCClF_2 was very low. Retention of organic material was observed in all reactions, up to 80% for extended exposure times. Samples of chlorinated γ-alumina that had been pretreated with CCl_2FCClF_2 showed no dehydrochlorination activity towards CH_3CCl_3, indicating that the Lewis acid sites required for dehydrochlorination had been blocked by the pretreatment.

Discussion

The elements of the model proposed to describe the dynamic behaviour of CCl_2FCClF_2 in the presence of solid aluminium(III) chloride at room temperature can be represented by the following:

(a) Adsorption (equation 1)

$$CCl_2FCClF_2\ (g) \rightarrow CCl_2FCClF_2\ (ad) \tag{1}$$

The experiments using [^{36}Cl]-labelled CCl_2FCClF_2 indicate that adsorption is rapid, that organic material is retained strongly at the surface and that desorption is slow. These conclusions are supported by mass balance data; analyses of product mixtures indicate that chlorination, isomerization and fluorination (albeit to a very small extent) occur.

(b) Chlorination (equations 2, 3 and 4)

$$CCl_2FCClF_2\ (ad) + AlCl_3\ (s) \rightarrow CCl_3CClF_2\ (ad) + \text{‘}AlCl_2F\text{’}\ (s) \tag{2}$$

$$CCl_3CClF_2 + AlCl_3\ (s) \rightarrow CCl_3CCl_2F + \text{‘}AlCl_2F\text{’}\ (s) \tag{3}$$

and

$$CCl_3CCl_2F + AlCl_3\ (s) \rightarrow C_2Cl_6\ (s) + \text{‘}AlCl_2F\text{’}\ (s) \tag{4}$$

Product analyses indicate that equation (2) represents an important reaction in the system. The reactions represented by equations (3) and (4), although less important, do occur as shown by the behaviour of solid CCl_3ClF_2 towards solid aluminium(III) chloride. The chlorination reactions lead to a build-up of organic material on the inorganic surface but they do not result in the rapid blocking of active sites for the isomerization of CCl_2FCClF_2.

Chlorination of C–F bonds by aluminium(III) chloride is well documented[9,10,15–17] although such reactions are usually performed above room temperature. The formation of an uncharacterized material, AlF_xCl_{3-x}, active for isomerization and dismutation of fluorohalocarbons, was reported[15] during a reexamination of the reaction of refluxing CCl_2FCClF_2 with aluminium(III) chloride. More recently, the very active Lewis acid catalyst, amorphous $AlF_{2.8-2.9}Cl_{0.2-0.1}$, has been described.[10] It is prepared from aluminium(III) chloride and CCl_3F in a reaction moderated by CCl_4. Calculated fluoride ion affinities of monomolecular aluminium(III) halides, $AlCl_{3-n}F_n$, $n = 0$–3, are high and from these it has been inferred that amorphous aluminium(III) chlorofluoride has surface sites having similar very high fluoride affinites.[10] The material described in equations (2)–(4) as ‘$AlCl_2F$’, although not characterised, may be similar.

(c) Isomerization (equation 5)

$$CCl_2FCClF_2\ (g) \rightarrow CCl_2FCClF_2\ (ad) \rightarrow CCl_3CF_3\ (g) \tag{5}$$

It is proposed that isomerization occurs at an ‘$AlCl_2F$’ site, *i.e.* a surface Al^{III} in a disordered F/Cl environment, rather than at $AlCl_3$ which is therefore the catalyst precursor rather than the catalyst itself. Isomerization *via* a long-lived surface (or other) intermediate is inconsistent with the IR results and the absence of substantial [^{36}Cl] incorporation into CCl_3CF_3 in the presence of labelled aluminium(III) chloride is less easily visualized if an intermediate of the type, $CClF_2CClFCl$ - - - $AlCl_3$, was involved. Therefore, it is reasonable to suggest that CCl_2FCClF_2 adsorbed at $AlCl_3$ results exclusively in chlorination while isomerization occurs exclusively at ‘$AlCl_2F$’ sites.

Consistent with this view is the inhibition of isomerization activity by trace H_2O, in agreement with an earlier observation,[15] as similar behaviour has been reported for amorphous aluminium(III) chlorofluoride.[10]

(d) Fluorination

Although fluorination does occur, it is relatively unimportant and was not detected in the initial study.[9] Conversion of a C–Cl bond to C–F by Al–F is thermodynamically unfavourable (unlike the analogous Cr^{III}/F/Cl system where the energetics are more balanced) and therefore extensive fluorination is not to be expected.

Conclusions

The most obvious way of modifying the catalytic properties of the archetypal solid Lewis acid, aluminium(III) chloride is by treatment with H_2O vapour even at a trace level. Experimentally this can be demonstrated by a change in the [^{36}Cl] exchange behaviour of $H^{36}Cl$ toward the solid (Table 3) and can result in complete inhibition of activity towards the room temperature dehydrochlorination of CH_3CCl_3. It is also likely to be a factor in explaining the degree of irreproducibility observed in the behaviour of CCl_2FCClF_2 towards aluminium(III) chloride samples (Table 1). More subtle is the modification of the surface that results from chlorination of CCl_2FClF_2 by aluminium(III) chloride which, we have argued, is required for the catalytic isomerization of CCl_2FCClF_2 to CCl_3CF_3 to occur. In this situation aluminium(III) chloride is the catalyst precursor rather than the catalyst and we speculate that the active site for isomerization is a surface Al^{III} atom in a disordered chlorofluoride environment. In view of the calculated F^- ion affinities of molecular binary and mixed aluminium(III) halides,[10] it is a moot point whether surface Lewis acidity is promoted by the fluorination process.

Somewhat surprisingly, the organic layer, comprising unsaturated oligomers derived from $CH_2{=}CCl_2$ which coats aluminium(III) chloride as a result of its exposure to CH_3CCl_3, has little or no effect on the CCl_2FCClF_2 isomerization reaction. The active sites required are still accessible, presumably due to the quasi-liquid nature[11] of the surface layer and deactivation by adventitious H_2O is still possible.

We have previously used the dehydrochlorination behaviour of CH_3CCl_3 at an inorganic solid as an operational probe for the Lewis acidity of its surface.[12] Using this criterion is was expected that the γ-alumina chlorinated using CCl_4 would be active in catalysing the isomerization of CCl_2FCClF_2 at room temperature. This material would be an attractive alternative to aluminium(III) chloride particularly for large scale use, since it is hydrolytically less sensitive and has a greater surface area. However its isomerization activity is negligible although organic material, which blocks the sites at which CH_3CCl_3 dehydrochlorination occurs, is retained by the solid. The behaviour of CCl_2FCClF_2 in the presence of this material differs from that exhibited in the presence of aluminium(III) chloride, either bulk or sublimed onto calcined γ-alumina. A possible reason is that the chlorinating ability of chlorinated γ-alumina is inferior to that of aluminium(III) chloride, presumably for kinetic rather than for thermodynamic reasons. We conclude that the intrinsic Lewis acid strength of surface sites in heterogeneous catalyses involving halocarbon compounds is only one of the factors that must be considered.

Experimental

Standard vacuum and glove box techniques were used throughout. Mass balance experiments were carried out using an evacuable, thin Pyrex bulb equipped with a side arm and designed to enable aluminium(III) to be transferred directly by sublimation *in vacuo*. Solid transfers were also carried out in a glove box but such samples had lower activity for isomerization. [^{36}Cl]-Radiotracer experiments were performed in a Pyrex counting cell equipped with two intercalibrated Geiger Müller counters, a moveable Pyrex boat which could be positioned under either counter, an ampoule from which a solid could be dropped directly into the boat *in vacuo* and a gas handling system. The principles that underlie the technique and the application of the method for the study of [^{36}Cl]-halocarbons at inorganic surfaces have been described elsewhere.[13,18] Studies of the isomerization of CCl_2FCClF_2 to CCl_3CF_3 by IR spectroscopy were carried out in a Pyrex cell fitted with an evacuable ampoule from which solid was dropped into a depression at the bottom of the cell. Windows were either KBr or AgCl. Spectral changes were monitored over 24 h, the cell holder ensuring that positioning of the cell in the spectrometer was reproducible. Instrumentation was: IR, PE 983; ^{19}F NMR, Bruker WP200 or AM200; GC, PE Sigma with FID and PE 8410 with hot-wire detection, 2 m packed column, calibrations being determined experimentally for all compounds; CGMS, VG 7070F.

Aluminium(III) chloride was sublimed before use (several times if required) as previously described.[11] Calcined γ-alumina (Degussa) was chlorinated with CCl_4 at 503 K for 6 h as described elsewhere.[18] Samples of resublimed aluminium(III) chloride and chlorinated γ-alumina were treated with CH_3CCl_3 vapour at room temperature in the mass balance or radiochemical counting cells as appropriate. Both solids behaved as previously reported.[11,18]

[^{36}Cl]-Labelled compounds were prepared as follows: CCl_2FCClF_2 by photolysis (medium pressure Hg lamp, silica vessel) of a 3:1 mixture of Cl_2 and CH_2FCHF_2, CCl_4 by the thermal reaction of a 1:1 mixture of Cl_2 and $CHCl_3$,[19] CH_3CCl_3 by the iron(III) chloride-catalysed addition of HCl to $CH_2{=}CCl_2$,[18] HCl by the reaction of Cl^- with conc. H_2SO_4[20] and Cl_2 by $KMnO_4$ oxidation of HCl.[21] Solid aluminium(III) chloride was labelled with [^{36}Cl] by exchange with CCl_4 at 60 °C for 24 h.[22]

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Paper a908406a

Catalytic cracking reactions of polyethylene to light alkanes in ionic liquids

Christopher J. Adams,[a] **Martyn J. Earle**[b] **and Kenneth R. Seddon***[b]

[a] *Institute of Applied Catalysis, PO Box 32, Prenton, Wirral, UK L43 5XT.*
E-mail: Chris.Adams@iac.org.uk; http://www.iac.org.uk/
[b] *The QUILL Centre, The Queen's University of Belfast, Belfast, Northern Ireland, UK BT9 5AG.*
E-mail: k.seddon@qub.ac.uk or m.earle@qub.ac.uk; http://www.ch.qub.ac.uk/krs/krs.html

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Summary

The cracking of polyethylene to light alkanes can be achieved in ionic liquid systems, such as 1-ethyl-3-methylimidazolium chloride–aluminium(III) chloride. The major products of the reaction are C_3–C_5 gaseous alkanes (such as isobutane) and branched cyclic alkanes, all of which are useful feedstocks.

Introduction

The catalytic cracking of polyethylene has been used as a process for its recycling and conversion into other valuable products.[1] To date, several different methods have been employed, which include pyrolysis,[2] catalytic cracking with zeolites or mesoporous materials,[3–5] use of supported chloroaluminate(III) catalysts[6] and reaction with supercritical water.[7] Here we report a new method for the cracking of polyethylene, using chloroaluminate(III) ionic liquids, which gives a significantly different spectrum of hydrocarbon products.

Room temperature ionic liquids such as [emim]Cl–$AlCl_3$ (X = 0.67)† ([emim]$^+$ = 1-ethyl-3-methylimidazolium cation, see Fig. 1),[8] have been found to be promising solvents for a wide range of industrial applications from petrochemicals,[9] bulk chemicals,[10,11] fine chemicals[12] and the treatment of nuclear waste.[13]

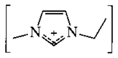

Fig. 1 Structure of the [emim]$^+$ cation.

Results and discussion

We have found previously that chloroaluminate(III) ionic liquids were capable of causing isomerisation and cracking reactions of fatty acid derivatives,[11] and we considered that similar reactions might occur with high molecular weight alkanes, such as polyethylene. The cracking reactions of polyethylene were investigated by suspending powdered low density polyethylene (LDPE) or high density polyethylene (HDPE) samples in several ionic liquids (typical data are included in Table 1). An acidic co-catalyst was added, such as [emim][HCl_2][14] (1 mol%) or concentrated sulfuric acid (2 mol%), and the mixtures were stirred at 90–250 °C for 1–6 days. It should be noted that the addition of a proton source to an acidic chloroaluminate(III) ionic liquid results in Brønsted superacidity of the proton.[15,16] The product distributions appeared to be independent of the ionic liquid cation used (ionic liquids tested include 1-butylpyridinium ([C_4py]) chloride–$AlCl_3$ (X = 0.67), [emim]Cl–$AlCl_3$ (X = 0.67), 1-butyl-3-methylimidazolium ([bmim]) chloride–$AlCl_3$ (X = 0.67) and LiCl–$AlCl_3$ (X = 0.67, and $T > 150$ °C) for a given temperature and time. Also, the type of proton source made little difference to the outcome of the reaction. For example, concentrated H_2SO_4 gave similar results to [emim][HCl_2] or water for concentrations less than 2 mol%. During the reaction, a gas was evolved from the surface of the polyethylene, which was collected in a cold trap (-196 °C) and analysed by gas chromatography and by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ (sealed tube). The volatile hydrocarbons isolated were all alkanes and had the chemical formula C_nH_{2n+2} (see Table 2). The reaction temperature appears to affect the composition of the volatile products formed. Typical compositions are given in Table 2, for reactions carried out at 120 and 200 °C. At the higher temperature, a higher proportion of propane, and less pentanes were formed (Note: gas chromatographic analysis gave no evidence for the formation of methane or

Green Context

The cracking of polyethylene is one of the most important plastic recycling processes. Several methods have been reported for this process including catalytic reactions although the wide range of products can be a problem. Here the novel use of ionic liquids for polyethylene cracking is described. Apart from the inherent advantages of using these involatile liquids (see for example the article on p. 1 of this issue from Rogers' laboratory), the method is quite selective towards low molecular weight feedstocks—the best possible products from this cracking reaction. ***JHC***

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† The composition of a chloroaluminate(III) ionic liquid is best described by the apparent mole fraction of $AlCl_3$ {$X(AlCl_3)$} present. Ionic liquids with $X(AlCl_3) < 0.5$ contain an excess of Cl^- ions over $[Al_2Cl_7]^-$ ions, and are called 'basic'; those with $X(AlCl_3) > 0.5$ contain an excess of $[Al_2Cl_7]^-$ ions over Cl^-, and are called 'acidic'; ionic liquids with $X(AlCl_3) = 0.5$ are called 'neutral'.

ethane in this reaction). It is also interesting to note that the amount of hexanes and heptanes formed was less than 2%. A plausible explanation for this shift to alkanes of lower molecular weight and the increased amount of *n*-butane as the temperature increases is as follows. These cracking reactions probably involve the formation of carbocationic species,[17] as fragments are broken off from the polyethylene chain. This has a high activation energy barrier. This activation energy is lowered if the cations formed are tertiary cations, as is the case with $[C(CH_3)_3]^+$ or $[(CH_3)_2CC_2H_5]^+$. The formation of secondary cations (leading to propane or butane) has a higher activation energy and hence lower quantities are observed. As the reaction temperature is raised, it becomes easier to overcome the activation energy barrier to form the secondary carbocations and hence more of the products derived from secondary carbocations are observed. Products derived from primary cations (methane and ethane) are not observed.

The low-volatility liquid products of the reaction (resembling turpentine spirit in smell) floated on the surface of the ionic liquid and were collected by washing the ionic liquid with an inert solvent (such as cyclohexane). The amount of low-volatile products formed appeared to show a slight temperature dependence. At higher temperatures, more volatile products were formed, as would be expected, because of the increase in entropy due to the formation of gaseous products. Analysis of this low-volatility liquid by ^{1}H and ^{13}C NMR spectroscopy showed that it was composed of a large number of alkanes. The spectra suggested that the alkanes possessed cyclic structures and that a considerable amount of branching had occurred. These products typically consisted of a large number of hydrocarbons that contain features such as cyclohexyl and cyclopentyl rings, methyl groups, attached to aliphatic rings, isopropyl groups and short CH_2 chains. Integration of the ^{1}H NMR spectra revealed that approximately 33% of the hydrogen atoms occurred in terminal methyl groups (mostly as doublets at 0.85 to 0.90 ppm), and the remainder were in methylene or methine groups. The low-volatile alkanes were further analysed by GCMS to identify individual components of the mixture. There is strong evidence here for the presence of numerous polycyclic aliphatic hydrocarbons, with several fused rings per molecule. The molecular weights of the products were all above 162, which corresponds to $C_{10}H_{18}$ (perhydronaphthalene). It is of interest to note that over 10 isomeric compounds with the formula $C_{17}H_{28}$ were detected. This formula corresponds to the aliphatic backbone of many steroids. Based upon the NMR and GCMS evidence, possible structures as shown in Fig. 2 would be typical of the compounds present.

An important feature of these ionic liquid reactions is that there is no evidence for significant formation of aromatic compounds or olefins. The only non-alkane product observed, usually at temperatues above 200 °C, was a black solid of high carbon content. The ionic liquid process contrasts with the cracking reactions carried out in the presence of supercritical water[7] where a mixture of *n*-alkenes and *n*-alkanes are formed, or with zeolites[3,18,19] where a wide range of hydrocarbons are formed, including aromatics, alkenes and alkanes. The volatile compounds produced in the ionic liquid reactions have the formula C_nH_{2n+2}. In order for the hydrogen balance to be maintained, in going from $(CH_2)_n$ to C_nH_{2n+2}, compounds must be formed that have a hydrogen to carbon ratio of less than 2. This is achieved in the reaction by the formation of cyclic and particularly fused cyclic alkanes as in Fig. 2. This type of behaviour has been observed in the reactions of methyl oleate[11] and methyl stearate[20] in [emim]Cl–$AlCl_3$ (X = 0.67), where oligomerised products (particularly the trimer of methyl oleate or methyl stearate) contain several carbocyclic rings.[11,20] An explanation as to why no alkenes are observed is that alkenes (*e.g.* methyl oleate) rapidly

Table 1 The reaction of polyethylene in several ionic liquids

Entry	Polymer	Ionic liquid	T/°C	t/h	Yield (%)	Low-volatility to volatile product ratio
1	HDPE	[emim]Cl–$AlCl_3$ (X = 0.67)[a]	120[b]	72	95	1.2
2	HDPE	[emim]Cl–$AlCl_3$ (X = 0.67)[a]	200	72	90	0.8
3	LDPE	[emim]Cl–$AlCl_3$ (X = 0.67[a]	120[b]	72	68	0.8
4	LDPE	[C_4py]Cl–$AlCl_3$ (X = 0.67)[a]	120[b]	72	62	1.0
5	LDPE	[bmim]Cl–$AlCl_3$ (X = 0.67)[a]	120[b]	72	60	1.0
6	LDPE	[bmim]Cl–$AlCl_3$ (X = 0.67)[c]	200	48	85	0.9
7	LDPE	LiCl–$AlCl_3$ (X = 0.67)[c]	250	24	95	0.6[d]

[a] 1 mol% of [emim][HCl_2] used as co-catalyst. [b] Reaction heated to 90 °C for 72 h before being heated to 120 °C. [c] 2 mol% of concentrated sulfuric acid used as co-catalyst. [d] Some decomposition to carbon observed due to the high reaction temperature.

Table 2 Composition of the volatile hydrocarbons in the cracking of polyethylene in Table 1

Volatile alkane product	Composition at 120 °C for entry 1 (%)	Composition at 200 °C for entry 2 (%)	Composition at 200 °C for entry 6 (%)
Propane	10	35	30
2-Methylpropane	55	50	45
2-Methylbutane	20	5	5
Butane	5	10	15
Others	10	5	5

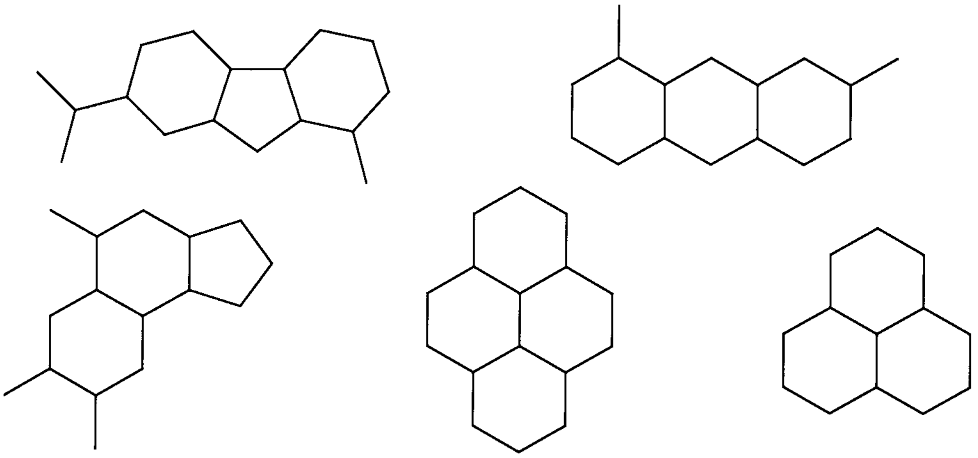

Fig. 2 Proposed typical structures of low-volatility alkanes obtained.

oligomerise in acidic chloroaluminate(III) ionic liquids.[11] So if alkenes are formed during the reaction, they would rapidly polymerise as soon as they are formed.

Conclusion

The cracking of polyethylene to gaseous alkanes and low-volatile cyclic alkanes in chloroaluminate(III) ionic liquids provides an effective means of converting polyethylene into useful low molecular weight feedstock hydrocarbons. Yields as high as 95% with HDPE have been obtained. The reaction is thought to be superacid catalysed, as a proton source is needed.[15–17] Another attractive feature of this reaction is that the products are very easily separated from the ionic liquid by solvent extraction or other physical separation processes, enabling the ionic liquid to be reused in further reactions. A final point to note is that the rates of these reactions are highly dependant upon the surface area of the polyethylene in contact with the ionic liquid. This means that the polyethylene must be finely powdered for the reaction to succeed. Between 130 and 180 °C the polyethylene melts and the surface area in contact with the ionic liquid is reduced. Above 180 °C, efficient stirring must be employed to disperse the molten polyethylene in the ionic liquid.

Acknowledgements

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Paper a908167d

A solvent-free Jacobs–Gould reaction

Teresa Cablewski, Paul A. Gurr, Peter J. Pajalic and Christopher R. Strauss*

CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia

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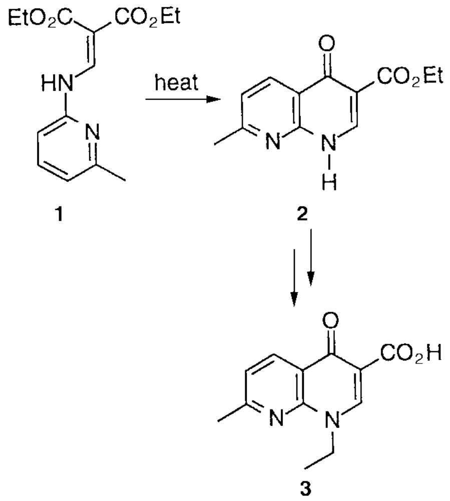
Summary

The Jacobs–Gould intramolecular cyclisation of diethyl *N*-(6-methyl-2-pyridyl)aminomethylenemalonate (**1**) to 3-ethoxycarbonyl-7-methyl-1,8-naphthyrid-4-one (**2**) was conducted without solvent. Empirical kinetic data were extrapolated to determine optimal reaction conditions. In contrast with established methods employing heat transfer oils, the reaction proceeded in high conversion, rapidly, predictably and controllably, at temperatures near 400 °C. Since dilution was unnecessary, the procedure facilitated high throughput, was energy efficient, low polluting and offered convenient work-up. A continuous Jacobs–Gould reaction (of **1** to **2**) was demonstrated for the first time.

Introduction

Oils derived from biphenyl and diphenyl ether are commonly employed as diluents and heat transfer media for reactions at temperatures above 180 °C, and typically around 250 °C.[1] However, solidification of the individual components (biphenyl, mp 69–71 °C; diphenyl ether, mp 26–30 °C) or the eutectic mixture (mp 12 °C), can complicate isolation of products, particularly on the industrial scale. Losses of oil occur during recovery and purification, owing to penetration through valves, pumps and flanges and by evaporation through vents.[2] The vapours are disagreeable even at concentrations below 10 ppm and acceptable replacement oils are sought.[3]

However, a limited range of alternatives has led to such oils being used extensively for thermal processes *e.g.* in Jacobs–Gould reactions,[4] by which the quinolone ring systems of quinolone antibacterials can be formed.[1,5,6] To explore the feasibility of avoiding heat transfer oils, we have investigated the cyclisation of diethyl *N*-(6-methyl-2-pyridyl)aminomethylenemalonate (**1**) to 3-ethoxycarbonyl-7-methyl-1,8-naphthyrid-4-one (**2**), which is the key intermediate toward the first commercial quinolone antibacterial, nalidixic acid (**3**; see Scheme 1).[5]

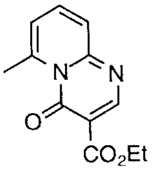


Scheme 1

Results and discussion

The roles of solvents, their function and selection criteria for environmentally benign chemistry were recently reviewed by Nelson.[7] For intramolecular transformations in particular, high dilution is employed to inhibit competing intermolecular processes. Clearly, if achievable, solvent-free intramolecular processes would be preferable.

To explore that possibility, neat methylenemalonate **1** was heated in Pyrex glass vessels for up to 50 min at 260, 270, 280, 290 and 300 °C. Low heating rates and temperatures facilitated formation of significant proportions of the pyrimidinone byproduct **4** by an alternative intramolecular ring closure. The highest conversion to naphthyridone **2** was 44% at 300 °C, after 5 min.[8] Although the maximum conversion increased with reaction temperature, extended heating, even at 260 °C, led to decomposition.



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From these experiments, the times required to achieve 10%, 20%, 30% and 40% conversions were plotted as a function of

Green Context

There are a limited number of suitable solvents for thermal processes such as the Jacobs–Gould reaction which can be used to form the quinolone ring system of quinolone antibacterials. High temperature solvents such as biphenyl and diphenyl ether are solids under ambient conditions, which complicates work-up and recovery. Ideally such reactions would be carried out in the absence of solvent which would simplify the procedure and minimise waste. In this article an effective solvent-free thermal reaction is described which leads to multiple green chemistry improvements, notably greater energy efficiency, simpler work-up and waste minimisation. The process has also been successfully extended to a continuous system. ***JHC***

temperature (see Fig. 1; semi-log scale). Extrapolation of the reaction times indicated the shorter periods and higher temperatures required for comparable conversions. These conditions were verified experimentally, as shown by data points for temperatures above 300 °C. Also, the plots for 30 and 40% conversion were more nearly co-linear than the 10 and 20% plots in Fig. 1. This suggested that as the yield increased, relatively minor changes in temperature and time substantially affected the outcome. A conversion of 40% or greater was only obtained at 290 °C and above (note that the 30% and 40% conversion plots do not meet the *y*-axis in Fig. 1) and decomposition occurred with longer heating times, so the useful heating period and temperature range both narrowed with increasing yields. These results indicated that optimal conditions would lie near the bottom right hand corner of Fig. 1, with temperatures of at least 370 °C and reaction times of less than 1 min.

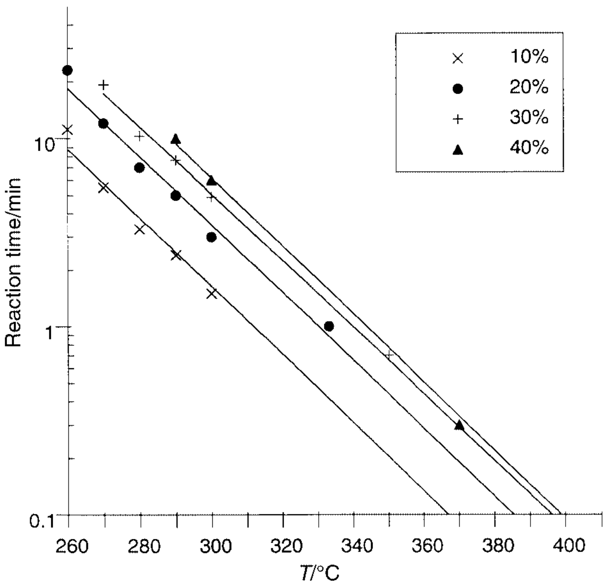


Fig. 1 Plots of reaction time against temperature for 10, 20, 30 and 40% conversions of **1** to **2**.

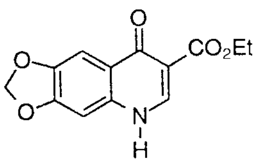
When such conditions were employed, greater conversions (over 80%) to **2** were obtained than over any time interval explored at lower temperatures. High precision was necessary, as the product polymerised if the heating was continued for even seconds beyond the required time. The optimal conditions (45 s at 385 °C) afforded **2** in 86% conversion.

The short heating periods enabled adaptation of the process for flowthrough operation. To our knowledge, this is the first example of a continuous Jacobs–Gould reaction and **2** was obtained in 79% conversion (see experimental).

From this work, Jacobs–Gould reactions can proceed in high conversion, rapidly, predictably and controllably, without a diluting heat transfer medium. Surprisingly, the optimal conditions involved considerably greater temperatures than have been employed traditionally. Since dilution was unnecessary, far less processing than before was needed to obtain a similar amount of product. Hence, the procedure was energy efficient, low polluting, convenient to work-up and afforded high throughputs of reactant. Interestingly, the mixture of biphenyl and diphenyl ether slowly decomposes near 400 °C and so it could not be used routinely at the optimal reaction temperatures anyway.[2]

Naphthyridone **2** has a high melting point and is insoluble in common solvents. Such characteristics are typical for crystalline compounds with extensive hydrogen bonding. Since recrystallisation was impractical, crude **2** was triturated and the impurities were leached at room temperature by acetone, diethyl ether or ethyl acetate, all of which could be recycled. By this process, **2** could be obtained in high purity.

Quinolone antibacterials constitute an important commercial class of antibiotics and there are now several such compounds on the market, with others undergoing clinical trials.[9] Some have a broader spectrum and are at least an order of magnitude more potent than nalidixic acid **3**. We have applied the developed methodology to the preparation of **5** and **6**. Both could serve as intermediates for analogues. Although the conversions were lower, the results were consistent with those for the cyclisation of **1** to **2**.



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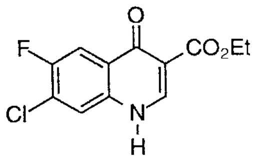

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We hope that these results and the methodology involving the extrapolation of empirical kinetic data to determine optimal reaction conditions, will encourage investigation of further thermal intramolecular processes under solvent free conditions.

Experimental

General

General procedures have been described previously.[10] Methylenemalonate **1** was produced by a literature method.[11] Physical data for products or synthesised reference compounds, agreed with literature values.

Continuous process

Methylenemalonate **1** at 170 °C, was pumped at a rate of 14 g per min through a stainless steel coil (14.8 mL, 3.8 m long, 2.8 m of which was immersed) heated in a fluidised sand bath at 380 °C. The product (effluent temperature 290 °C), which contained naphthyridone **2** (79%), **1** (8%), pyrimidinone **4** (5%) and unknown(s) (8%) was collected in chilled stainless steel vessels.

A sample (20 g) of the crude product was ground with a mortar and pestle and suspended in Et_2O (60 mL). The mixture was stirred at room temperature for 1.5 h and the solid removed by filtration. The leaching procedure was repeated twice more with Et_2O (48 and 40 mL, respectively), to afford naphthyridone **2** (15.4 g) in 94% purity, by ^1H NMR analysis.

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An efficient synthesis of 5-hydroxy-2(5*H*)-furanone

using a titanium silicate molecular sieve catalyst

Pradeep Kumar* and Rajesh Kumar Pandey

Division of Organic Chemistry: Technology, National Chemical Laboratory, Pune-411008, India.

E-mail: tripathi@dalton.ncl.res.in

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Summary

Titanium silicate molecular sieve, having MFI (TS-1) topology, efficiently catalyses the oxidation of furan to the corresponding 5-hydroxy-2(5*H*)-furanone in excellent yields, using dilute hydrogen peroxide (25%) as an oxidising agent; mechanistically the intermediacy of $^1O_2$ is proposed.

Introduction

Owing to the environmental and economic concerns in recent years, there has been a considerable upsurge of interest in the application of atom efficient catalytic methodologies to industrial organic synthesis. The synthesis of fine chemicals and complex organic molecules involving multisteps is normally associated with the production of large yields of by-products. As a result, the *E*-factor (weight of by-product per unit weight of product) is large and in the range 5–100.[1] The development of alternative environmentally benign synthetic routes is thus of primary concern. In the context of developing processes with low *E*-factor and high atom efficiencies, the use of environmentally friendly heterogeneous catalysts assumes significance as it results in waste minimization, safe and simple operations and easy work-up. The use of solid acids such as clays and zeolites as 'green' catalysts has been well established.[2,3] We have also exploited the catalytic potential of zeolites, mainly titanium silicate molecular sieve (TS-1), for various organic synthetic transformations.[4]

5-Hydroxy-2-(5*H*)-furanone is a key constituent in a number of biologically active compounds such as manoalide (a nonsteroidal anti-inflammatory agent), secomanolide, luffariellin, thoreotolide and cacospongiolide[5] *etc.* It has been used as a useful synthon in the total synthesis of portulal,[6] (*d*,*l*)-pyrenophorin, (*d*,*l*)-strigol[7] and camptothecin.[8]

Various methods for the synthesis of 5-hydroxy-2(5*H*)-furanone have been reported in the literature. The dye-sensitised oxygenation of furfural in ethanol followed by acid hydrolysis of the 5-ethoxy analogue is known to give 5-hydroxy-2(5*H*)-furanone.[9] The hydroxy furanone and its derivatives have also been prepared by the oxidation of 2-furoic acid *via* singlet oxygen generated by photochemistry[10] or by the reaction of furfural and hydrogen peroxide in the presence of a catalyst consisting of group V and VI metals of the periodic table.[11] The photoinduced oxidation of furan/furfural in ethanol in the presence of eosin for 9–18 d is reported to give 5-hydroxy-2(5*H*)-furanone in reasonably good yield.[12] However, many of these methods have several limitations: expensive and stoichiometric amount of the reagent, tedious work-up procedures, high temperature, multistep synthesis, low substrate concentration and long reaction times. Consequently there is a need to develop alternative reagents for this reaction. Here we report an efficient, high-yielding synthesis of 5-hydroxy-2(5*H*)-furanone by oxidation of furan over a TS-1/H_2O_2 system.

Experimental

Titanium silicate molecular sieve (TS-1) was prepared from tetraethylorthosilicate, tetrabutylorthotitanate, tetrapropylammonium hydroxide and water following the literature procedure.[13] The Si : Ti molar ratio of the sample was 33. The X-ray powder pattern of the calcinated sample of TS-1 is characteristic of the MFI structure. The Al-free titanium silicate (TS-1) retained its orthorhombic symmetry after calcination. A scanning electron micrograph of the TS-1 sample showed the absence of any amorphous material. The particle size of the cuboid-shaped crystallites range from 0.2 to 0.3 μm. The UV–VIS spectrum of TS-1 showed a band at 209 nm and the IR spectrum showed a characteristic absorption at 960 cm^{-1}.

In a typical experimental procedure, to a cooled solution (0 °C) of furan (2 g, 29.4 mmol) in acetonitrile (10 ml) were added TS-1 catalyst (0.4 g) and 25% H_2O_2 (9.6 g, 71 mmol). The mixture was stirred for 8 h and allowed to warm to room temperature. The catalyst was filtered off and the filtrate was concentrated and extracted with ethyl acetate, washed with aq. Na_2SO_3 and brine. The organic layer was separated and dried over anhydrous Na_2SO_4. Removal of solvent and subsequent silica gel column chromatography using light petroleum (bp 60–80 °C) : ethyl acetate (3 : 2) gave a colorless viscous oil which solidified on cooling. The solid was recrystallised from diethyl ether–light petroleum to afford 2.98 g (98.3%) of 5-hydroxy-2(5*H*)-

Green Context

The selective oxidation of simple precursors is one of the fundamental operations in chemistry. Many methods for these transformations are known, but are often associated with large quantities of transition metal waste. This paper demonstrates a highly selective and clean functionalisation of furan using titanium silicate TS-1, one of the most efficient solid catalysts for the selective oxidation of small molecules (channel diameter *ca.* 0.5 nm), and hydrogen peroxide, a cheap and clean oxidant. The product is a versatile intermediate in the synthesis of several bioactive compounds. ***DJM***

Table 1 Oxidation of furan by H_2O_2 over TS-1. Effect of the furan : H_2O_2 mole ratio

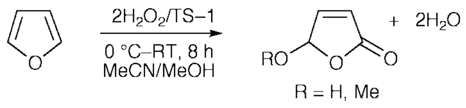
		Substrate		
Entry	H_2O_2/Furan (mole ratio)	Furan	H_2O_2 (25%)	Product yield[a]
1	0.6	2 g (29.4 mmol)	2.4 g (17.647 mmol)	0.876 g (29.8%)
2	1.2	2 g (29.4 mmol)	4.8 g (35.29 mmol)	1.74 g (59.2%)
3	2.4	2 g (29.4 mmol)	9.6 g (70.58 mmol)	2.89 g (98.3%)

Reaction conditions: acetonitrile (10 ml), 0 °C–room temperature, 8 h, catalyst wt% with respect to furan = 20. [a] Yields refer to isolated pure product.

furanone,[14] mp 56–58 °C, (lit.,[15] 58–59 °C). The physical and spectroscopic data were in full agreement with the literature data.[16,17]

Results and discussion

When furan **1** was treated with aq. hydrogen peroxide in acetonitrile in the presence of TS-1, the corresponding hydroxy lactone **2** was obtained in excellent yield (Scheme 1). Thus, furan reacted smoothly with the TS-1/H_2O_2 system and this transformation is first of its kind in the literature. Under similar conditions, cyclic 1,3-dienes containing other heteroatoms, *e.g.* thiophene, mainly gave the sulfoxide and sulfone as major products and the hydroxy enones were not formed. The reaction with 1,3-acyclic and cyclic dienes failed due to the consecutive and multiple reaction pathways open to these dienes.



1 2

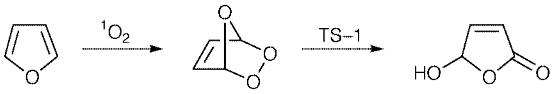
Scheme 1

The influence of furan/H_2O_2 mole ratio on the conversion and product selectivity is presented in Table 1. With the increase in H_2O_2/furan ratio from 0.6 to 2.4, there was a significant increase in the product yield. Thus the reaction gave almost a quantitative yield of the desired hydroxy lactone **2** with the use of excess of hydrogen peroxide (*ca.* 2.4 equiv.).

Similarly, the effect of different solvents on furan conversion and product selectivity was studied. Aprotic solvents like acetone and acetonitrile seem to favor the formation of the hydroxy lactone *vis-à-vis* protic solvent like methanol. It was observed that when methanol was used as solvent, apart from the hydroxy lactone (25%), another major product, 5-methoxy-2(5*H*)-furanone (75% yield), characterised by spectroscopic data, was formed due to the subsequent methylation of the corresponding hydroxy compound.

A time dependent study of the oxidation of furan with H_2O_2 in the presence of a varying concentration of the TS-1 catalyst indicated that even a small amount of catalyst (7.5 wt%) can significantly catalyse and accelerate the rate of reaction. As the concentration of the catalyst was increased, the reaction became faster. Thus 20 wt% (on the basis of furan) catalyst was sufficient to oxidise furan completely affording the corresponding hydroxy lactone. The use of other catalysts such as Sn-silicalite-1, vanadium silicates such as VS-1 or VS-2, and Cr-silicalite-1 failed to accomplish the same transformation.

Regarding a possible mechanism, some of the reactive species, *e.g.* hydroxyperoxy, peroxy in the presence of H_2O_2, are routinely being proposed for oxidation processes involving TS-1.[4,18,19] Alternatively, one could invoke the intermediacy of singlet oxygen[20] in the oxidation of furan. Presumably, the generation of singlet oxygen could be visualised from the hydroperoxo or peroxo titanium species. Indeed, when the endoperoxide[17] of furan was treated under TS-1 conditions, the formation of the hydroxy lactone **2** was observed indicating the intermediacy of $^1O_2$ in TS-1/H_2O_2 chemistry (Scheme 2). It should be mentioned that the oxidation of furan by singlet oxygen generated photochemically[17] or *via* the nonphotolytic method,[21] *e.g.* by the reaction of sodium hypochlorite and hydrogen peroxide, has also been widely investigated.



Scheme 2

Conclusion

In summary, a facile heterogeneous catalytic method for the oxidation of furan to the corresponding hydroxylactone has been developed. This method offers a practical alternative to conventional methods and the process itself is environmentally friendly with minimal waste.

Acknowledgements

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D-Gluconolactone

as a precursor to new environmentally benign tensioactive agents

Florence Garésio,[a] Nathalie Kardos,[a] Christian Bonnevie,[a,b] Serge Petit[b] and Jean-Louis Luche*[a]

[a] *Laboratoire de Chimie Moléculaire et Environnement, Université de Savoie-ESIGEC, 73376 Le Bourget du Lac Cedex, France. E-mail: Jean-Louis.Luche@univ-savoie.fr*

[b] *Laboratoire de Chimiométrie, Université Claude Bernard de Lyon, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France. E-mail: petit@cpe.fr*

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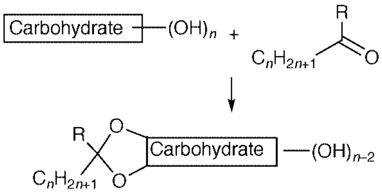
Summary

The conditions for the preparation of acetals with tensioactive properties from γ- and δ-gluconolactones and dodecanal and tetradecanal were studied. The role of the solvent, the catalyst and the influence of sonication on the yields (up to 60–80%) were examined, and a mechanistic interpretation is formulated.

Introduction

The chemical stability of conventional tensioactive agents synthetised from fossil resources is at the origin of many environmental problems,[1] making their replacement by eco-friendly substitutes highly desirable. This observation has prompted a research effort aimed at the exploitation of raw materials from renewable resources, and their transformation to new types of surfactants easily decomposed in the natural environment. A strategy was developed using a carbohydrate derivative as the polar hydrophilic part, and a fatty chain compound for the apolar part of the molecule.[2] The link between the two parts can be, among others,[3] an acid-labile acetal group (Scheme 1), and a number of compounds derived from such basic structures were shown to have excellent tensioactive properties. Cleavage to non-tensioactive fragments offers advantages both at the usage stage by permitting a progressive delivery of a bioactive substance, or the disposal due to their decomposition to products with minimised environmental impact.



Scheme 1 Acetalic carbohydrate-based tensioactive.

Among the carbohydrates tested, sucrose itself can be ketalised with diverse carbonyl compounds.[4] The reactivity is low, however, and indirect procedures from aldehyde dimethylacetals were used,[5] in some cases under sonication,[6] but even with this activation the yields remain modest. Another problem is the selectivity, due to the number of hydroxy groups, and protection steps are sometimes required.[5] The acetals derived from the available and cheap glucono- **1** or galactonolactones, which can undergo a nucleophilic ring opening to introduce a second apolar chain,[7] can be prepared in good yields,[8,9] but some drawbacks persist such as long reaction times, high amounts of catalysts, and the requirement for expensive (DMF) or toxic (benzene) solvents. All these elements prompted us to undertake an optimisation of the reaction shown in Scheme 2. Previous work in this laboratory[10] established that the experimental conditions published[9] can be improved by replacing benzene by hexane. Nevertheless, a few other parameters (catalyst, solvent, time, . . .) deserved examination to reach further improvements. This paper reports our recent findings.

Results and discussion

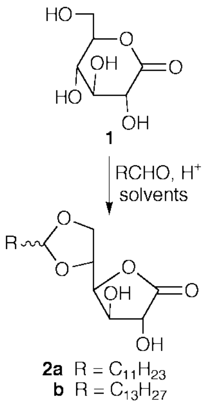
First, we found that the toxic hexane can be changed for cyclohexane, and toluene-4-sulfonic acid for methanesulfonic acid (MsOH), which is known to exhibit interesting characteristics in terms of green chemistry.[11] Thus, MsOH and cyclohexane have been systematically used in this work. Since the reaction medium is heterogeneous, all the experiments were duplicated under ultrasound irradiation.[12]

It was found that the optimal solvent composition corresponds to a DMF : cyclohexane ratio of 3 : 17 (Table 1). A further decrease of the DMF amount (2 : 18) slows down the process and degradations predominate. The sonochemical reactions provide satisfactory results, even if their advantage is not obvious. Despite extensive experimentation, reaction using octan-2-one gave the expected acetal in a disappointing 13–16% yield.

A most important question is that of the acetal structure. In a previous study,[10] we established that, contrary to literature data,[9] the product is a dioxolane (1,4-DGLA, **2**) derived from the

Green Context

Surfactants are used in great quantities in many applications, but suffer from several drawbacks. For example, their stability to biodegradation can often cause difficulties in the environment, and the reliance on fossil fuel as a source of raw materials is also a problem in the longer term. The development of novel surfactant structures derived from renewable sources is described in this article. The products are designed to degrade to materials without surfactant properties, making them less of a problem environmentally. Several experimental parameters are investigated with a view to optimising the environmental impact of the production of these new surfactants. ***DJM***

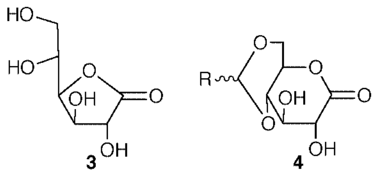


Scheme 2 Acetalisation of D-gluconolactone **1**.

Table 1 Acetalisation of D-glucono-1,5-lactone **1**

Entry	Aldehyde	Solvent[a]	Conditions	Yield[b] (%)
1	Dodecanal	A	Reflux, 4.5 h	67
2	Dodecanal	A	Reflux, 2.5 h	69
3	Dodecanal	A	Reflux, 0.5 h	37
4	Dodecanal	A	)))), 1.5 h	79
5	Dodecanal	A	)))), 0.5 h	42
6	Dodecanal	B	Reflux, 2 h	79
7	Dodecanal	B	Reflux, 0.5 h	38
8	Dodecanal	B	)))), 2 h	74
9	Dodecanal	B	)))), 0.5 h	33
10	Tetradecanal	B	Reflux, 2 h	60
11	Tetradecanal	B	Reflux, 0.5 h	56
12	Tetradecanal	B	)))), 2h	61
13	Tetradecanal	B	)))), 0.5 h	47

[a] Solvent A = DMF–cyclohexane (5:15, v:v); Solvent B = DMF–cyclohexane (3:17, v:v). [b] Isolated yield.



Scheme 3 Isomeric gluconolactone acetals **2** and **4**.

Table 2 Acetalisation of D-glucono-1,4-lactone **3**

Entry	Aldehyde	Conditions[a]	Yield[b] (%)
1	Dodecanal	Reflux, 2 h	70
2	Dodecanal	Reflux, 0.5 h	65
3	Dodecanal	)))), 2 h	70
4	Dodecanal	)))), 0.5 h	38
5	Tetradecanal	Reflux, 2 h	60
6	Tetradecanal	Reflux, 0.5 h	47
7	Tetradecanal	)))), 2 h	45
8	Tetradecanal	)))), 0.5 h	34

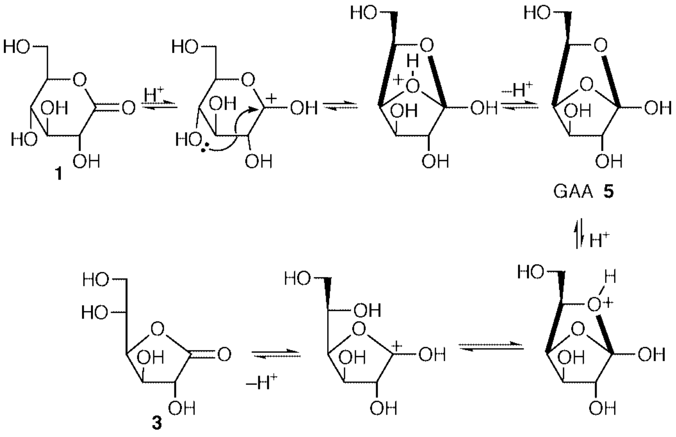
[a] Solvent = DMF–cyclohexane (3:17, v:v) in all the cases. [b] Isolated yields

1,4-gluconolactone **3** and not the 1,5-lactone derivative (1,5-DGLA, **4**) (Scheme 3).[13]

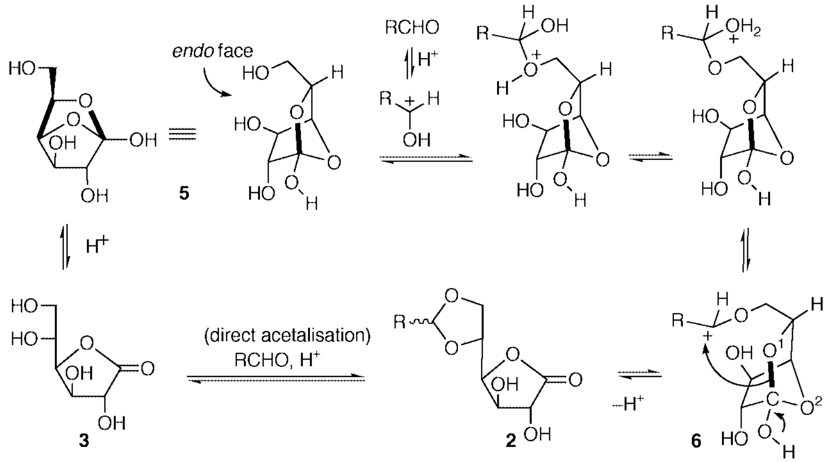
It can thus be envisaged that the formation of **2** occurs in two consecutive steps, a ring contraction followed by the acetalisation, making the lactone **3** a potentially better starting material. Therefore a second series of experiments was undertaken from this compound, prepared from the commercial lactone **1** by an acid catalysed ring contraction.[14] This translactonisation (a transesterification) should most probably proceed by a AAC2 process *via* the bicyclic GAA **5** as the tetrahedral intermediate known to be involved in such mechanisms (Scheme 4).[15]

Experiments run from **3** (Table 2) demonstrate that no obvious advantage results from its use to prepare **2** as compared to its isomer **1**, in terms of rates and yields. These results should mean that the pathway does not necessarily involve the sequence '**1** to **3** then **3** to **2**', which led to the proposal of an alternative interpretation (Scheme 5).

The key intermediate in these reactions should be **5**, formally an intramolecular acetal of gluconic acid, or a 'hemi-orthoester'. Thus, the **1** to **3** isomerisation implies a simple opening of the 6-membered ring of **5**, as shown in Scheme 4. On the other hand, the reaction of a carbonyl compound with the latter compound is actually a transacetalisation, the first step of which is the addition of the primary alcohol to the protonated aldehydic C=O group. Further steps consist in the elimination of water to give a carbocation which rearranges to the acetal in a rather straightforward manner. Two observations give substance to this proposal:



Scheme 4 Mechanism proposal for the ring contraction of **1** to **3**.



Scheme 5 Mechanism proposal for the formation of **2**.

(i) the steric crowding on the *endo* face of the transient **5** explains the poor reactivity of octan-2-one; (ii) the formation of 1,5-DGLA **4** is disfavoured since it would require the cleavage of the C–O^2 bond (see structure **6** in Scheme 5) to achieve the cyclisation on the cationic site on the opposite side of the molecule. If the direct acetalisation remains possible, it does not appear to be particularly favoured in terms of rates in comparison to the other route.

To conclude the present study, the results to be underlined are: (i) the acetalisation of the two isomeric lactones **1** and **3** provides the same product **2**, (ii) it is possible to achieve this transformation from commercially available materials, without the need to convert them to potentially more reactive compounds (including the use of aldehyde dimethylacetals), (iii) the use of a catalyst and solvents known to be more eco-friendly than in the previously published procedures, and (iv) the yields, up to *ca*. 80%. A more accurate view on the mechanism provides an unified explanation of the ring contraction leading to **3** and the acetalisation itself as well.

Experimental

D-Glucono-1,5-lactone **1** (from Aldrich, 1.07 g, 6 mmol, 1.2 equiv.), dodecanal (from Accros, 0.920 g, 5 mmol, 1 equiv.), MsOH (64.8 μL, 0.2 equiv.), and the solvents (total volume 20 mL) are refluxed (*ca*. 80 °C) in a round-bottom flask with a Dean-Stark water trap. The reaction is monitored by TLC. After completion and cooling, MsOH is neutralised with triethylamine (140 μL, 0.2 equiv.), the mixture is filtered through a 1:1 silica–alumina pad (1 g each) and the solvents evaporated *in vacuo*. The residue is purified on a silicagel column, eluting with cyclohexane–ethyl acetate (2:3) containing 1% NEt_3.

An alternative work-up can be used. After neutralisation, the two phases are separated. Water (10 mL) is added to the DMF (lower) layer, and the apolar products (residual aldehyde and other contaminants) are extracted with cyclohexane. The remaining milky suspension is then extracted with diethyl ether (3 × 15 mL). The ethereal phases are dried ($MgSO_4$) and the solvent evaporated.

The yellowish solid obtained after one of these work-ups is recrystallised from cyclohexane, providing the 1:1 mixture of stereoisomers of **2a** as white crystals, mp 108–109 °C (lit. 105–107 °C);[9a,16] ν(KBr)/cm^{-1} 3455, 2923, 2849, 1754, 1470, 1245, 1220, 1215, 1100, 1065, 962. δ_H(200 MHz, DMSO-d$_6$) 6.38 (dd, 1 H), 5.79 (dd, 1 H), 4.92 (t, 0.5 H), 4.80 (t, 0.5 H), 4.68 (t, 0.5 H), 4.57 (t, 0.5 H), 4.32 (m, 1 H), 4.2–3.69 (m, 4 H), 1.54 (m, 2 H), 1.25 (m, 18 H) and 0.86 (t, 3 H); δ_C(50.32 MHz, DMSO-d$_6$) 175.2, 103.6, 103.5, 81, 73.5, 73.3, 72.7, 72.5, 72.1, 71.9, 65.9, 65.4, 33.3, 33.2, 31.2, 28.9, 28.7, 23.5, 23.4, 22.0 and 13.9. MS (electron impact) for $C_{18}H_{32}O_6$: 344 (M$^+$), 343, 227, 189, 160, 143 (100%). **2b** from tetradecanal is obtained by the same procedures: mp 112–114 °C (lit., 112–115 °C);[16] ν(KBr)/cm^{-1} 3440, 2956, 2850, 1763, 1470, 1226, 1107, 1059 and 961. δ_H(200 MHz, DMSO-d$_6$) 6.40 (dd, 1 H), 5.78 (dd, 1 H), 4.90 (t, 0.5 H), 4.80 (t, 0.5 H), 4.68 (t, 0.5 H), 4.55 (t, 0.5 H), 4.35 (m, 1 H), 4.25–3.70 (m, 4 H), 1.70–1.45 (m, 2 H), 1.45–1.10 (m, 22 H) and 0.85 (t, 3 H); δ_C(50.32 MHz, DMSO-d$_6$) 175.2, 103.6, 103.5, 81.3, 73.5, 73.3, 72.7, 72.6, 72.1, 71.9, 65.9, 65.5, 33.3, 33.2, 31.3, 29.0, 28.9, 28.7, 23.4, 23.4, 22.0 and 13.9. MS (electron impact) for $C_{20}H_{36}O_6$: 372 (M$^+$), 371, 255, 189, 160, 143 (100%). The sonochemical experiments were performed in a glass vessel equipped with a condenser, using identical amounts of materials and solvents, with a Ultrason-Annemasse 30 kHz generator delivering an energy of 14 W, estimated calorimetrically.[17]

Acknowledgements

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Semi-continuous recovery of chromium from waste water

Kalarical Janardhanan Sreeram, Jonnalagadda Raghava Rao, Ramasubbu Sundaram, Balachandran Unni Nair* and Thirumalachari Ramasami*

Central Leather Research Institute, Adyar, Chennai, 600 020, India. E-mail: clrimd@vsnl.com

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Summary

The use of chromium(III) salts is under review by global industries. One of the options for better management of chromium is through recovery and reuse. Batch type processes for the recovery of chromium and subsequent use in tanning has already gained importance in the tanning industry. Here we describe a novel semi-continuous method for the recovery of chromium(III) from tannery wastewaters containing the metal ion. In this system, sodium carbonate is used as the alkali to precipitate chromium(III) as chromium(III) hydroxide, instead of magnesium oxide, which is preferred for batch type systems. The hydrostatic pressure build-up and turbulence within the reactor is modulated to achieve online separation of chromium(III) hydroxide. Under steady state conditions, the inflow into the reactor is matched by the outflow. The outflow from the reactor can be discharged without causing ground-water hardness.

Introduction

The manufacturing processes of leather tanning requires considerable quantities of water and discharges nearly 30–35 L of water for every kilogram of leather processed.[1] Nearly 90% of the leathers manufactured and currently used contain at least a minor quantity of chromium either as a tanning material or in dyes. The biotoxicity of chromium has been a subject of active discussion. The biological implications of chromium are known to vary with the oxidation state of the metal ion.[2,3] Oxyanions like chromates are well-established human carcinogens.[4] Numerous studies have attempted to determine the intracellular status of chromium as well as the chemical nature of the ultimate carcinogen or mutagen.[5] It has been reported that, once inside the cell, Cr^{III} species can be mutagenic and genotoxic.[6] The ability of Cr^{III} to (*a*) crosslink DNA and proteins, (*b*) participate in non-enzymatic phosphorylation and (*c*) influence calcium transport channels has been discussed.[7–9]

In view of the potential toxicity of some forms of chromium, the environmental regulatory norms stipulate that the levels of chromium in waste waters are controlled. The discharge norms for industrial waste waters in different countries specify permissible concentrations of chromium in the range of <0.3–2 ppm.[10] Such strict norms demand technological interventions for abating chromium pollution.

Chromium(III) recovery–reuse processes have now been accepted as the commercially most attractive.[11] It is now well established that the nature of alkali used in precipitating chromium(III) hydroxide influences the settling characteristics of chromium(III) hydroxide.[12] The characteristics of colloidal chromium(III) hydroxide particles are closely related to the zeta potential. Distribution of particle sizes, extent and degree of aggregation as well as settling behaviour and morphological properties of chromium(III) hydroxide vary markedly with the nature of alkali employed.[12]

Although chromium(III) hydroxide can be generated from aqueous solutions of Cr^{III} salts with almost any alkali at pH 7–10; the use of magnesium oxide is most extensive.[13] This is because of its high bulk density and good settling of particulate matter. The particle characteristics enable easy handling of chromium(III) hydroxide generated using MgO from solutions of basic chromium sulfate. The process is batch type and is simple.[14] The batch type process enjoys the advantages of (*a*) minimum process change in tanneries, (*b*) repeated recyclability of recovered chromium, (*c*) acceptable quality of leather after reuse of chromium and (*d*) a relatively short cost-recovery period of the initial installation investment.

MgO being a partially soluble alkali (0.00062 g/100 ml water), 2–3 h is required for raising the pH to desired levels of 8.0–9.0. Owing to the poor solubility of MgO, rapid addition of alkali may lead to the use of higher amounts of MgO rather than that required stoichiometrically. Commercially available magnesium oxide samples contain significant amounts of calcium salts as impurities. This could result in the generation of calcium sulfate, which is known to co-precipitate along with chromium(III) hydroxide. If inferior grades of MgO are employed in chrome recovery, special steps would be required to remove calcium sulfate from the

Green Context

The use of chromium in oxidation processes and in *e.g.* tanning applications is still widespread, and for many applications, suitable green alternatives are not likely to be ready for several years. The recovery of chromium is thus a current and significant problem. Precipitation using magnesium oxide can be used, but has limitations. For example it cannot be used on a very large scale, and if the waste water is contaminated with oils (used in tanning to produce soft leather) it is of limited efficiency. The process also produces a lot of magnesium sulfate. This article describes the development of a method based on the use of sodium carbonate, which is more tolerant of organic contamination. Furthermore, the process has been designed to run semi-continuously. This is difficult to do with the magnesium oxide process for a number of reasons: the particle morphology obtained with sodium carbonate is better; the precipitated chromium from the new process does not contain as much oil as in the original process; the rate of neutralisation is much faster and sodium does not form ‘soaps’ with the oils used in the tanning process. *DJM*

recovered chromium.[15] Further, the magnesium sulfate generated during the process is expected to render the ground water harder. At certain concentration levels the magnesium ion is a soil micronutrient. It is necessary to assess the carrying capacity of the region and balance the amounts of magnesium salts being added to the soil and ground water prior to the wide scale adoption of chromium(III) hydroxide recovery process in tannery clusters.

The volume of leather processing activity using chromium(III) tanning is increasing. Batch sizes of chromium(III) tanning activities are also on the increase. Large batch sizes of spent chromium(III) tanning liquors are becoming available for chromium(III) hydroxide recovery. Even when small production systems are involved, waste water management processes adopted are based on common effluent treatment plants. Logical support to common waste water treatment concepts demands common chromium recovery plants. Newer trends in high exhaust chromium(III) tanning as well as stringent regulations on chromium discharge would result in large quantities of spent liquors bearing lower concentrations of chromium. There is now a need to develop continuous chromium(III) hydroxide recovery concepts.

It is now a common practice to use oils and fats during the chromium(III) tanning process to obtain soft leathers. In these cases, magnesium oxide based recovery systems could result in the formation of magnesium soaps, which adversely influence the recovery and reuse processes.[16]

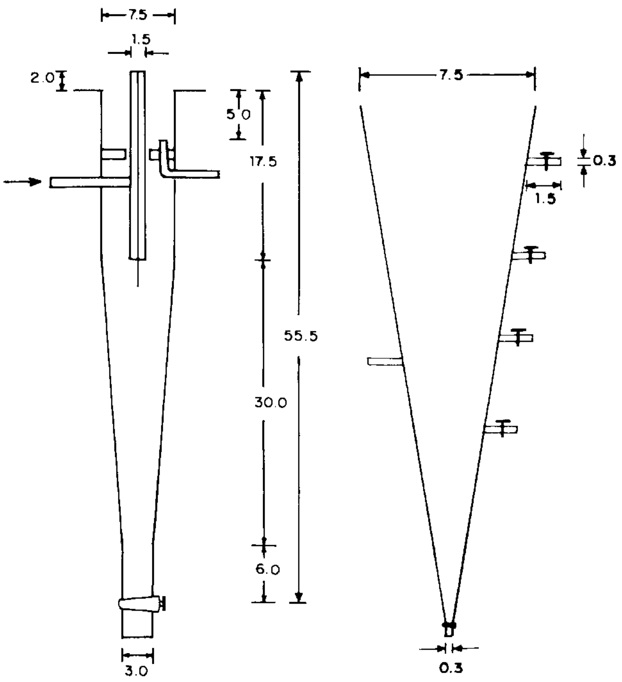
The higher bulk density of magnesium oxide based chromium(III) hydroxide favors its use over sodium carbonate or sodium hydroxide based systems. Since MgO is a low soluble alkali, the equilibrated pH after addition of MgO to the reaction media is not immediately established. Continuous chromium(III) hydroxide recovery systems demand the use of an alkali for which the equilibrated pH is established more or less immediately.

Experimental

Spent chromium liquor was generated from a typical chromium(III) tanning process. The solution was filtered through a Whatmann filter paper No. 1 and the concentration of chromium estimated spectrophotometrically as per standard methods.[17] The solution was then diluted to have an effective concentration of 1000 ppm Cr.

A semi-continuous chromium recovery process would need two vessels, one for the neutralization of the chromium liquor and the other for settling. While a cylindrical vessel was used for neutralization, a hopper bottom geometry was used for the settler. For efficient design of the equipment, the inflow of chromium bearing effluent into the settler and the outflow of chromium free supernatant need to be matched. The ratio of the volume of settler and that of spent chromium liquor was chosen to be one third of the total volume of spent chromium liquor being treated. A secondary settler of one-third the volume of the primary settler was included in the design as earlier investigations have reported that 30% of the chromium(III) hydroxide particles are fine (0.1–10 μm).[12] The secondary settler was included to trap the particles escaping from the primary settling tank without sedimentation. The geometry of the primary settler took into consideration the hydraulic pressure head, turbulence in a flowing reaction medium and buoyancy forces. The ratio of the height of cylindrical to the cone regions of the primary settler was 0.58.

A typical amount of spent chromium(III) liquor used for chromium(III) hydroxide recovery using the semi-continuous process was 3 L. A cylindrical neutralization tank (150 ml) was placed over a magnetic stirrer with an outlet at 1.5 cm from the bottom of the vessel. The height of the neutralization tank was set at 14 cm. A pressure head of 5 cm over the outflow tube of the neutralization vessel was employed. The primary settler had a cylindrical top and a hopper bottom. The height of the cylindrical portion was set at 17.5 cm. The bottom portion of the primary settler was the shape of a frustum of a cone with a 3 cm diameter at the bottom of the settler. The fluid receiving mechanism of the primary settler includes a well that modulated flow turbulence. The design of the primary and secondary settler is given in Fig. 1.



(*a*) All dimensions are in cm
Scale 1 : 2

(*b*) All dimensions are in cm
Scale 1 : 5

Fig. 1 The semi-continuous chromium(III) hydroxide recovery system. (*a*) Primary settler and (*b*) secondary settler.

A schematic drawing of the reactor setup is shown in Fig. 2. The chromium(III) bearing solution and alkali were pumped at predetermined velocities into the neutralization tank (4 and 0.6 ml min^{-1} respectively) into the neutralization tank and the reaction stream flowed through a pipeline with surface friction and under hydrostatic pressure. The suspension was passed through a primary settler. The reactor was designed to modulate the forces of buoyancy which could influence the settling of the finer particles of chromium(III) hydroxide. Under steady state conditions, the flow rates of fluids into and out of the settler need to be equal. The total volume of fluid which could be handled by the settler is correlated to the bulk volume and settling behavior of the precipitate being obtained.

Two different alkalies *viz.* sodium carbonate and sodium hydroxide were used in this study. Either 0.1 M NaOH or 0.05 M Na_2CO_3 was employed for pH adjustment. The density and particle size of chromium(III) hydroxide were measured as per procedures reported earlier.[12,18] The settling velocity was calculated using Stokes law[19] after determining the density, viscosity and temperature.

The capacity of the settler and the rate of fluid inflow determine the available residence time of chromium(III) hydroxide for settling. The flow rate of chromium(III) bearing effluent into the mixing tank was varied from 2 to 10 ml min^{-1}.

The efficiency of the reactor design has been studied over a range of chromium(III) concentrations of 400–2000 ppm. The settled volume of chromium(III) hydroxide and chromium(III) content in the supernatant was studied.

The influence of anionic polyelectrolytes on the settling characteristics of chromium(III) hydroxide was studied using a commercial polyelectrolyte (Synfloc 110 A of Chemical Specialties India (P) Ltd.) and varying its concentration from 0.2 mg L^{-1} of chromium liquor treated to 1.0 mg L^{-1}. The settled volume was measured and the polyelectrolyte concentration optimized.

To the spent liquor, 1% acid stable anionic fatliquor (Lipoderm Liq SA of BASF India) was added. The resulting mixture was treated with alkali in the neutralization tank and chromium(III) hydroxide settled. The sludge obtained was analyzed for oils and fat content by standard procedures.[20] A comparative assessment of the oil and fat content was made with a standard batch type system using magnesium oxide as the precipitant alkali.

The aggregation characteristics of chromium(III) hydroxide were studied in a flow tube (Fig. 3). The tube had sampling outlets at constant intervals. Chromium(III) solution and alkali were flown along the two arms of the Y tube. Aggregation and formation of particles of chromium(III) hydroxide along the flow path were monitored by turbidometric techniques and a UV–VIS spectrophotometer. The flow rate of chromium liquor ($[\mathrm{Cu}^{\mathrm{III}}]$ = 200 ppm) was maintained at 6 ml min^{-1}, while that of the alkali varied and adjusted the pH to 7.5, 8.5 and 9.5. Samples were drawn through the outlet positioned at various distances from the point of mixing of chromium solution and alkali. Optical density was measured at 400 nm after the solutions had been allowed to flow for 45 min. The rate of particulation of chromium(III) hydroxide was considered to be first order and the rate constant for the particulation of chromium(III) hydroxide can be given as $k = 2.303t^{-1}$ [log(Δturbidity)], where 't' is the time taken to travel a distance 'd'. The rate constant was estimated by plotting the logarithmic values of changes in absorbance or turbidity against the time taken to travel a distance d, by flowing suspension at a given flow rate. The data were analyzed using a non-linear least squares fit program.

Results and discussion

The particle size distribution and settled volume of chromium(III) hydroxide generated using NaOH and Na_2CO_3 under the conditions used in the study are presented in Table 1. One important observation is that when the sludge generated settles under gravity overnight in the primary settler, the sludge volume was reduced to 11 and 12.5% with respect to NaOH and Na_2CO_3. This volume can be compared with 9–10% obtained with magnesium oxide based batch processes.[15] The velocity of settling calculated using Stokes' law was found to be 381 and 314 $\times 10^{-3}$ m^{-1} respectively, indicating that settling under the semi-continuous system is independent of the alkali employed.

The settled volume under dynamic conditions will be influenced by the time available for settling. Hence, in principle the optimum inflow rate of solution will be limited by the settling characteristics of the chromium(III) hydroxide precipitate and the settler volume. Employing a chromium concentration of 1000 ppm and maintaining a pH of 8.0–8.5 using 0.05 M Na_2CO_3 the flow rate was varied from 2 to 10 ml min^{-1}. The settled volume was found to increase from 21% for 2 ml min^{-1} to 34% for 10 ml min^{-1}, while the chromium content in the supernatant increased from 1.3 to 4.0 ppm. The results are presented in Table 2. Factors like turbulence and forces of buoyancy may be responsible for the relatively higher volumes of chromium(III) hydroxide being precipitated at higher flow rates. From the experiments conducted in this study a flow rate of 6 ml min^{-1} could well be employed, resulting in a sludge volume of 25%. Thus for a reactor capacity of 1.2 L and a continuous operation the reactor can treat approximately 7 times its volume per day.

The settled volume of chromium(III) hydroxide and the chromium(III) content in the supernatant for varying concentrations of spent chromium(III) solutions are presented in Table 3. The settled volume was found to be dependent on inflow chromium(III) concentration and varied from 14–40%. However, when the chromium(III) hydroxide was dewatered using a basket centrifuge, the differences in the settled volume of chromium(III)

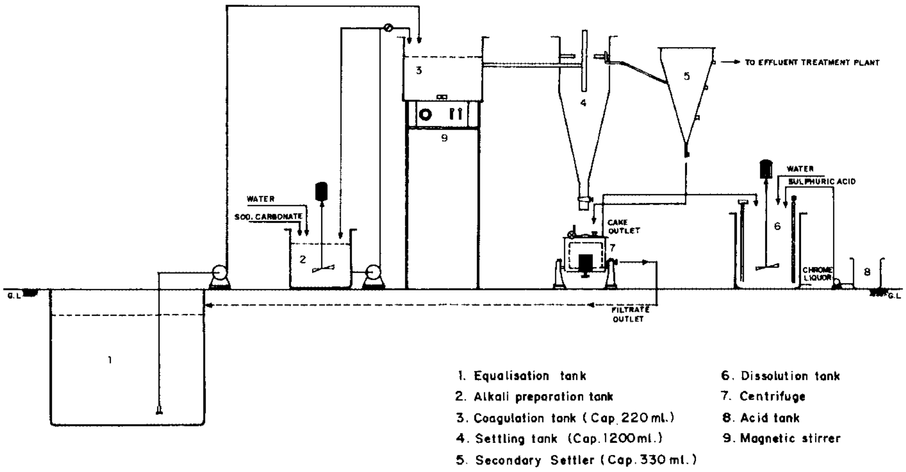


Fig. 2 A semi-continuous chromium(III) hydroxide recovery plant.

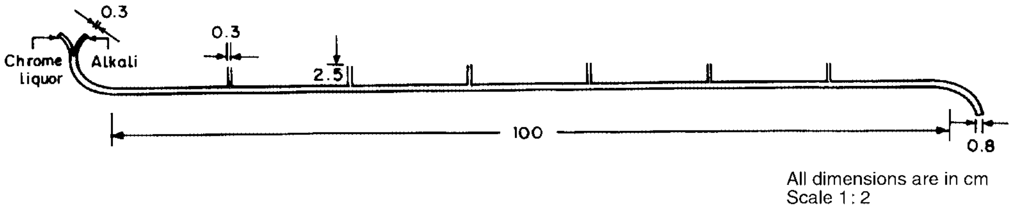


Fig. 3 Continuous flow tube configuration adapted to investigate the rate of particulation of chromium(III) hydroxide.

Table 1 Influence of the nature of the alkali on the settled volume of chromium(III) hydroxide

Alkali	Settled volume (%)	Density/ kg m^{-3}	Particle size distribution/µm < 5	5.1–10	10.1–15	> 15
NaOH	22	2220	28	56	14	2
Na_2CO_3	23	2130	22	54	22	2

Flow rate 4 ml min^{-1}. [Cr^{III}] = 1000 ppm

Table 2 Influence of flow rate and flocculent on the settling characteristics of chromium(III) hydroxide

Flow rate/ml min^{-1}	Flocculent concentration/ ppm	Settled volume (%)	Cr content in supernatant/ ppm
2	0	21	1.3
4	0	23	1.8
	0.2	21	1.9
	0.4	19	1.9
	0.6	18	1.8
	0.8	18	1.8
	1.0	20	1.9
6	0	25	2.3
8	0	29	3.2
10	0	34	4.0

Inflow [Cr^{III}] = 1000 ppm. Alkali employed = 0.05 M Na_2CO_3. Flow rate of chrome liquor = 4 ml min^{-1}

hydroxide was only marginal. The reactor design, for operational convenience, has not incorporated the roughness parameter. In commercial practice, the use of fibre reinforced plastic would bring in such parameters and this would reduce the chromium(III) content in the supernatant to stipulated levels.

The effect of a commercial anionic flocculent on settling characteristics of chromium(III) hydroxide has been studied. Data on settled volume of chromium(III) hydroxide as a function of flocculent concentration is presented in Table 2. It has been observed that the reduction in sludge volume is only marginal when the flocculent concentration is increased above 0.4 ppm. A flocculent concentration of 0.4 ppm appears optimum. When the flocculent concentration was raised to 1.0 ppm, an increase in the sludge volume was observed. A mechanism suggested for this action of an anionic polyelectrolyte on the settling behavior of a surface active colloid involves desolvation, favorable ionic environment for particulate aggregation and bridging of particulate matter by a polymeric flocculating aid. When a higher than optimum dose of polyelectrolyte was employed, surface loading of the colloid by the polymer could well increase the ionic charge of the colloidal particles and promote solvation. In other words, restabilization of colloid by polymer is likely.

The influence of oils and fats present in the spent chromium liquor on chromium(III) hydroxide recovery has been examined by analysis of oils and fats contained in the chromium(III) hydroxide sludge after precipitation of chromium(III) hydroxide. The oils and fats content in the chromium(III) hydroxide sludge obtained by the batch process was 47% as against 22% in the case of the sodium carbonate based continuous process. The oils and fat content in the chromium(III) hydroxide sludge was further reduced to 9.8% after dewatering, *i.e.* a 79% decrease when compared to the MgO based batch type process. This indicates that the continuous chromium recovery system based on sodium carbonate as the alkali for precipitation is a viable option for treatment of spent chromium(III) liquors from wool-on leather industries. Dewatering does not seem to influence the oils and fat content of chromium(III) hydroxide sludge generated by employing MgO. Since chromium(III) hydroxide sludge generated using Na_2CO_3 affords a fluffy precipitate, dewatering using a basket centrifuge reduces the oils and fats content more significantly.

The rate constants for particulation of chromium(III) hydroxide for varying pH conditions are reported in Table 4. It can be seen from the data given in the table that under the conditions employed in this study a pH of 8.5 is marginally preferable for achieving higher rates of particulation of chromium(III) hydroxide.

Conclusions

The present study demonstrates a feasible semi-continuous chromium recovery system based on sodium carbonate or sodium hydroxide as alkalies in preference to an MgO based batch type system. Sodium carbonate or sodium hydroxide provides a fluffy precipitate free of contamination but requires dewatering using appropriate mechanical devices such as a continuous centrifuge or

Table 3 Influence of inflow chromium(III) concentration on the settling characteristics of chromium(III) hydroxide

Inflow chromium(III) concentration/ppm	Settled volume of chromium(III) hydroxide(%) Before dewatering	After dewatering	Cr content in supernatant/ppm
400	14	9	1.4
750	21	15	1.9
1250	30	20	2.3
1500	35	22	2.5
2000	40	24	3.1

Alkali employed = 0.05 M Na_2CO_3. Flow rate of chrome liquor = 4 ml min^{-1}

Table 4 Influence of pH on the rate of particulation of chromium(III) hydroxide

pH	Rate constant for particulation/s^{-1}
7.5	$2.67 \pm 0.5 \times 10^{-3}$
8.5	$4.50 \pm 0.9 \times 10^{-3}$
9.5	$2.50 \pm 0.4 \times 10^{-3}$

Flow rate = 6 ml min^{-1}. [Cr^{III}] = 200 ppm.

filter press. The present investigation provides a viable design for a semi-continuous chromium recovery process based on the use of relatively more cost effective alkalies like Na_2CO_3 or NaOH. The salient features of the present investigation are the findings that (*a*) the settled volume of chromium(III) hydroxide generated using NaOH–Na_2CO_3 can be effectively reduced to match that obtained in MgO based process through equipment modifications, (*b*) cleaner chromium(III) hydroxide sludge can be continuously generated and dewatered using appropriate devices and (*c*) a supernatant which could be discharged without causing ground water hardness.

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