Green Chemistry

Editorial

The first year of the 21st century will see a further increase in the number of major awards for achievements related to green chemistry. I am now aware of awards in the USA, Italy, Germany, Australia and, as from 2000, in the UK. There are other national awards which can and do sometimes recognise green chemistry achievements such as those of the Japan Chemical Industry Association (JCIA). I believe that this increase should be welcomed, although it is not all good news—the Chemical Industries Association (CIA) in the UK, for example, recently held its awards ceremony for advancing the public understanding and appreciation of chemistry for the last time (see page G53 in this issue). I very much hope that the new decade will see the successful launch of new trans-national green chemistry awards and in view of this it seems appropriate to briefly review the national programs in terms of their scope and purpose.

USA

The first awards programme started in the United States and it is appropriate that many of the national programs that have followed have been modelled on the US awards. President Clinton announced the Presidential Green Chemistry Challenge in March 1995. This was to include research grants and educational activities as well as annual green chemistry awards to highlight the concept, and to encourage companies and researchers to work towards its goals. Specifically the US awards recognise outstanding *chemical technologies that incorporate green chemistry principles into chemical design, manufacture, and use.* I think that the expression “incorporate green chemistry principles” is particularly important and well-chosen. Green chemistry is not a subject but a concept that should influence chemistry at all levels—school and university teaching, research, and the manufacture and use of chemicals. There are five award categories in the US program covering industries, SMEs, and individual academics as well as covering the three focus areas alternative synthetic pathways, alternative reaction conditions and the design of chemicals. The recipients rightly receive national and increasingly international public recognition (*Green Chem.*, 1999, **1**, G174) for their accomplishments in the research, development, and/or implementation of green chemical technologies. Such rewards can and should be an incentive to individuals and organisations to describe their innovations and this provides another very important benefit from these awards—the publication of real and exciting examples of the incorporation of green chemistry principles into education, research and industry (see for example, *Green Chem.*, 1999, **1**, G41).

Italy

The Italian Green Chemistry award had its first deadline early in 1999. The 50 nominations were judged on scientific merit and economic and environmental impact. The first awards were given in March 1999 in the categories (1) processes, (2) products, and (3) recycling. The inclusion of recycling perhaps goes beyond the original scope of green chemistry, although it is interesting to note that the new Japanese Green and Sustainable Initiative led by the Japan Chemical Innovation Institute also includes recycling in its coverage. The ceremony for the 2000 awards was held recently in Rome and we look forward to hearing about the chemistry behind these new awards.

Germany

In Germany the Haltermann Innovation Prize started in 1998 and is awarded every two years for chemical-technical developments in the areas of product and process integrated environmental protection. The special emphasis is on processes for substance separation and environmentally sound products based on renewable resources. I strongly support the specific reference to renewable resources. We are now in the century that even the most optimistic of the energy companies recognise as being when we will no longer be able to rely on hydrocarbon feedstocks for the chemical industries. This is also an area where we can see some of the greatest challenges for new chemistry in terms of processes and products (see, for example, C. Okkerse and H. van Bekkum, *Green Chem.*, 1999, **1**, 107).

Australia

The Royal Australian Chemical Institute (RACI) inaugurated its Green Chemistry Challenge Awards in 1999. Nominated technologies should be an example of one or more of the focus areas (1) alternative synthetic pathways, (2) alternative reaction conditions, and (3) alternative chemicals. These are the same as the key areas of the US awards program and reinforce their importance.

UK

The latest national green chemistry award program is in the UK. There are no specific focus areas although the nominations should be for technology that offers significant improvements in chemical processes, products and services through research and commercial exploitation of novel chemistry, so as to achieve a more sustainable, cleaner and healthier environment as well as creating competitive advantage. It is important to reflect the belief that environmental benefit can go alongside economic (as well as societal) advantage in green chemistry awards. The awards will be given annually to a young academic as well as to companies and this should help to encourage our younger scientists to direct their research along green chemistry lines. The award winners will be expected to describe their innovations both in an article in *Green Chemistry* and in a lecture at the Green Chemistry Conference in Swansea in 2001.

I look forward to new green chemistry awards in the coming years and particularly to trans-national awards that help reflect the global nature of chemistry today. Hopefully, future awards can learn from the still recent but valuable experiences of existing programs.

James Clark,
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Green algae as fuel factories

Photo courtesy of University of California, Berkeley

Anastasios Melis and Liping Zhang of the University of California at Berkeley, and Michael Siebert, Maria Ghirardi and Marc Forestier of the National Renewable Energy Laboratory (NREL) in Golden, Colorado, have shown that, in the absence of a supply of sulfur and oxygen, the green algae *Chlamydomonas reinhardtii* can switch from oxygen production to hydrogen production. A joint patent has been filed by UC Berkeley and NREL for this new technique for capturing solar energy, which was presented on 21 February at the annual meeting of the American Association for the Advancement of Science in Washington D.C. and published in the January 2000 issue of *Plant Physiology* (*Plant Physiol*., 2000, **122**, 127-135).

Green algae normally employ the same photosynthetic process as any other plant, converting sunlight, water and carbon dioxide to chemical energy, and emitting oxygen as a waste product. It has long been known since the 1940s that after a period of darkness and in the absence of oxygen, an alternative anaerobic process catalyzed by hydrogenase kicks in, producing molecular hydrogen. The problem has been that in order for the algae to survive, illumination is required, even for the hydrogen-generating pathway. Once that happens, photosynthesis resumes, the algae start making oxygen again, and the oxygen deactivates the hydrogenase. Researchers have tried continuously purging the oxygen with inert gases, but that makes the process too expensive and impractical for large algae cultures. Attempts to destroy the oxygen chemically have often resulted in destroying the algae as well. These stumbling blocks discouraged research into using algal cultures as a source of renewable energy.

The current advance is a way to alternate back and forth between the oxygenic and hydrogenase processes. Instead of incubating the algae culture in darkness, the metabolic switch is the removal of sulfur from the growth medium. In a stoppered bottle, the algae have no access to outside oxygen, and the absence of sulfur prevents it from producing its own by photosynthesis. Under these anaerobic conditions, a one-liter algae culture produces about 3 ml of hydrogen per hour, which bubbles to the top and is collected in tall glass tubes. After about four days of hydrogen production, the algae must be allowed to return to photosynthesis; the process can be repeated two or three days later. In their experiments, the researchers tested algae cultures through three full cycles, but believe the culture could go back and forth many more times.

The process has still to be tested in small-scale industrial and commercial operations, and larger utility photobioreactor facilities, but the new discovery opens up the possibility of harnessing nature's own tool, photosynthesis, to produce hydrogen as an alternative fuel from sunlight and water. (http://www.urel.berkeley.edu/urel_1/CampusNews/PressReleases/releases/01-27-2000b.html)

EU chemical industry CO_2 emissions remain absolutely constant

Recent figures from CEFIC, the European Chemical Industry Federation, show that, in absolute terms, the industries' CO_2 emissions have remained fairly constant during the period 1990–1997. However in relative terms the industry has made significant strides forwards both in terms of energy efficiency and CO_2 releases per unit of production. Industry production output has increased by over 20% during this period but energy consumption has risen by only 6%. In relative terms CO_2 emissions have be gradually falling and were over 18% lower per unit of production in 1997 than in 1990 (http://www.cefic.be/).

ICI to reduce mercury discharges

ICI Chlor-Chemicals has set up a Waste Brine Treatment 2000 project to reduce the amount of mercury discharged from its mercury cell chlorine plants. Planned improvements will be phased in over several years at a total cost of over £3.5M. (http://www.chlor-chemicals.com/)

Paints and coatings

Two main environmental factors are currently driving innovation in the paint and coatings sector. The phase out of tributyl tin as an antifouling additive, and the control of VOCs are both issues which are the subject of ever-tightening legislation. Some recent developments in this industrial sector are outlined here.

The control of VOCs is currently the focus of the EC, and proposals for emission standards are being discussed. The likely cost of implementing the proposals (along with controls on ozone air quality standards is thought to be around EUR 7.5bn in addition to the EUR 58bn already committed (*CEPE News*, 1999, **2**, 30—secretariat@cepe.org; *Farbe und Lack*, 1999, **105**(11),19).

The Norwegian government has recently announced its plans to create a cleaner paints and lacquers industry by a mixture of tax penalties and outright bans on the most harmful components, and voluntary reductions in the use of other harmful components by the industry. The Government intends to involve all parties (manufacturers, dealers, consumers, and authorities) in order to encourage a more environmentally acceptable industry to evolve (*Polym., Paint, Colour J.*, 1999, **189**(4422) 5).

Tributyl tin phase-out

In November, the International Maritime Organisation made the decision to phase out tin-based paints in 2003. This means that the use of paints containing tributyl tin will be banned in 2003, with a phase out ending in 2008 (*Eur. Chem. News*, 6 December 1999). Tributyl tin has been shown to cause marine pollution, and was banned on ships over 25m length in 1987. However, 85% of ships worldwide still use tributyl tin as an anti-fouling additive, and its ban will have significant repercussions on the paint industry in India, where tributyl tin paints still account for 5% of the total market (*Chem. Weekly*, 1999, **45**(16), 74). This decision was made on the basis that suitable alternative paints are available.

The Japanese company NOF have announced that their tin-free paints will now be marketed globally (*Eur. Paint Resin News*, 1999, **37**(11), 14). The paints are based on silylated monomers (silyl acrylate and methacrylate, and sales are expected to reach 10000 tonnes per annum.

Specialty chemicals manufacturer Rohm and Haas Company based in Philadelphia, Pennsylvania, is one company that has developed an alternative to tributyltin in marine paints for large commercial vessels. SEA-NINE® 211 marine antifoulant employs isothiazolone chemistry as a more environmentally acceptable ingredient in marine paints. The new marine antifouling agent was rewarded with the "Green Chemistry Challenge Award" from the U.S. Environmental Protection Agency in 1996. The company has just completed a modernisation of its site in Jarrow, UK, which produces these compounds. Improvements include equipment to reduce emissions into air and water.

Water-based paints and coating resins

Two Japanese companies have announced that they have developed water-based products to replace solvent–based paint and coating systems. Toyota has devised a new technology which allows them to use water-based paints on their cars (*Eur. Paint Resin News*, 1999, **37**(10), 14). The technology is in place at the company's factory in Takaoka, and has resulted in a reduction in VOC emissions of 50%. This makes Toyota the first Japanese car manufacturer to use water-based paint technology (http://www.toyota.com/).

Nippon Kasei has also developed a water-based coating resin, based on three co-monomers—dimethyrol butyrate, dimethyrol propionic acid and diacetone acrylamide. All three monomers will be produced at a new facility in Onahama (*Eur. Paint Resin News*, 1999, **37**(11), 14). The products will be launched soon in Western markets.

Greener green

Heubach GmbH has announced that it will build a second plant to produce its phthalocyanine green pigment in India on a 3000 tonnes per year scale (*Eur. Paint Resin News*, 1999, **37**(10) 5). The plant will incorporate new technology to reduce the quantity of solid waste produced.

Shell takes steps to cut emissions

Mark Moody-Stuart, Group Managing Director of Anglo-Dutch oil major the Royal Dutch/Shell Group highlighted the companies commitment to climate care and wider issues of sustainability during his opening speech at the World Economic Forum in Davos in January. "Shell companies believe that the best approach to climate care is to make it part of a sound business rational, and that a strong commitment to a sustainable future is the best basis for a sound business," he said.

Although Shell International Renewables is looking at commercially viable opportunities for solar cells, biomass and wind power, Moody-Stuart believes that hydrocarbon energy sources will still have a major role for most of the 21st century. The commercial viability for renewable energy sources, on the scale needed to make a significant impact, is still many years away.

Shell have been working towards meeting the objectives set up under the Kyoto protocol and recently launched an internal trading system to help meet greenhouse gas emission reduction targets. The Shell Tradeable Emission Permit System (STEPS) will help the group meet an overall 10 percent cut in greenhouse gas emissions by 2002 compared with 1990 levels. Mark Moody-Stuart said "STEPS is going to be a key factor in reaching or exceeding the emissions reduction targets we have set ourselves."

The system will allow group businesses involved in chemicals, refining and exploration and production as well as in different countries to trade permits worth 100 tonnes of carbon dioxide or methane equivalent over an internal web site.

Each business unit will be able to buy or sell permits over the next three years to hit a two percent reduction target from 1998 emissions levels, the last available date for data. The system will work similarly to the Kyoto Protocol proposals whereby units succeeding in cutting emissions would be able to sell them to those not so successful.

Emissions covered by STEPS make up 30% of the Group's total emissions. Chemicals, refining and exploration and production businesses, from North America, Europe and Australia, are all represented in the system.

Further information about STEPS can be found at http://www.shell.com/steps

Shell is also involved in a consortium called Blyth Offshore Wind Limited to raise two of the world's most powerful wind turbines off the UK north east coast. The turbines, each of two Megawatt-capacity (enough in total to power 3000 average households), will be the largest erected offshore in the world and the first to be built in such a demanding position, subject to the full forces of the North Sea. First electricity is expected to be generated in August 2000.

Improvements in packaging

Improvements in packaging have led to reductions in waste production. For example, a survey by the Association of Plastics Manufacturers in Europe (APME) has shown that plastic packaging has been reduced in weight by 28% in the decade ending in 1997. This is predominantly through improvements in the performance (*High Perform. Plast.*, 11 November 1999, 8) which have allowed better levels of performance, and thus reduced weights of plastic. The major reductions have been achieved in palletizing films, where a remarkable 73% reduction in thickness has been achieved.

AgrEvo of Germany has just won an award for environmental protection for a new packaging system for some of its pesticides. The system is aimed at avoiding spills during application of the pesticides of farms. The company was also commended for its waste management scheme, where users can return used packaging.

The German Packaging Federation (IVP) has proposed a new autodisposal system which it claims will be cheaper to run than the current Green Point system. A proposal produced in consultation with the Recycling Association (VfW) could lead to a reduction in cost for recycling of, for example, 1000 polythene bags from DM58.66 to DM36.89

Degradable plastics are making inroads in China (*China Chem. Reporter*, 1999, **10**(37) 9–11). Over 100 facilities now exist in China for the production of such plastics, with the capacity to produce 20,000–30,000 tonnes per year of products derived from degradable plastics. While this is still small compared to the total amount of plastic produced (*ca.*15 M tonnes p.a.) it is a growing part of the market. The necessity for such changes is underlined by the 2 M tonnes of hard-to-recover plastic waste which is predicted for this year.

Renewable plastics

The production of polymers from renewable resources is an area of continued activity, although several processes have been proven technically, production economics have prevented wide scale commercialisation.

Dow Chemical and Cargill (as the joint venture company CPD) believe they have found the solution and have recently announced their intention to build a large scale ‘renewable plastics’. Called NatureWorks, the technology allows the company to process natural plant sugars from crops such as corn and wheat and rice, rather than traditional petroleum based materials, into polylactide polymers (PLA). The first plant (14,000 te) is to be built in Nebraska as part of a $300 million investment business. A further plant is also being planned for Europe within the next few years (http://www.cdpoly.com/natureworks/default.asp).

One of the main applications of the polymer will be in fibres for clothing where attributes such as wrinkle resistance and good moisture management properties together with its compatibility with downstream processing equipment should ensure success. Other potential applications for the polymer include carpets and food containers.

The key elements of the process involve fermentation of unrefined dextrose, obtained from the crop, to lactic acid. This undergoes a condensation process to produce a cyclic dimer intermediate which is purified by distillation. The final step involves a ring opening polymerisation in a solvent free melt, conditions of this process can be varied to produce a range of molecular weights and crystallinities. It is this novel manipulation of polymer properties which CPD will ensure the success of the project, enabling the product to be sold into a variety of markets.

Other green credentials of the product are that it is fully compostable and that 30% less fossil fuels are required to produce it than with conventional plastics (http://www.cdpoly.com/home.asp).

Making money from old diapers (nappies)

The waste recycling company Knowaste have opened a $20M plant in Arnhem to recycle diapers and adult incontinence products. The local waste disposal costs of $150–400 a ton allow for a profit to be made on the recycling process. Ironically the company had earlier found it impossible to make a profit in the North American market. When they started in Ontario, Canada 10 years ago the company flourished thanks to the policies of the then Socialist Government who raised landfill dumping fees to encourage recycling. Since then free market policies have dominated and Knowaste have been unable to compete. The new owners of Knowaste sought new business opportunities in Boston and San Francisco but again could not make their processes competitive with local dumping. Fresh from there new success in Europe Knowaste is planning to take on the North American market with a new lower-cost diaper recycling process. This relies on the deactivation of the super adsorbing polymer from the pulp which it can then sell to paper companies. A new plant will soon begin operating in Mississauga where it will service a local residential operation that delivers disposable diapers and then takes them away for a fee. It is competitive with local landfill despite these being only $50 a ton. Further developments in the US are planned (http://www.knowaste.com/).

Pollution

Ozone in the European Union

The EU report for 1999 shows that despite a small reduction in Central Europe there is still not a global reduction in population and ecosystems exposure to ozone in the Union. The main points in the report concern peoples health, and protection of the vegetation. In 1998 the indicative ceiling of 110 micrograms per cubic meter during 8 hours was on average exceeded during a 20-60 day period in Mediterranean countries and by 10-35 times in countries located in the centre of the Union. The danger level of 360 micrograms per cubic meter was exceeded several times in Greece, Italy and France. In 1999 no exceeding of the danger level occurred but the ceiling for informing the public (180 micrograms per cubic meter during an hour) was exceeded by all member countries except Ireland, Denmark, Sweden and Finland. The most critical occurrences were in France, Greece, Italy and Spain where the population was informed of the high ozone levels during a 40–60 day period. The vegetation limit has been established at 200 micrograms per cubic meter and this was exceeded for more than 200 days in 94 separate observation posts located in 13 member states.

Contrary pollution levels in the UK

While pollution in the UK is falling, the level throughout the UK is rising dramatically. A report from Friends of the Earth shows the biggest deterioration in air quality since modern records began. The number of days on which pollution broke health standards rose by 20% in cities and by 53% in the countryside compared with 1998. In North and Mid-Scotland and North Yorkshire, the number of days of moderate or high pollution has risen by 50% in 3 years largely due to increased levels of traffic. The Department of Health in the UK says that in London the health costs of pollution are very low—only 0.2% of the health budget compared to 2% in dealing with road accidents. They also point out that lead emissions have been almost eliminated, sulfur dioxide and particulates have fallen dramatically and ozone levels are lower in London than in most other parts of the country despite heavier traffic. A report "Transport and Health in London" produced for the Department of Health has concluded that "The efforts now in progress at national and local level to introduce national air quality standards and to put in place low-emission zones (from which heavily polluting vehicles are barred) do not appear to have been given a justification on grounds of saved health costs" (*Reuters News Service*, January 2000; *The Independent*, 17 January 2000).

New developments in catalysis

News relating to enzymatic methods involves the polymerisation of natural products such as syringic acid and cardanol (*CHEMTECH*, 1999, **29**(10), 22–28). Japanese workers have used the oxidative polymerisation of these materials to produce polyphenolic resins, which are normally produced using toxic monomers such as formaldehyde. Reaction conditions are mild, and the process generates relatively benign waste streams.

Improvements in titanium dioxide photocatalysts have also been reported. Ecodevice of Tokyo has developed a new photocatalysts which can absorb and use visible light as well as UV (*Jpn. Chem. Week*, **40**(2049), 3). The new material can use 50% of solar energy, compared to the 5% which is amenable to existing photocatalysts. The company is currently planning to build a plant to exploit the breakthrough.

A second report on photocatalysis (*CHEMTECH*, 1999, **29**(10), 55) indicates the potential of photocatalytic process for the destruction of pollutants in waste water.

Wako Pure Chemi has announced the commercialisation of a new range of encapsulated *catalysts (Jpn. Chem. Week*, **40**(2050), 3). These new catalysts are based on the microencapsulation of *e.g.* osmium tetroxide or scandium triflate in polystyrene matrices. The encapsulated materials often have remarkable chemical and catalytic properties, but are difficult to handle and recover. The new materials circumvent these difficulties. The commercialisation of these materials follows on from articles written by Shu Kobayashi and his group in the last year or two (S. Kobayashi and S. Nagayama, *J. Am. Chem. Soc.*,1998, **120,** 2985).

As reported in a recent issue of *Catalysis Today*, researchers at Ohio State University have developed a new method to remove toxic nitric oxide emissions from stack gases. With the help of a palladium-based catalysis methane reacts with the nitric oxide to form nitrogen, carbon dioxide and water. Work is proceeding to improve the formulation of the catalyst, especially to minimise inactivation by sulfur dioxide present in flue gases (http://www.acs.ohio-state.edu).

Cleaner cars

Clean cars a step nearer (see *Green Chem.*, 2000, **2**, G9)

Cars and trucks that run on a combination of electricity and other fuels—known as hybrids—could comprise 20 percent of vehicle sales by 2010, William Clay Ford Jr., chairman of Ford Motor Co, said recently. But Ford predicted that both hybrids and vehicles powered by traditional internal combustion engines will eventually be replaced by clean-burning fuel cell engines.

"It's going to be a winning situation all the way around—consumers will get an efficient power source, communities will get zero emissions, and automakers will get another major business opportunity—a growth opportunity," Ford said.

Automakers have been introducing more electric and alternative fuel vehicles in the last few years as they experiment with new ways to build more efficient engines.

Hybrids now make up a tiny fraction of vehicles sold. Toyota Motor Corp and Honda Motor Co. Ltd currently sell hybrid vehicles in Japan, and are expected to start sales in the United States early this year. Ford Motor, General Motors Corp and DaimlerChrysler AG are scheduled to introduce hybrid vehicles that get 80 miles per gallon by 2003 as part of a U.S. government-sponsored programme (*Reuters News Service*, January 2000).

Western Australia leads new cleaner fuel regulations

Western Australia has introduced new tougher cleaner fuel standards ahead of the rest of the country. Leaded fuel has been replaced with a new fuel containing an additive substitute. Additionally the permissible sulfur level has been reduced from 5000 ppm to 500 ppm for some parts of the state with the rest following by 2001. The federal Government has ruled that refineries nationally must produce diesel fuel with a sulfur level of only 500 ppm by the end of 2002 and 50 ppm by January 2006. The industry average is currently *ca.* 1300 ppm (*Reuters News Service*, January 2000).

Hybrid-electric car for Australia

A new hybrid-electric car, the aXcessaustralia has been developed by CSIRO's Australian Automotive

The aXcessaustralia car. The drive motor and transmission are at the front. In the rear is the internal combustion engine surrounded by the supercapacitor pack. The battery pack is located underneath the rear seats. Photo courtesy of CSIRO, Australia.

Technology Centre (AATC) and will be launched in June 2000. The aXcessaustralia car uses a novel, compact internal combustion engine to drive a CSIRO Generator in a Series hybrid configuration. The Surge Power Unit comprises CSIRO supercapacitors and CSIRO batteries. The traction motor is a CSIRO water-cooled electric motor that also acts as a generator when braking. During most of the operating time, power is supplied from the batteries, supplemented by the supercapacitors for acceleration. The internal combustion engine generally operates in response to the needs of the storage system. However, for extreme power needs, all three sources of energy are available to the drive motor enabling vehicle performance to be equivalent to a conventional car. The aXcessaustralia will reduce fuel consumption by half and lead to a 90% reduction in greenhouse gas emissions.

The supercapacitors, which use a carbon coating in an organic electrolyte to form what is termed a ‘double layer capacitor’, absorb energy and deliver stored energy very quickly, while battery pack provides enough energy storage to allow the car to complete an urban drive cycle under electric power only. This means that the car gives the range and performance and low emissions of other hybrid cars, but also will run in zero-emission, all-electric mode in areas that are particularly environmentally sensitive such as city centres. In this way the aXcessaustralia car combines the performance and very good emissions of other hybrid vehicles with the zero emission of an electric vehicle. The car can also be charged overnight on low tariff electricity to reduce running costs further (http://www.csiro.au).

Nissan claims cleanest gasoline car

The Japanese car manufacturer Nissan has claimed the worlds cleanest gasoline driven car, the Sentra CA. They say that the emissions from the car after a 16KM drive are less than from a normal car standing on a drive all day (cars still emit vapours after the engine is turned off or due to heating from the sun). The car has been given “super ultra low emission” status by the Californian authorities but unlike the Honda Accord, it has also been given partial zero emission credits. California requires that 10% of all vehicles sold in 2003 should be “zero emission”. The Sentra will initially only be sold in California which is the only US state to offer low sulfur gasoline (http://www.nissan-na.com/).

Sustainable development in hard surface cleaners

Unilever believes that, for the detergents industry to be sustainable, it must raise its resource conservation by a factor of 4, meaning a 75% reduction in resource consumption for any unit of production. The European Detergent Association (AISE) has established a code of practice with four key objectives to be reached over a 5-year period beginning from the base year of 1997. Among these are targets for energy savings, reduction of product consumption, reduction of packaging consumption and biodegradability. According to life cycle studies, much of the environmental impact of laundry detergents is in their use and subsequent disposal. Chlorinated solvents are effective cleaners and are non-flammable, but they are increasingly the subject of strict environmental standards and this is a challenge for hard surface cleaners that involve environmental indicators for a more sustainable approach to chemical production and use. These indicators include ozone depletion potential, global warming potential, presence of volatile organic compounds, toxicity, and reactivity. Consequently water-based cleaning formulations are being marketed by companies such as Alconox, Northern Products, Watson Technical, and Safe Science.

A new method to recover metal from acid wastes

MARS Technology Inc has proposed a new two-stage process to recover metal from acid waste. The process is environmentally friendly since it offers an alternative to deep well disposal and can recover useful metal salts from hydrochloric acid solutions that can be purified into chemical commodities. Metal chlorides are absorbed in a standard ion exchange resin in a column and then stripped by a patented system that uses tap water.

Phytoremediation

Crabgrass, a plant considered a noxious weed by gardeners, is being investigated at dozens of US institutions as a means to clean up sites contaminated with hydrocarbons. Scientists at the University of Washington and Washington State University have developed hybrid poplar trees which extract the widely used solvent trichloroethylene, breaking to down into harmless compounds. Sunflowers have also been used to remove radioactive contaminants from a pond of water near Chernobyl, and the US Army is investigating several plants to extract explosive compounds, including TNT from several test sites. For general information and a large number of weblinks on phytoremediation see http://www.engg.ksu.edu/HSRC/phytorem/home.html.

A cheaper and greener way to make nylon

RPC Inc. and Fluor Daniel are making a new cost-effective and environmentally friendly nylon 66 production technology available. Oxygen and a cobalt catalyst are used to oxidize cyclohexane to adipic acid. The production of cyclohexanone and cyclohexanol by-products is limited. Nitric acid is not involved, so there are no NOx emissions and no nitrates produced; raw material costs are reduced. An analysis comparing a theoretical unit with an existing unit (both 135,000 tonnes/y) indicated potential capital cost reductions of over 30% and operating cost reductions of 20%.

Adhesives

Europe – The Solvent Emissions Directive

In March 1999 the Solvent Emissions directive was adopted by the European Council of Ministers and should be implemented by member states within 2 years. The adhesives industry uses about 130,000 tonnes/y of solvents in its products and has a major part to play in meeting the Directive’s target, both in the production of adhesives and their application by adhesive coaters. The principal objective of the legislation is to limit volatile organic compound (VOC) emissions from solvents from industrial sources. It is expected that the Solvent Emissions directive will reduce overall emission of VOCs in 2007 to 67% of the 1990 level. All adhesive coaters using more than 5 tonnes/y of solvent are covered by the Directive. A table shows the requirements as set out in the directive for the adhesive industry. There are two bands of solvents use considered: 5–15 tonnes/y and more than 15 tonnes/y. Coating of leather and footwear manufacture have specific limits in the Directive. Also affected are adhesive manufacturers using more than 100 tonnes/y of solvents. The principal impact on the industry arises through compliance. Instead of restricting the use of specific solvents, the Directive allows the user the flexibility to reduce emissions through abatement or use of alternative technologies or a combination of both. Among the options are an Emissions Limits Option, a Reduction Scheme Option, and a National Plan. A second table gives the selection criteria for choice of adhesive.

North America – switching to water-based adhesives

According to the Pacific Northwest Pollution Prevention Resource Center, there are many issues involved in switching from solvent-based adhesives to water-based systems. The successful application of new adhesive technology requires the input of multiple decision-makers, especially product development engineers, adhesive suppliers, application equipment vendors, and end-product customers. The overall quality required for the product being produced is ultimately determined by the customers. Some of the most important issues regarding water-based adhesives are: performance requirements including bond strength, process adaptability, and durability; application issues; mixing options; and curing technology. There are numerous advantages of water-based adhesive technologies over solvent-based adhesives. The principal advantages include the removal of hazardous air pollutants and volatile organic compounds from the process; a complete removal of explosion risk; and the reduced generation of hazardous waste. The limitations include the need for an oven to cure the adhesive which takes up space and possibly increases energy costs; increased generation of wastewater and sludge; more stringent production run requirements; and a limitation on complete substitution of water-based adhesives for solvent-based adhesives.

Cleaner fuels

Methanol fuel

In experiments that combine methane photolysis and catalytic photolysis of water, methane and water have been converted to methanol, hydrogen, and acetic acid by a doped semiconductor photocatalyst (platinum-doped tungsten oxide) at temperatures of ~94 °C and at atmospheric pressure. The reaction was enhanced in the presence of hydrogen peroxide, which is consistent with the postulated mechanism that invokes a hydroxyl radical as an intermediate in the reaction sequence. Such that the hydroxyl radical reacts with a methane molecule to produce a methyl radical and the methyl radical then reacts with an additional water molecule to produce methanol and hydrogen. Experiments also indicate that the photocatalyst operates under visible light rather than UV (*New developments in the photocatalytic conversion of methane to methanol*, *Catal. Today*, 2000, **55**(3), 259-267).

Fuel cells

Global Thermoelectric Inc. have announced a new prototype fuel cell aimed at the residential market using natural gas as its energy source. It is also developing manufacturing facilities in Calgary, Canada. The successful test of the design using natural gas will allow development of power systems in the 1–5 KW range to supply electricity and heat in homes or in remote industrial locations. It hopes to begin remote system testing in early 2001. Another fuel cell company Ballard Power Systems Inc announced in January an agreement with Tokyo Gas Co. Ltd. and Ebara Corp to develop one KW fuel cell cogeneration systems for residential use in Japan (http://www.globalte.com/).

Funding for clean fuels

The US Energy department is to provide $75 million in research grants to develop clean fuels and better pollution control devices for cars and trucks. The research money is part of the government's efforts to cut sulfur levels in gasoline. In December the administration proposed new regulations requiring the nations refineries to reduce sulfur levels in gasoline to an average 30 ppm by 2005 (current levels are at *ca*. 300 ppm). The Department is asking for proposals in the following areas:

- the production of clean fuels from different energy sources—crude oil, petroleum coke, refinery waste, natural gas or coal
- innovative emission control systems and verification in engine tests
- new fuel making processes or technologies that refineries and automakers could use in future fuel, engine and emission control systems

Funding will be available from 2000 to 2005 and will require participants in the research to share 35–50% of the cost of each project. The Department will evaluate proposals over two time periods: those received by 1 June 2000 and those received by 1 December 2000 (*Reuters News Service*, February 2000)

Washington court rules out EPA extension of reformulated gasoline rule

A US court has ruled that the EPA cannot extend its rule on the use of reformulated gasoline to areas with little or no pollution problems. Reformulated gasoline contains additives that increase the oxygen content of fuel so that it burns more completely thereby reducing air pollutants. The American Petroleum Institute and the National Petrochemical and refiners Association claimed that the EPA exceeded its authority in September 1998 when it issued the rule opening the program to more communities. The US Court of Appeals for the District of Columbia agreed that the EPA exceeded its statutory authority and ordered a review. The API have stated that they support clean fuels " based on need, sound science and cost effectiveness" (*Reuters News Service*, January 2000).

Soybean fuel additives

Researchers from the University of Kansas in the USA have shown that fuel additives made from soybean oil improve the performance of diesel fuel and, in particular, of diesel fuel containing ethanol (so-called 'diesehol'). Using a blend of 10% ethanol and 90% diesel in a Volkswagen test engine, it was found that the soybean-oil based cetane improvers reduced the amount of particulate matter in the engine by more than 30–50% compared with unblended diesel (http://www.ukans.edu).

US farmers push for ethanol to replace MTBE

US farmers are pushing the government to replace the controversial oxygenate MTBE with ethanol in California's clean burning gasoline program. In the US most ethanol is made from corn and farmers see a huge new market in California with the State concerned over the effect of MTBE on water quality. The EPA has classified MTBE as a potential human carcinogen. However, California argues that the use of ethanol will increase emissions and cost compared to other blends of reformulated gasoline it could make without oxygenates. It is seeking a waiver from the federal requirement that all reformulated gasoline must contain at least 2% oxygen. The EPA is currently considering this request (*Reuters News Service*, February 2000).

Unleaded gasoline phaseout in the Philippines

Manila is to phaseout leaded gasoline by April 2000, 9 months ahead of the original schedule set out in the 1999 Clean Air Act. The first unleaded gasoline was sold in the Philippines in 1994 but sales had initially been poor due to a public perception that the fuel gave lower power. Reduced taxation on unleaded fuel ahs however helped to remedy this and sales of unleaded fuel now amount to 45% of the total across the nation. The law has stipulated that all gasoline sold in the Philippines from 2003 must contain no more than 35% aromatics and 2% benzene so as to reduce airborne pollution (*Reuters News Service*, January 2000).

California adopts gasoline rules banning MTBE

The California Air Resources Board has brought in regulations which will ban the use of methyl tertiary butyl ether (MTBE) in fuel after 31 Dec 2002. The addition of oxygenates to gasoline had been required as part of the Clean Air Act in areas which could not meet air quality standards. However, the environmental impact outweighs air quality improvements. Under the new rules, refiners will have to cut the level of sulfur in fuel. Changes in distillation standards will allow refiners to substitute MTBE with other additives.

German accord on lower sulfur in gasoline

Germany has approved tax concessions for producers of low-sulfur fuels in a move that will raise the pressure for stricter regulations on the sulfur content of gasoline throughout Europe. German motorists will receive concessions for clean fuels, first at 50 ppm, in keeping with the EU's Auto-Oil proposals, and then at 10 ppm, well under any formally agreed limit. The shift toward ultra low levels of sulfur in German gasoline appears to be all one way. The government has declared its position with the new tax laws and the automobile manufacturers are keen to see as little sulfur as possible at the fuel pump. Germ refiners are also cooperating. For example, refiners DEA and Veba Oel both say they will support the 10 ppm level. It is still possible however that the support for the lower level of sulfur might bring long term benefits to some refiners already commitment to large investment projects involving sulfur removal technology when other cannot afford to follow the trend under pressure. With effect from 1 November 2001, the German oil industry will voluntarily introduce gasoline with 50 ppm sulfur at all their pumps. In exchange, the German government will introduce a DM 0.03/litre tax concession. Veba says its refineries would be ready to deliver gasoline with 10 ppm in 2002. The German government, however, must convince the European council of finance ministers that it had the right to introduce a further tax incentive to support the additional reduction.

New clean air technologies for the automotive sector

According to developers, two catalyst systems for car exhausts are unaffected by the level of sulfur in fuel. A division of the UK's AEA Technology has revealed a diesel particulate filter that utilises a low temperature plasma for self-cleaning. Delphi Automotive Systems, US, announced a device that performs partial oxidation of nitric oxide to nitrogen dioxide followed by catalytic conversion to nitrogen with reduced levels of diesel particulates and hydrocarbons. The Delphi system applies to diesel, lean-burn and direct injection gasoline engines.

Sulfur silanes for green tyres

From 1999-2002, $106 M is to be invested by Degussa-Huels to expand its production capacity for organofunctional sulfur silanes which are compounded with rubber used for production of so-called green tyres with low rolling resistance. A production unit is to be built at Antwerp, Belgium. Global capacity will be increased by two-thirds. Capacity is also being increased at an existing facility in Antwerp and at its facilities in Mobile, AL. In Termoli, Italy, capacity for organofunctional sulfur silanes is to be more than doubled by CK Witco, at a cost of $50 M. Completion is due by mid 2001. 17% of passenger car tyres now manufactured are green, and there has been a 10%/y increase in the use of silica-based compounds in tyres.

Potential 'breakthrough' battery technology

Exide Corp has acquired a controlling interest in Lion Compact Energy, a privately held company conducting research in dual-graphite battery technology that could dramatically advance the search for cleaner, less expensive and more efficient batteries. Under the terms of the acquisition, Exide paid $3.5 M in cash upon closing and could pay $11.5 M, plus certain royalty fees, over the next several years depending upon the performance of Lion Compact Energy and its product. Lion Compact Energy has thus far produced several prototype batteries using graphite in different forms as the electrode material. Exide Corp, with revenues of about $2.4 bn/y and operations in 19 countries, is the world's largest manufacturer of automotive and industrial lead-acid batteries (http://www.exideworld.com)

Fuel cell advance

Researchers at the University of Pennsylvania led by Professor Raymond Gorte say that they have devised a fuel cell that uses a compound of copper and cerium oxide. Currently fossil fuels must be converted to hydrogen before fuel cells can be used, otherwise the cell is choked by carbon deposits. The new dry hydrocarbon fuel cell eliminates the wasteful conversion to hydrogen and resolving the carbon deposit problem. Tested on ethane and butane, the new fuel cell produces clean power, and emits only water and tiny amounts of carbon dioxide. This new development, reported in *Nature*, 2000, **404**, 265, opens up the possibility of smaller, cheaper and more efficient fuel cells for applications in homes and cars.

Achieving practically zero discharge for an acrylic acid plant by a metalorganic precipitation process

G. Y. Guo of Shanghai Jiao Tong University and Y. L. Chen of Shanghai University (Peoples' Republic of China) show that while none of the established extraction and separation techniques (distillation, solvent extraction, adsorption, ion exchange and membranes) are suitable for efficiently separating carboxylic acid mixtures such as acetic acid from acrylic acid, a novel metalorganic precipitation process is practical and can help to achieve a near-zero discharge level in the production of acrylic acid.

Acetic and related acids are, often at relatively low concentrations, found in effluents from a variety of industrial processes. For example, the plant which manufactures acrylic acid generates the effluent containing acrylic and acetic acids. Acetic and acrylic acids are highly refractory low-molecular-weight carboxylic acids. Their volatility is close to that of water in aqueous solution. It is, therefore, difficult to deal with such effluent by ordinary means. Incineration appeared to be only an option for the effluent in order to meet the discharge legislation set by countries. Nevertheless, during the last decade an active research has been undertaken in different laboratories, in order to find new methods for recovering dilute acetic acid from fermentation broth and wastewater. As a result of the intensive work done, several separation processes such as solvent extraction, adsorption and ion exchange have been explored for the recovery of acetic acid.[1–5] Most of these studies, however, have concentrated on the extraction of acetic acid from simple synthetic solutions. Very little work has been reported on the effectiveness of those processes for dealing with the effluent from a chemical plant and for separating acetic acid from its homologues, *e.g.*, other carboxylic acids, and on the economical and environmental aspects of these processes. Here we present a wasteless treatment for the effluent from an acrylic acid plant, *i.e.*, a metalorganic precipitation technology, which has the double advantage of both recovering acetic acid from the effluent and obtaining a precursor of advanced zirconia ceramics, and which may, therefore, be considered as a potential alternative to the existing incineration process.

> 'metalorganic precipitation technology may be considered as a potential alternative to the existing incineration process'

Process Development

A wide variety of isomeric and non-isomeric organic acidic or basic compounds are encountered in plant effluents from the manufacture of chemical and pharmaceutical products. These compounds have very similar physical and chemical properties. Their molecules are structurally simple and lack the suitable specific functional groups required to develop a highly selective recovery process. In addition, the desired organics, *e.g.* acetic acid, are usually present at relatively low concentration in a complex effluent containing these compounds. The volatility of acetic acid is close to that of water in aqueous solution. Distillation cannot fractionate among the low-volatility acids, and distillation is energy-intensive for dilute aqueous solutions. It is, therefore, difficult to separate acetic acid from these closely related compounds by conventional methods such as distillation, solvent extraction, adsorption, ion exchange, or membrane processes.

The low aqueous activity of carboxylic acids results in low distribution coefficients of the acids into conventional solvents such as ketones and alcohols. Although neutral organic phosphorus compounds and long-chain tertiary amines are effective extractants for carboxylic acids and have reasonably high distribution coefficients at low acid concentrations, only low selectivities among carboxylic acids can be achieved with these extractants giving favourable distribution coefficients, and for low-volatility acids the regeneration of the extractants is challenging. While a number of approaches to regeneration have been explored, all these developments in extraction and regeneration are at the research level to date—few have found their way into commercial practice. The reasons for the apparent lack of success in industrial developments are:

- the toxicity of the solvents
- the poor selectivity of the extractants for the separation of, *e.g.*, acetic acid from carboxylic acids with similar pK_a values
- the difficulty of cost-effective regeneration of the extractants
- the residual solvent present in the processed water

Membrane processes in principle can avoid costly phase changes. At the present time, however, hydrophobic membranes with a high selectivity for aqueous organics can only offer a low permeability, whereas the more permeable membranes are not sufficiently selective. The separation of acetic acid from carboxylic acids, *e.g.* acrylic acid, cannot be achieved by membrane processes such as reverse osmosis and ultrafiltration since both acetic and acrylic acids are low-molecular-weight carboxylic acids and since membranes do not usually have pores that are small enough to separate acetic acid from the raw waste water.

Adsorption with activated carbon or, sometimes, with adsorbent resins is frequently used in wastewater treatment for the clearing of organic water constituents, which are difficult to biodegrade or are not biodegradable. These adsorbents, however, lack selectivity in the separation. Acetic acid can be adsorbed on activated carbon, but the adsorption is lack of selectivity and the irreversible adsorption may make reuse of activated carbon difficult.

While ion-exchange resins have been extensively used for separation and purification in hydrometallurgy, there has been increasing interest in applying ion-exchange technology to environmental remediation and waste minimization. This is because ion-exchange resins are totally insoluble in water, there is no release of toxic solvents to cause problems with environment, and because a relatively concentrated product stream can be obtained by ion-exchange process with low energy consumption. A weakly basic ion-exchange resin in the free-base form could be used to extract acetic and related acids from the effluent. The percentage extraction is extremely high, since the extraction is based on the neutralization of a base by an acid. However, the extraction suffers from low selectivity. All the homologues of acetic acid are extracted and eluted together. In addition, large volumes of regeneration solution will be produced during resin regeneration. The costs for ion-exchange or adsorption process are decisively influenced by the desorption, since this determines the expenditure not only of the adsorption–desorption cycle, but also of the subsequent process steps.

Overall, it may be realized from the above review that none of the present commercially significant extraction and separation techniques may be used to separate acetic acid from acrylic acid with a good combination of selectivity, economy, and environmental allowance. It is necessary to seek techniques that invoke differences in microproperties of molecular structure of a component in the mixture. Most of the techniques now available for difficult separations are tentative; they depend on the addition of a third component that changes the physical properties or created a new phase. For example, extractive or adductive crystallization, reactive distillation, dissociation extraction, extraction with supercritical fluids, and precipitation from a hydrotropic solution have been presented.[6–11] We believe that selective complex formation reactions may be useful for developing economically viable and environmentally benign processes. The strong interest in precipitation is spurred by its potential no waste discharge. It should be, however, pointed out that it is impossible to recover acetic acid from fermentation broth or wastewater by conventional calcium salt precipitation process because calcium acetate is soluble in aqueous solution. We propose a metalorganic precipitation process, by which both practically pure acetic acid and a precursor of advanced zirconia ceramics can be obtained from the effluent of an acrylic acid plant, as a potential alternative to the existing incineration treatment of the effluent.

Theoretical considerations

In the preparation of zirconia ceramics the very important and frequently used chemicals are zirconium oxychloride and carboxylic acids,[12–14], since metal carboxylates are the interesting precursors for the preparation of ceramic oxides and films. Acetic acid may be used as a chelating agent to stabilize the precursor for zirconia, whereas acrylic acid can form a precipitate with zirconyl chloride under suitable conditions and very finely divided zirconia could be obtained from the precipitate.[15–16] The thought spawned the work described in this paper.

The aqueous solution chemistry of zirconium(IV) has proved to be quite complicated due to the hydrolytic behavior of group IV complexes even in strong acid solutions. It may be expected that both $ZrOOH^+$ and $[Zr_4(OH)_8]^{8+}$ with water of hydration are present in the solution because of the following factors. When ZOO (zirconium oxychloride octahydrate) is dissolved in water it gives rise to $[Zr_4(OH)_8]^{8+}$. This species goes into the solution phase with water of hydration and forms basic zirconyl ion, $ZrOOH^+$. Both $[Zr_4(OH)_8]^{8+}$ and $ZrOOH^+$ may react with acetate ion. Acetate can complex zirconium(IV) and displace the hydroxyl groups in the tetranuclear species $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ present in the Zr(IV) acidic aqueous solution, resulting in soluble hydroxoacetatozirconium chlorides.

On the other hand, most carboxylic acids are weak acids. Carboxylic acids in aqueous solution mainly exist as monomers because the intermolecular hydrogen bonding between acids is destroyed due to their preferential hydrogen bonding with water molecules. They will partially ionize in aqueous solution according to eqn. (1)

$$HA \Longleftrightarrow H^+ + A^- \quad (1)$$

The concentrations of dissociated (A) and undissociated acids (HA) are affected by the concentration of hydrogen ion or pH. The polymerization of acrylic acid depends strongly on the degree of ionization of acrylic acid in solution, *i.e.*, pH. When the basic zirconyl cation $ZrOOH^+$ comes in contact with acrylate ion in an acidic solution, they would

Dr Guo carrying out a precipitation experiment on the effluent from an acrylic acid plant at Shanghai Jiao Tong University

combine to form a precipitate, which consists of cross-linked polymer chains bridged by zirconium ion.

Results and discussion

The raw materials for our studies were effluents from the Shanhai Gao-Qiao Petrochemical Plant which manufacture acrylic acid. The effluent contains low molecular weight carboxylic acids (acrylic and acetic acids) which show resistance to biological and chemical oxidation. Acid concentrations were measured using a gas chromatograph. Technical zirconium oxychloride was used for the metalorganic precipitation process with the resulting zirconia precursor being calcined at 650 ºC. Fig. 1 shows the precipitation dependence of acrylic acid and acetic acid on pH values. It may be noted from Fig. 1 that the percentage precipitation of acrylic acid with a given concentration of aqueous zirconium oxychloride solution follows an increasing trend as pH value increases. When pH value is around 6.0, the percentage precipitation of acrylic acid can approach 100%. Then, it drops off at pH >6.0. on the other hand, the percentage precipitation of acetic acid exhibits a gradually rising tendency with an increase in pH value and even at pH 6.0 or higher it only has about 10%. These results suggest that precipitation which proceeds at pH 5.5–6.5 should be favourable for removing acrylic acid and retaining acetic acid. At these pH values, the percentage precipitation of acrylic acid may be over 80% while acetic acid is precipitated to a lesser extent (~10%).

In the case of acrylic acid alone, the pH value at which precipitation occurs is 1.2, and an appreciable amount of precipitate is produced by the present process at pH 3.7. It is evident that these pH values are lower than the corresponding values in the presence of both acrylic and acetic acids. As indicated earlier, acetate ion can complex zirconium(IV) and displace the hydroxyl groups in the tetranuclear species $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ present in aqueous zirconium oxychloride solution to form soluble hydroxoacetatozirconium chlorides so that the pH value at which acrylic acid is allowed to be precipitated in the presence of acetic acid is increased.

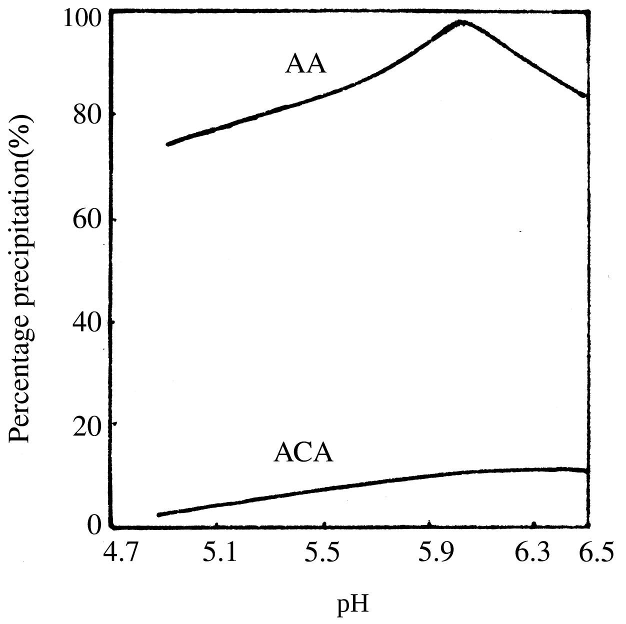

Figure 1. Percentage precipitation of acrylic acid (AA) and acetic acid (ACA) with zirconium oxychloride as a function of pH value.

When precipitation proceeds at pH 5.5~6.5 which exceed the pKa value of acetic acid, it is present very largely as acetate ions in the aqueous solution. This just is what is required for the complexation of zirconyl chloride because this complexation is achieved by the linkage of carboxylate ions and not of carboxylic acid molecules. The coordination of acetate ions on zirconium ions in zirconyl chloride aqueous solution leads to a soluble complex, as indicated above. On the other hand, acrylic acid is a polymer precursor with added active sites for the formation of large gel network structures. Basic zirconyl cations can combine with acrylate ions in acidic solution to form a precipitate, which consists of cross-linked polymer chain bridged by zirconium ion. This is the reason why acrylic acid can, with a high yield, be precipitated by the present process while most of acetic acid remain to be retained in the effluent. In addition, it should be indicated that zirconium hydroxide precipitate can be produced by the hydrolysis of zirconium oxychloride in aqueous solution with an addition of ammonia at pH *ca.*2, but in the presence of acrylic acid a basic zirconium acrylate would result rather than zirconium hydroxide. At higher precipitation pH values (>6), however, the formation of some zirconium hydroxide appears to be inevitable, resulting in a relatively low percentage precipitation of acrylic acid.

The solution after precipitation contained some inorganic constituents determined by inductively coupled plasma-atomic emission spectroscopy (Zr was measured by EDTA-complexometric titration), as shown in Table 1. Their concentration is low, depending on the pH value at which precipitation proceeds. It is understandable that as the pH value increases the concentrations of inorganic constituents decrease. At the pH values which are favourable for both acrylic acid removal and acetic acid retention, total the content of inorganic constituents may be less than 100 ppm in the solution after precipitation. Subsequent recovery of free acetic acid by cation exchange treatment of the solution should prove straightforward, whereas the precipitate obtained by the present process is a precursor which may result in advanced zirconia ceramics and this will be reported elsewhere.

Conclusions

It is shown from the assessment of the existing and potentially applicable

Table 1. Compositions of the effluent.

pH	Organic acids(wt%)		Inorganic constituents (ppm)						Remarks
	acrylic	acetic	Zr	Fe	Al	Ca	Si	Na	
1.9	0.68	3.67	1762.8	39.64	20.8	9.9	5.9	0.72	before precip.
5.3	0.12	3.46	1488	0.55	13.81	9.75	1.19	0.45	after precip.
5.8	0.07	3.35	61.7	0.11	4.6	6.92	0.79	0.29	after precip.
6.1	.03	3.27	4.74	0.05	1.36	0.79	0.39	0.16	after precip.

processes for the extraction and separation of carboxylic acids that none of the current commercially significant extraction and separation techniques (distillation, solvent extraction, adsorption, ion exchange and membrane process) may be used to separate acetic acid from acrylic acid with a good combination of selectivity, economy, and environmental allowance. This study demonstrates that both practically pure acetic acid and a precursor of advanced zirconia ceramics can be obtained by the metalorganic precipitation process using zirconium oxychloride at pH *ca.* 6.0 from the effluent of an acrylic acid plant, suggesting that near-zero discharge can be achieved in the production of acrylic acid by the simple, environmentally friendly, and cost-effective process.

Acknowledgements

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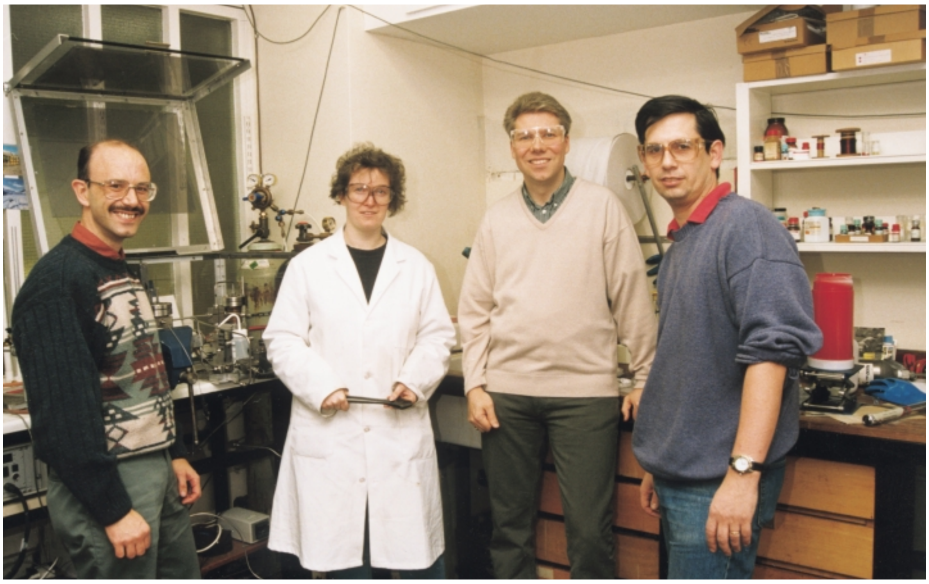
Green Chemistry at Leicester University

Mike Lancaster of the Green Chemistry Network reports

In many university chemistry departments across the world more attention is being focussed on green chemistry issues and there is a gradual increase in the establishment of Green Chemistry or Clean Technology Centres. Leicester is no exception, but what is somewhat unusual about Leicester, at least in the UK, is that the recently established Green Chemistry Group (LGCG) is focusing on applying several of the principles and techniques of green chemistry to solve problems rather that specialising in one particular aspect of the subject.

LGCG
LEICESTER GREEN CHEMISTRY GROUP

The three people mainly responsible for setting up the group are Drs. Andrew Abbott, David Davies and Professor Eric Hope who have wide ranging experience in such diverse areas as supercritical fluids, catalysis, electrochemistry and ionic liquids. The group has been strengthened by the recent appointments of Drs. Sandeep Handa (asymmetric catalysis) and Phil Dyer (polymer-supported catalysis). Research in these areas is core to the greening and cleaning of many current and future industrial processes. Industrial interest in the groups ionic liquid work has already led Abbott and Davies to set up a new company, Scionix, a joint venture between the University and Genasys (part of Whyte Chemicals). The company has patented important, novel ionic liquid technology (unfortunately information is not yet in the public domain) which will hopefully lead to inexpensive cleaner processes.



Supercritical fluids

Supercritical fluids are increasingly being used in extraction processes and reaction technology is now being introduced through companies like Thomas Swan and others. Much of the research on scf's is done using CO_2, which in many ways is the ideal solvent, being non-toxic, non-combustible and readily available. However, for many potential applications the solvent properties of $scCO_2$ are poor due to its low polarity. This inevitably leads to larger more complex and costly industrial plant. Hope and Abbott are looking at alternatives to CO_2 for reactions requiring polar substrates.

In particular the Leicester group are studying hydrofluorocarbon solvents that have readily attainable critical points (*e.g.* HFC 134A has a Tc of 101 °C and a Pc of 40.6 bar).[1] The solvent properties of these fluids have been studied by measuring the solvatochromatic shifts of indicator solutes as a function of temperature and pressure and these measurements used to predict the solubility of other species in these fluids. Under supercritical conditions HFC's have solvent properties similar to diethyl ether. Under these conditions polar molecules such as salicylic acid are more then 100 times more soluble in scHFC's than in $scCO_2$.

The Leicester group has also pioneered the study of electrochemical processes in this country. The main interest is to develop electrochemical sensors for measuring solubility *in situ* during supercritical extraction processes. Because most processes are diffusion controlled, the reduced viscosity of these media means that diffusion limited currents are increased by an order of magnitude, improving sensitivity.

HFC solvents allow high solubilities of electrolytes and also have exceptionally high electrochemical stability and this property is being used to study extreme oxidation reactions such as:-

$$Xe \longrightarrow Xe^{2+} + 2e^{-}$$

Catalysis

Catalysis is one of the cornerstones of the green chemistry movement, with approximately one third of the GNP of industrialised countries being dependent on catalysis. The Leicester group are focussing on three key areas, asymmetric catalysis, polymer supported catalysis and fluorous biphase catalysis.

Asymmetric catalysis continues to be of great academic and industrial importance, for the green chemist their use can potentially give rise to simple clean production of enantiopure materials of great value to the pharmaceutical industry. One of the areas the Leicester team is studying is the use of asymmetric catalysts for the conjugate addition of diorganozincs to unsaturated carbonyls (Figure 1).

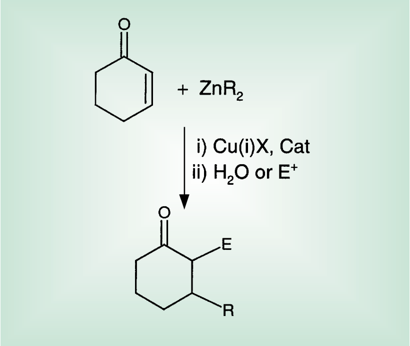
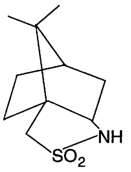


Figure 1. Conjugate addition of diorganozincs to unsaturated carbonyls. Reagents and conditions: 0 °C, 2 h Cat concentration <0.01 mol equiv.

These reactions are particularly useful to study since they are high yielding and catalyst turnovers are generally very high. The research work involves using a combinatorial approach to synthesise and screen a library of chiral sulfonamide catalysts in order to examine the steric and electronic factors which influence catalyst efficiency and enantioselectivity. For example, sulfonamide catalyst **1** gives an unoptimised enantiomeric excess of 24% (Figure 1, R = Et, E = H).



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A further area of interest to Davies is the use of asymmetric catalysts in enantioselective Diels–Alder reactions. Both asymmetric Rh and Rh catalysts have been employed[2,3] and have produced ee's of over 70% for the reaction of dicyclopenta-diene with methacrolein. The reaction takes place at room temperature in quantitative yields; at lower temperatures the enantioselectivity is even higher.

The use of catalysts on insoluble solid supports helps retain the potentially toxic metal, preventing contamination and aiding recovery. One of the holy grails of catalysis research is to combine the green aspects of traditional heterogeneous catalysts with the generally higher selectivities and efficiencies achieved with homogeneous catalysts. It is advances in this area the group are hoping to achieve.

The approach being taken involves synthesising catalysts consisting of a polymeric 3D scaffold to which is attached a pendant spacer group containing a functionalised site for attachment of the catalyst. Initially polystyrene is being used as the support, largely due to its ease of polymerisation and the ease and versatility of introducing functionality and morphology variations through incorporation of, for example, divinylbenzene as crosslinking agent.

Since the first reports in 1994[4] interest in fluorous biphase catalysts has continued to grow. The concept involves derivatization of the catalyst with long perfluorinated aliphatic ponytails, which renders the reagent soluble in the perfluorinated hydrocarbon phase. This allows facile separation of the products which remain in the organic phase. One major advantage of the system is that it can be tailored such that the fluorinated and organic phases are imiscible at room temperature but completely miscible at elevated temperature, this, of course, leads to the possibility of having the advantages of both homogeneous and heterogeneous catalyst systems.

The main focus of work at Leicester is in the synthesis of phosphorus ligands containing perfluoroalkyl chains. One of the main possibilities for this work is the development of clean selective technology for the hydroformylation of alkenes, which conventionally employs a rhodium / phosphine catalyst.

Model studies on the hydroformylation of hexene (Figure 2) have proved highly encouraging with very high yields and selectivities being achieved. One interesting observation is that the normal / iso ratio can be varied significantly by changing the ligand, for example a n/i ratio of up to 8.4 can be achieved with $P(OC_6H_4\text{-}4\text{-}C_6F_{13})_3$.

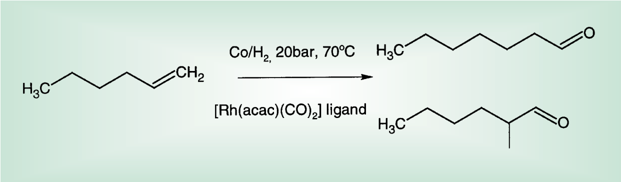

Figure 2. Hydroformylation of hexene. Reagents and conditions: solvents – toluene/1,3-perfluorodimethylcyclohexane.

Ionic liquids

The search for benign, easily recoverable alternatives to volatile organic solvents is of great industrial significance. Ionic liquids (along with supercritical fluids) are at the forefront of much research in this area. Ionic liquids offer a very large liquid range (up to 300 ºC), no effective vapour pressure and good solvent properties for a range of organic and inorganic materials. Potential applications of ionic liquids include catalysis, metal deposition, extraction and batteries; the cost and moisture sensitivity have hindered the commercialisation of ionic liquids in many of these areas. The Leicester Green Chemistry Group have, however, developed a range of inexpensive materials that are highly water-resistant. The physical and chemical properties of these materials as well as potential applications are being investigated, with three postdoctoral fellows working in the area.

Most of this work is currently being patented and is commercially sensitive, however the group will be posting regular updates on their web site—http://www.le.ac.uk/chemistry/lgcg/.

Education and research

Leicester is beginning to introduce aspects of Green Chemistry in their undergraduate courses. A practical project on supercritical fluids looking at the effects of catalyst, time and solvent on Friedel–Crafts reactions is proving popular with students. Although at the early planning stage it is hoped to introduce a full Green Chemistry module within the undergraduate course.

In general, Abbott, Davies and Hope are relatively happy with current options for obtaining funding for green chemistry research. One issue that has caused problems with EPSRC funding is that often green chemistry proposals cross the traditional organic/inorganic/ physical boundaries and as such it is sometimes difficult to find the correct 'home' for applications.

The concept of the multi-disciplinary approach to solving green chemistry problems is obviously one that appeals to industry. The LGCG may be breaking new ground in the UK but it is a model that will surely become more popular.

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The LMCCCO– Green chemistry in Montpellier

Duncan Macquarrie† **from the University of York and Daniel Brunel from the LMCCCO describe the work on the rational design of catalysts and adsorbents being carried out at Montpellier in France.**

Photo credits: Christine Oberlinkels - ENSCM

Professor François Fajula (Head of the LMCCCO Laboratory) and Dr Anne Galarneau (Synthesis Group) in front of the LMCCCO Laboratory in Montpellier.

The Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique (LMCCCO) at Montpelier, France, was set up in 1982 by the merging of a synthetic organic chemistry group and a materials chemistry group. Since then the combination of these two areas of expertise has promoted the rational design of catalysts and adsorbents for many applicational areas.

The LMCCCO is situated on its own site (La Galéra) in the Parc Euromédecine, a high tech science park, mostly concerned with medical research—a theme of great strength in Montpellier, ever since the founding of the medical university (now Montpellier I) in 1232. The lab complex is close to the Science and Technology University (Montpellier II), with which it has many links.

The group, headed by Professor François Fajula, consists of 25 permanent researchers, and 39 post-doctoral workers and students. Within this groups there are four sub-groups, specialising in different areas, and working to combine theoretical modelling studies on zeolites and related materials with the synthesis of optimally designed solids for adsorption and catalysis. This part of the work is then coupled to the utilisation of the materials in processes of industrial importance. Fundamental work on kinetics and characterisation of the different catalytic systems leads to further understanding and improvements in the performance of the systems.

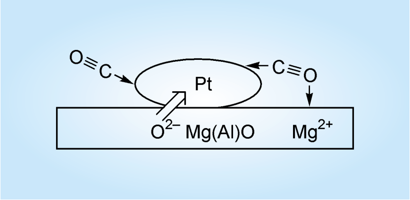
The research themes are divided into the following four areas:

Catalytic reduction

This area is headed by Bernard Coq and Annick Goursot, and is concerned with the development of supported metal catalysts for the reduction of NOx and pollution control, and also for the reductive cleavage of N- and S-containing pollutants in fuels. Both areas of research are underpinned by theoretical chemical modelling of the catalysts and processes involved. Typical catalysts are based on zeolitic materials exchanged with various transition metal cations such as Cu, Ru and Rh, often with co-cations to further enhance activity.

They also study metal - support interaction which affects the properties of bifunctional catalysts for hydrogenation (Scheme 1).

For further information see refs. 1–4



Scheme 1. Interactions of carbon oxide with platinum supported on Mg(Al)O.

Acid-base catalysts and adsorbents

The use of zeolites and hydrotalcites in catalysis and adsorbency are the major themes within the group led by François Fajula, Francesco Di Renzo, Dan Lerner and Annick Goursot. Again benefiting from theoretical studies, the group prepares novel zeolites and mesoporous solids for acid-base catalysis and redox catalysis. Additionally, there is a great deal of interest in the development of hydrotalcites as basic materials. Hydrotalcites are layered Mg-Al oxides which display a significant degree of basicity. They have been used in many base-catalysed reactions with success.

The preparation of Micelle Templated Silicas (MTS) is a second major area of current activity. These materials stem from the discovery of MCM-41 in 1992, and the Montpellier group has carried out a substantial amount of work into their mechanism of formation. The understanding of the influence of synthesis conditions on the properties of the material is crucial to their application, and is a complex function of many factors (Scheme 2).

The group has autoclave systems capable of routinely producing kilo quantities of MTS materials, allowing large quantities to be prepared in a single batch.

The catalysts prepared in this group are used for applications relating to the petrochemicals industry, in base catalysis applications, and as supports for the materials prepared as part of the activities of the next group.

For further information see refs. 5–7

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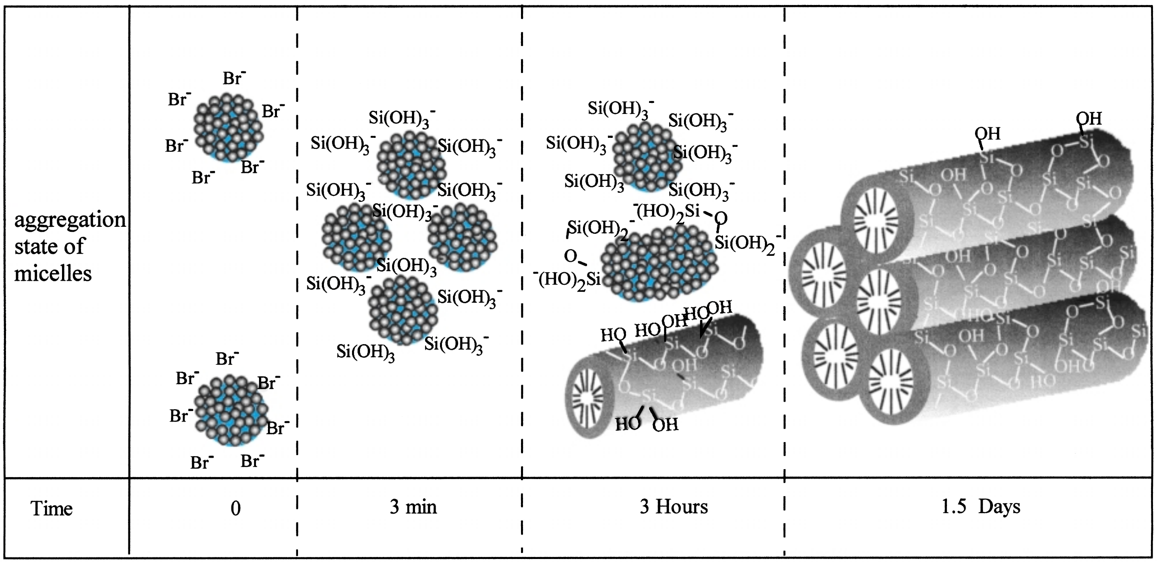
† DM recently spent a Royal Society-funded 3-month study visit at the LMCCCO



Scheme 2. Mechanism of formation of ordered hexagonal mesophase by condensation of silica-coated micelles. (A. Galarneau, F. Di Renzo, F. Fajula, L. Mollo, B. Fubini and F. Ottaviani, J. Colloid Interf. Sci., 1998, ***201****, 105-117).*

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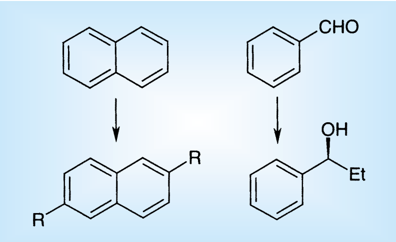
Acid-base catalysis in fine chemicals production

Patrice Moreau and Daniel Brunel are in charge of the application of novel solid catalysts to fine chemicals synthesis. Their areas of research are predominantly acid catalysis and base catalysis, but increasingly enantioselective, transition metal-centred reactions are being investigated.

The acid catalysis work centres on electrophilic aromatic substitution, one of the major problem areas in industrial chemistry. In particular, the group has contributed greatly to both acylation and alkylation of aromatics using acid zeolites as catalysts—novel routes to the 2,6-dialkylnaphthalenes obtained *via* the novel dialkylation technology using zeolites. The products are used as precursors to monomers for high-performance plastics. The research uses tailor-made zeolites, are often based on a combination of computer modelling and wet chemical results.

Base-catalysed research has involved hydrotalcites, modified zeolites, and most recently, organically modified MTS materials. The approach used here has been to graft amine functions onto the highly ordered MTS supports to provide uniform catalytic materials for use in a range of C–C bond forming reactions. Other, more powerful bases continue to be investigated.



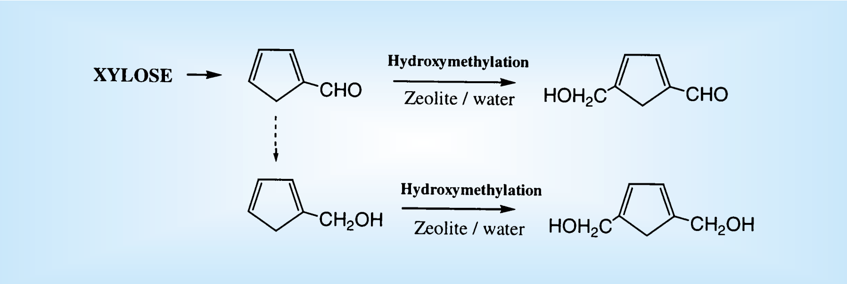
Oxidation and enantioselective catalysts have also been prepared by grafting more complex functionalities, such as supported ephedrines and heterocyclic ligands onto the supports, leading to catalysts for oxidation and the addition of diethylzinc to aldehydes, an important C–C bond forming reaction.

For further information see refs. 8–12

Catalysis for feedstock sugar chemistry and for remediation

The final area of investigation is led by Claude Moreau and Jean-Louis Olivé, and is concerned with two diverse areas—the first is the use of sugar chemistry as a contribution to the development of natural renewable resources as alternative feedstocks. In particular, the use of heterogeneous catalysis is investigated. The treatment of *e.g.* starches, hemicelluloses, and cellulose with acids leads to both C5 and C6 sugars which can then be converted into a range of useful materials including bifunctionalized furan derivatives which are precursors to polymeric materials.

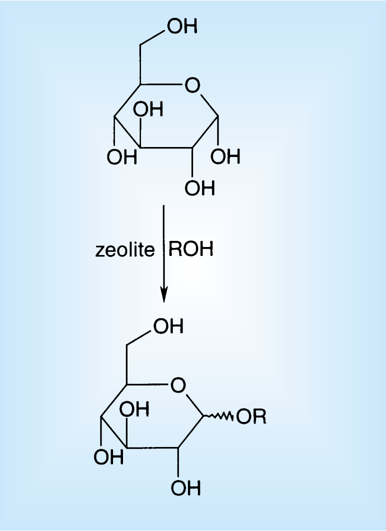
For further information see refs. 13–15



Francesco Di Renzo (Synthesis Group) and Dr Daniel Brunel (Functionalization of Materials and Catalysis) in the organic chemistry room at LMCCCO, Montpellier.

Photo credits: Christine Oberlinkels - ENSCM

The second area involves environmental remediation by the use of photocatalysis in presence of TiO_2 and TiO_2/Zeolite for oxidative degradation of chloro compounds in aqueous solution.



For further information see ref. 16

To aid the research carried out in Montpellier, the group has many collaborations both with industry (Elf-Aquitaine, Air Liquide, IFP, Rhodia, Givaudan-Roure, Roquette and CEA) as well as with over 20 universities and research establishments around the world (within Europe—Spain, Italy, the UK, Switzerland, Belgium, Russia and Romania), Asia (China and India), North Africa (Morocco) and North and Central America (Canada and Mexico). The group publishes around 50 articles per year, as well as several book chapters and patents.

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Green Chemistry Institute

The Green Chemistry Institute (GCI) is a not-for-profit entity established to support and promote the development, understanding and use of green chemistry for the purpose of protecting human health and the environment. The organization is made of institutions representing all aspects of the chemical enterprise industry, academia, non-governmental organizations and government. Participants and partners are located all over the world.

Recently, a series of agreements have been executed which formalize the relationship between the CGI and several institutions worldwide. The new international affiliate chapters of the CGI are:

Australia
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The Green Chemistry Institute

New affiliate chapters are under negotiated in at least five more countries and will be announced in the near future.

Chapter Rights

A chapter of the GCI is entitled to the following rights and privileges as a member of GCI:

- Each chapter is entitled to identify itself as an affiliate of the GCI in any publicity, outreach or promotional activities.
- Each chapter will have one (1) voting member on the GCI Board that will be entitled to participate on all decisions before the board including projects, products, budgets, and strategies.
- Each chapter is eligible to receive benefits such as funding, products or other benefits from GCI as appropriated by the GCI Board.
- Each chapter will be entitled to participate in all GCI activities such as conferences, workshops, meetings and product developments listed on the GCI Web page.

Chapter Responsibilities

- Each chapter is expected to actively engage in the furtherance of green chemistry through appropriate mechanisms available to the chapter.
- Each chapter's activities associated with green chemistry will fall within the scope of chemical products and processes designed to reduce or eliminate hazardous substances (other environmental activities such as waste treatment, control, remediation, etc will not be considered green chemistry).
- Each chapter is encouraged note their affiliation with the GCI in any materials, presentations, etc. that are part of their green chemistry activities.
- Each chapter will communicate activities in green chemistry to the headquarters location in Washington DC for dissemination to the general GCI membership.
- On regular basis, each chapter is expected to report on green chemistry activities in order to facilitate information exchange.

For more information or if interested in establishing and international chapter, please contact:

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e-mail: dennish@lanl.gov
or visit the Green Chemistry Institute website
(http://www.apt.lanl.gov/projects/green/)

EPA BEACH program

The EPA, recognizing the need for consistent and improved monitoring systems, has announced the Beaches Environmental Assessment, Closure and Health (BEACH) Program. The goal of this program is to reduce the risk of disease to users of the nation's natural recreational waters through improvements in recreational water programs, communication, and through scientific advances. In response to the BEACH program, an Action Plan for Beaches and Recreational Waters was developed. The Action Plan addresses program development activities, risk communication activities and improvements in the science supporting recreational water monitoring programs. The latter includes water quality indicators research, modeling and monitoring research, and exposure and health effects research. Research areas of interest are identified in the Action Plan and three of these are described below. In this Request for Applications (14

February–15 May 2000), the EPA solicits applications that take new and innovative approaches to develop methods or exposure assessment information in three research areas associated with the nation's natural recreational waters (http://es.epa.gov/ncerqa/rfa/beaches4.html).

IChemE expand environment awards

The IChemE Excellence in Safety and Environment Awards, now in the seventh year of running, have been expanded to include a new award for Sustainability. The programme now includes award categories for engineering innovation, responsible care and sustainability as well as the ultimate award —The Cremer and Warner medal. The new sustainability award is being sponsored by Eutech Engineering Solutions, the consultancy company created by ICI in 1993.

Last years winners included Gardener Energy Management with its revolutionary Gem venturi orifice steam trap which promises to save industry a considerable amount of money on wasted energy and Solutia's Newport factory which demonstrated consistent environmental improvements. The top award went to ICI polyurethanes and du Vergia for a polyurethanes recycling pilot plant.

To register an interest in these awards see http://www.tce-online.com.

There is still time to enter this year's UK Green Chemistry Awards, nominations close on 31 May 2000. There will be 3 awards, one for a young academic preferably working with industry and two awards for industry (at least one being for an SME). The academic award is worth £10,000. For further details contact greennet@york.ac.uk.

Green software packages

Atrion, the environmental, health, safety and transportation software specialists have developed a new package to train employees in all aspects of the area and allows companies to introduce their own procedures and policies.

CHEMMATE is being marketed as much more than a training package however, it is claimed to be the most powerful and integrated solution for intelligent, enterprise-wide environmental, health, safety, and transportation management. Further information can be obtained at http://www.atrion-intl.com.

New software called WISARD has been developed for the UK Environment Agency by the Ecobilan Group. It is aimed at local authorities and the waste industry to enable decision-makers to use life cycle assessment techniques to help establish the best environmental options for managing waste.

Waste-Integrated Systems Assessment for Recovery and Disposal, claims to be the first system of its kind in the world to bring together a waste management database with a powerful and easy to use software package. It was designed as a part of an extensive £1.5 million research project undertaken by the Agency into the emissions and resource use of different waste management options, and to adapt life cycle techniques for waste management.

Designed with a user friendly, graphical representation of different waste management systems, WISARD allows users to simply model all the aspects of the systems, including the container system, collection, separation, recycling, incineration, composting and landfill and to compare their environmental impacts. For more information on WISARD see http://www.ecobalance.com/software/wisard/wisard_home.html

Steve Lee, Head of Waste at the Agency, said "Determining the systems that are best for the environment is very difficult, particularly when we need to take into account transport, infrastructure and other indirect effects. If we want to make sure the changes in waste management practice we are proposing will actually improve the environment, we have to assess all possible consequences across the life cycle. Life cycle assessment is an important technique in the context of sustainable development because it takes account of all the environmental emissions and resource uses that are attributable either directly or indirectly to waste management. For example, when assessing waste incineration, the electricity generated as well as the change in associated pollution must be compared to that produced from coal."

Grants

EPA to fund ecological classification schemes

The US EPA is soliciting grant applications for establishing ecological classification schemes and reference conditions to support development of biological criteria for aquatic ecosystem health in one or more of the following resources: wetlands, large rivers, ephemeral systems, reservoirs, lakes, streams, estuaries, near-shore coastal environments, and coral reef communities. Development of biocriteria for evaluating the condition of aquatic resources within the US is central to implementing the Clean Water Act's objective to "restore and maintain the chemical, physical and biological integrity of the Nation's water". Approximately $6M will be made available in 2000 and the closing date is April 17, 2000 (http://es.epa.gov/ncerqa/rfa/classific2000.html).

EPA's Global Change Research Program is assessing the potential consequences of climate change and climate variability for human health, ecosystems and social well-being in the US. The new call is for proposals that address the development of models that will enable assessors to consider the effects of human activities in tandem with the effects of climate change and climate variability. Up to $5M will be available for 2000 with a deadline of 26 April 2000 (http://es.epa.gov/ncerqa/rfa/00humanrfa.html).

Exploratory research to anticipate future environmental issues (EPA STAR programs)

Research conducted under the STAR program is an important mechanism for promoting a sound scientific foundation for environmental protection, one that addresses current problems and anticipates future problems. One of the approaches under STAR to build this foundation is the issuance of requests for applications (RFAs) for research that addresses gaps in today's science and engineering knowledge. A second approach is to allow open, investigator-initiated projects which apply new, novel, and highly innovative approaches to address environmental issues or the scientific or engineering principles that underlie them. Our objective in this announcement is to support innovative, and possibly high risk, research that may help define and understand significant emerging environmental problems. We seek novel approaches that can lead to significant breakthroughs which provide enhanced environmental benefit. This solicitation combines two former EPA STAR program areas, Exploratory Research and Futures: Detecting the Early

Signals. The emphases in this new program combine features of both, and provides mechanisms for both identifying a problem and conducting research to solve it. Applications are invited from 14 February to 6 July 2000 (http://es.epa.gov/ncerqa/rfa/explfuturefnl.html).

CIA Awards

The UK Chemical Industries Association has announced its awards for advancing public understanding and appreciation of science and the application of science and familiarity with chemicals and the chemical industry throughout the news media. The awards were announced at the Royal Society in London on 8 February 2000.

Pauline Newman of the BBC World Service won a £5000 Chemical Industry Media Presidents Award for her outstanding contribution to increasing the public understanding of science during 1999. She presented the chemistry the chemistry of cassava, coffee, cement, soap, rubber and paper in historical, humanitarian and economic contexts. The judges said that “she did this in such a clear and direct style that she showed us, even at our age, how much we still have to learn about the important role of chemistry in nature and the world about us”

Steve Connor, science editor of the *Independent* newspaper, also won a £5000 Chemical Industry Media Presidents Award for his outstanding contribution to increasing the public understanding of science in 1999. The judges pointed out that “In common with several other entrants, Steve Connor came to the rescue of readers by trying to make sense of the confusing debate over genetically modified foods. He displays a real talent for highlighting the ethical and scientific issues raised by a wide range of topical subjects, each of which he tackled in a thorough and painstaking way.”

The Association Award was won by Carol Allen of Dow Chemical, Kings Lynn, for the outstanding work she and her colleagues undertook to correct the factual errots in the news media originating from information provided by an environmental pressure group. The judges said “It is a credit to the team at Dow Chemical that they have secured acknowledgement from this pressure group, on the BBC Radio 4 *Today* program, of their 3-year investment in pollution abatement and praise for their 99% cut in emissions”

This was the sixth year of the awards. In previous years the Presidents award has been won by John Emsley, George Auckland, Roger Highfield, Ruth Prince and Paul Bader. Previous winners of the Association award are BP Chemicals in Hull, Lambson Group I Harrogate, Zeneca Plant Science in Bracknell, Tom Swan in Consett, and Jane Measures from BP Amoco in London.

An integrated approach to inherent safety, pollution prevention and green chemistry

The Center for Waste Reduction Technologies in the US organised a workshop on March 7 to review, critique and strengthen a preliminary approach for the development of a practical, integrated (or at least coordinated) approach to inherent safety, pollution prevention and green chemistry. The workshop was part of the AIChE Spring 2000 meeting in Atlanta. Further information is available from Dana Ponciroli at the CWRT, 3 Park Avenue, New York NY 10016-5991, USA (Tel +1 (212) 591 7462/Fax 8895; e-mail: danap@aiche.org; http://www.aiche.org/cwrt.

EPCA calls for co-operation on European water

The Director General of the European Crop Protection Association (ECPA) has called for more co-operation between European representative bodies to continue to improve the quality and safety of drinking water. The collaboration in Belgium involving the Belgian crop protection industry is seen as a model for this and similar initiative are underway in the UK, Ireland, Germany, France and Austria. The key players in these collaborations are seen to be the crop protection industry, regulators and legislators, regional water companies, and the farmers. Their activities should include promoting good crop protection practice such as Integrated Crop Management (ICM) and Integrated Pest Management (IPM), joint research projects, monitoring residue levels and addressing regulatory issues (*RSC, January 2000*).

RSC Green Chemistry Network

For those who haven’t visited the web site recently (http://www.chemsoc.org/gcn) it is now possible to register your membership interests online. We are also starting to update the current issues section more regularly, so it is worth visiting the site on a regular basis.

The network is currently involved in organising three events:

- A Young Persons Symposium in Leicester on 24 May 2000. The focus of the day will be presentations by Ph.D. and Postdoctoral students from local universities on such diverse Green Chemistry topics as fuel cells, catalysis, and supercritical fluids. Professor Keith Scott of Newcastle will give the Keynote lecture. This event is free to all students and academics.

- A 1½ day symposium on Clean Technology for the Speciality Chemicals Industry (26/27 September 2000 in Manchester) is being organised through the Speciality Chemicals Sector of the RSC. Speakers will be mainly from industry (UK and mainland Europe) and the conference will have a heavy focus on case studies, together with a flavour of emerging technologies.

- Green Chemistry—Speciality Chemicals & Processes (Swansea 2001) is the first major conference in the UK covering all aspects of Green Chemistry including Education and Chemical Engineering. The conference will be of equal value to industrialists, academics and educationalists.

Finally there is still just enough time to apply for the UK Green Chemistry Awards. More information can be found on the web site, there are awards for academics and industry and the application procedure has been designed to be as simple as possible.

CIA proposes new definition of energy intensive industry

In an attempt to break the impasse over the UK governments energy tax proposals the UK Chemical Industries Association (CIA) has suggested a new definition of energy intensive industry. This is designed to provide the government with a standard for judging a factory's eligibility for tax rebates, which are to be offered to heavy energy users. Members of the government's Integrated Pollution Prevention and Control (IPPC) scheme will be entitled to 80% discount on their tax. The CIA argues that this unfairly excludes some chemical companies who have large chemical demands but do not come under IPPC. Industrial gas companies for example fall into this category – they separate nitrogen from oxygen in air but their raw materials and end products are air and therefore are not part of IPPC (*Chem. Ind*., 24 January 2000).

Belgians urged to use tax system to develop greener economy

Belgium should use taxation to penalise pollution and reward "greener" practices in sectors ranging from transport to health to agriculture, government committee said in a report recently published. In a draft paper on environmentally sound policy-making which covers agriculture, energy, health and social policies, the advisory committee on sustainable development recommended increasing taxes on energy and reducing employment taxes.

Fiscal and other government policies should aim to reduce Belgium's demand for power by 7.5% of 1990 levels by 2010 and to double the market share of renewable energies such as wind power to two percent of total consumption, in line with European Union guidelines, the committee said.

The committee recommended making road transport more expensive to encourage the use of other modes. In the agriculture sector, policies should encourage the reduction of pesticide use and increase organic farming by 60% by 2004 *(Reuters News Service)*.

Environmental best practice guide for printed circuit board industry

The Printed Circuit Board (PCB) Industry uses considerable amounts of heavy metals, volatile organic solvents and other hazardous chemicals, as such, expenditure on environmental compliance is almost 6% of total industry costs compared to under 2% for UK industry as a whole. In an attempt to reduce these costs industry members have prepared a new guide under the Government's Environmental Technology Best Practice Programme (ETBPP).

The report advises on ways of dealing with releases of metals such as lead and copper as well as volatile organic compounds and chelating agents such as EDTA. In relative terms the industry has a heavy consumption of water, which is often added to effluent streams to bring metal concentrations within consent levels. The report highlights way of reducing metal content in effluent streams as well as giving advice on reducing water consumption through recycling and more effective rinsing. The report suggests that many PCB manufacturers could cut water consumption by up to 50%, saving up to £60,000 pa.

This report is available from ETBPP on Tel. 0800 585794, Fax 01235 463804; E-mail: etbppenvhelp@aeat.co.uk.

UN protocol to ensure polluter pays

The United Nations has established a new protocol setting out a liability and compensation regime resulting from the international movement and disposal of hazardous wastes. The aim of the protocol is to provide countries with compensation when damage results from the legal or illegal trade in waste. The protocol sets out a framework for determining who is financially liable in the event of an accident during all stages of movement across boundaries from the point at which waste is generated until it is exported, imported and disposed of. It will, however, take several years before the protocol is ratified by member nations.

NETI

Background

National Environmental Technology Institute (NETI) was established by Act of the Massachusetts Legislature in 1994 with key support from the Massachusetts Chemical Technology Alliance. Its focus is on the design and modification of processes and materials "upstream" to minimize pollution prior to ultimate treatment and disposal. Projects involve University of Massachusetts Amherst researchers from diverse departments and disciplines including chemical engineering, polymer science and engineering, chemistry, mechanical and industrial engineering, electrical and computer engineering, and public health and health sciences; and industry partners from large and small companies located in Massachusetts and nationwide. NETI's goal is to become a national leader in pollution prevention research, development, and technology transfer.

Mission

The conventional wisdom is that we must choose between environmental protection and economic growth. But what if innovation could simultaneously help companies reduce their environmental impacts and improve their operating efficiency? That's the goal of the National Environmental Technology Institute (NETI), at the University of Massachusetts Amherst. NETI's three-part mission, set by act of the Massachusetts Legislature, is to:

- **research and develop** new manufacturing process designs for pollution prevention and waste reduction
- **demonstrate and disseminate** existing and new process information and designs to industry and government
- **provide expertise** on industrial process design to government officials responsible for policy and regulations

Instead of conventional, costly, regulation-driven "end-of-the-pipe" waste treatment and disposal methods, NETI focuses on "green chemistry" research, designing and modifying processes to prevent pollution by either eliminating byproducts or finding productive uses for them within the manufacturing process itself. Projects involve UMass Amherst researchers from diverse fields including chemical engineering, polymer science and engineering, chemistry, mechanical and industrial engineering, electrical and computer engineering, civil and environmental engineering, and public health and health sciences. Since its creation five years ago, NETI has funded 27 research projects totaling $2.4 million, with industry partners providing an additional $1.2 million in direct and in-kind support.

NETI is a partner in the Massachusetts Strategic Envirotechnology Partnership (STEP), a collaboration between the University of Massachusetts, the Massachusetts Executive Office of Environmental Affairs, and the Massachusetts Department of Economic Development to promote research, development, and transfer of environmental technologies.

Workshop

From 11–12 June 1998 NETI and the Center for Industry Research on Polymers at the University of Massachusetts Amherst campus co-hosted a workshop on *The Role of Polymer Research in Green Chemistry and Engineering*; the event was sponsored by The U.S. Department of Energy, the U.S. Environmental Protection Agency, and the Green Chemistry Institute. The workshop predicted that. with adequate investments in research and application of green chemistry principles, the US chemical industry should be able to achieve, by the year 2020:

- A 50% reduction in the time it takes to bring new polymers to market.
- A 40–50% reduction in energy use in polymer manufacturing.
- Nearly 100% elimination of all emissions and raw material waste in the polymer manufacturing process.

Proposals for Fiscal Year 2000

Six individual projects have been selected for support in the areas of

- Radiation Curing of Polymers
- Prevention of Hazardous Solvents in Polymer Processing Using Supercritical Fluids
- Molecular Sieve Membranes: Processing-Microstructure-Separation
- Evaluation of Technologies for Achievement of Zero Discharge in the Textile Industry
- Environmentally Benign Processing of High Performance Fibers using Subcritical and Supercritical Carbon Dioxide
- Waste Minimization Through Integration of Process Design and Process Control

In addition there has been a commitment to continue funding for the two group projects underway:

- Environmentally Benign Products and Processes Based on Homogeneous Catalysis
- Green Chemistry, Physics, and Engineering of Polymers

More information on NETI can be obtained on http://www.umass.edu/tei/neti/

Non-Food Crops

IENICA

Early in 2000 IENICA (Interactive European Network for Industrial Crops and their Applications) launched a major, strategic document on the current status of industrial crops in Europe. This comprised 14 National Reports including a 200-page 'state of the art' review of the UK industrial crops arena completed by ACTIN (Alternative Crops Technology Interaction Network) early in 1999 (under the umbrella of IENICA) addressing science & technology, industry, market & environmental issues & barriers to progress. These individual reports, which form the basis of the IENICA document, will be available from the European Commission later in 2000. Executive summaries of all the Reports are already available on the IENICA website (http://www.csl.gov.uk/ienica/) or, in the case of the UK, locally at http://www.actin.co.uk/

During March 2000 the full Executive Summary to the IENICA project 1996 to 2000 reporting progress in detail will also be published on http://www.csl.gov.uk/ienica/

In March 2000 the IENICA partners submitted a bid to the EU Commission's DG Research, under Framework V, for funding for a further three years under the title IENICA MILLENNIUM; twenty-one countries will be involved. For more information on IENICA see *Green Chem.*, 1999, **1**(2), G39 and the IENICA website).

LINK Programme

The LINK programme 'Competitive Industrial Materials from Non-Food Crops' (CIMNFC), launched in June 1996 has provided funding for a wide variety of projects. VHEAR (Very high erucic acid rapeseed and THERMOSTARCH (Novel products from modified starches) projects came to an end in 1999. Work continues of the established projects: INDINK (Plant-derived indigo for industrial research); IONEX (Plant fibres as ion-exchange media); and SEMIOCHEM (Behaviour control from new crops). New projects include: STARPLAST (Biocompostable materials from starch); FIBRECLEAN (Improved cleaning machinery for flax fibre); RAPFI (Rosemary Antioxidants for the Pharmaceutical and Food Industries); and SEEDEX (Extraction of fixed seed oil products from novel crops by compressed carbon dioxide). For more information on any of these projects see http://www.dti.gov.uk/ost/link/foocim.html.

Research on oil crops

The oilseed Engineering Alliance, announced on 9 March 2000, between The Dow Chemical Company, Dow AgroSciences LLC, Michigan State University, Miami University, Washington State University and the U.S. Department of Energy's Brookhaven National laboratory, is pooling the expertise of a number of researchers to improve traits of specific oils and fatty acids in soybeans, canola, sunflower & other crops. Dow Chemical And Dow AgroSciences are committing more than $10 million to the Alliance over a 5-year period to hire additional researchers and fund new initiatives. According to John Ohlrogge and Mike Pollard, professors of botany and plant pathology at Michigan State – the project's coordinating university – the key to the research is the idea that plants can easily perform chemistry that is difficult for chemists. The research will coax plants to produce more acids and oils that are more stable and better suited to manufacturing needs. It could also make the oils easier to extract, reducing the cost of plant oils as compared to petroleum-based products.

Gas survivors at a rally commemorating the 15th anniversary of the Bhopal Disaster in December 1999, emphasising that suffering is still continuing.

Photo courtesy of Barbara Dinham, Pesticides Trust

Bhopal: 15 years on

The name Bhopal has become synonymous with industrial disaster. Now, a Greenpeace report has revealed severe environmental contamination around the former Union Carbide India Ltd (UCIL) pesticide plant. In the 15 years since the catastrophe at Bhopal, how has the chemical industry changed, and which issues still remain to be confronted? Becky Allen reports.

However many anniversaries pass, and however many times they are repeated, the statistics of the Bhopal disaster are still profoundly shocking: between 3000 and 10,000 killed and over 500,000 injured; 50,000 survivors totally or partially disabled; and over seven years’ litigation to achieve an out-of-court settlement of $470 million. To this human toll, Greenpeace has now added data on the environmental contamination in and around the UCIL plant: recent analysis of soil and water samples shows gross contamination with heavy metals and persistent organic pollutants.

According to the Greenpeace report[1], levels of tetrachloromethane of 1705 times above World Health Organization limits were found in some groundwater samples, as well as trichloromethane and chlorobenzenes. Analysis of soil samples revealed high levels of mercury, other metals and organochlorines. The report by the Greenpeace research laboratories at Exeter University concludes that as contaminated wells lie upstream of the plant, the pollutants reflect ‘long-term contamination of the aquifer’ due to routine use or spillages of chemicals on site. One the report’s authors, Ruth Singer, says: “The results of the survey indicate severe contamination by toxic chemicals at a number of locations within the old plant. The extent and nature of toxic chemicals found in the ground water indicate the need for immediate action to provide clean drinking water supplies for the local communities, and to prevent further releases of chemicals from the factory site itself.”

> ‘although the chemical industry made many changes after Bhopal—both voluntary and mandatory—there are many outstanding issues that remain to be addressed.’

Coming so soon after the controversy over genetically modified foods, and the dramatic public protests at the World Trade Organization’s negotiations in Seattle, the report will reignite debate about corporate responsibility. Nityanand Jayaraman, Greenpeace’s toxics campaigner in India, says: “The fact that Union Carbide has escaped without cleaning up the site exposes the gaping loophole in the legal and administrative infrastructure to ensure corporate responsibility. The contaminated condition of the Union Carbide site is a prime example of corporate irresponsibility and the inability or unwillingness of governments to rein in corporations at the cost of public safety and environmental health.” Although the chemical industry made many changes after Bhopal—both voluntary and mandatory—there are many outstanding issues that remain to be addressed.

National responses to Bhopal

Bhopal was a watershed for the chemical industry and a raft of legislation and voluntary initiatives followed the disaster. According to Jackson B. Brown, former head of Union Carbide’s health, safety and environment programmes: “At the time of Bhopal, the company was rated among those manufacturers with the best worker safety records. To a degree, we were smug about our record. Bhopal put an end to that attitude. It spurred new cycles of process monitoring and a fresh look at risk management . . . The impact of Bhopal went well beyond Union Carbide. It changed views and practices among the entire US chemical industry. It provided impetus to the development and enactment of federal laws requiring companies to notify government and the public about toxic substances they make or use. The EPA’s Federal Superfund Reauthorization, spurred by the Bhopal tragedy, helped bring about a network of local emergency planning councils, in which corporate specialists work with their neighbouring communities to safely deal with unthinkable environmental disasters.”[2]

> ‘Bhopal spurred new cycles of process monitoring and a fresh look at risk management . . .’

In the USA, the Emergency Planning and Community Right to Know Act 1986, the creation of the US Chemical Safety and Hazard Investigation Board as well as the Chemical Manufacturers Association’s Responsible Care® programme were all responses to Bhopal. According to Jon Holtzman, formerly of the Chemical Manufacturers Association (CMA): “The legacy of Bhopal has been to bring about fundamental change in the way the largest heavy manufacturing industry in the world does its job, as well as how it conducts its relationships with the public.”[3]

International action

Despite Bhopal’s impact on the way the chemical industry operates in the USA and Europe, critics argue that international action is urgently required to improve standards and accountability of multinational corporations. In a letter to the *Guardian* Richard Meeran, a UK solicitor and chair of the Solicitors for Human Rights Group, says: “There has been controversy at the World Trade Organization about the responsibilities of multinationals. The fact is that these powerful organisations operating across national boundaries are not liable under international law (including human rights law) because they are not states, although some of them are much wealthier and more powerful than many states. Nor is it easy for those, such as the Bhopal/Cape victims, to hold them to account under local law.”[4]

The United Nations Environment Programme (UNEP) and the Permanent People’s Panel (PPP) are two international organisations attempting to coordinate international improvements. In 1994 the PPP published the Charter on Industrial Hazards and Human Rights,[5] covering industrial hazards both in and outside the factory gate, and calls for:

- communities to have the right to refuse the introduction, expansion or continuation of hazardous activities
- rights to information and environmental monitoring
- rights to community emergency preparedness procedures, including warning systems and provision of adequate emergency services and relief efforts
- parent companies to be liable for the actions of subsidiaries
- individual rights to bring law suits in the forum of their choice

> ‘Greenpeace believes that –if ratified–the POPs treaty would ensure that the environmental contamination in Bhopal is finally addressed.’

In the environmental arena, negotiations began on an international Treaty on Persistent Organic Pollutants (POPs) in the mid-1990s under the auspices of

The accident

Late on Sunday evening, 2 December 1984, during routine maintenance of tanks containing methyl isocyanate (MIC) (an intermediate in the manufacture of the insecticide aldicarb), a large quantity of water entered one of the 60-tonne storage tanks. None of the safety systems was operating, and this triggered off a runaway reaction resulting in a tremendous increase of temperature and pressure. Just before midnight, a deadly cocktail of MIC, hydrogen cyanide, methylamine and other chemicals was carried by a northerly wind to the neighbouring communities. Over the next couple of hours close to 40 tonnes of the chemicals spread over the city of about one million people. People woke up surrounded by a poison cloud so dense and searing that they could hardly see. As they gasped for breath, the effects of the gas grew even more suffocating.

Official figures estimated over 500,000 people were exposed to the gas within a period of a few hours. This number was arrived at by totalling the population of residential districts where any fatalities occurred. An estimated 3000 people died in the immediate aftermath of the disaster due to acute complications of gas exposure; clinically manifested respiratory failure, pulmonary oedema, and adult respiratory distress syndrome. It is also estimated that well over 8000 people have died due to latent effects of exposure including chronic pulmonary disease and increased susceptibility to pulmonary infections.

UNEP.[6] An intergovernmental negotiating committee, due to meet again in Bonn as *Green Chemistry* goes to press, is drafting a global treaty to reduce or eliminate environmental emissions and discharges of POPs. In its current form, the treaty focuses on 12 highly toxic, persistent and bioaccumulative chemicals including aldrin, DDT, dioxin and PCBs. Greenpeace believes that —if ratified—the POPs treaty would ensure that the environmental contamination in Bhopal is finally addressed. "A global administrative and legal mechanism is required to address clean up of historical contamination, particularly in rapidly industrialising countries. This mechanism should make the polluter pay by placing financial obligations on the private sector and developed countries to clean up their pollution legacies. This mechanism should by included as a part of the United Nations Environment Programme POPs treaty," Greenpeace says.

> 'following the 1984 accident in Bhopal, the identification of inherently safer chemical processes has begun to accelerate and should be encouraged.'

Some, however, point out that the chemical industry needs to implement far more fundamental change in response to Bhopal. According to Dr Abe Mittelman, director of health assessment and technology transfer at Technical Resources International: "With increasing government and public interest in chemical safety following the 1984 accident in Bhopal, the identification of inherently safer chemical processes has begun to accelerate and should be encouraged. Indeed, the ultimate cost to industry may be high if it does not adequately address potential chemical risks that later become actual emergencies, with their resulting consequences."[7]

References

1 http://www.greenpeace.org/~toxics/toxfreeasia/press.html
2 http://www.bhopal.com/JBrowning.html
3 http://www.prcentral.com/rmjf95bhop.htm
4 http://www.guardianunlimited.co.uk/Archive/Article/0,4273,3938516,00.html
5 http://www.globalpolicy.org/socecon/envronmt/charter.htm
6 http://irptc.unep.ch/pops/POPs_Inc/press_releases/pressrel-99/NR99-8.html
7 http://ci.mond.org/9517/951710.html

Further reading

Websites

http://www.bhopal.org/
http://www.corpwatch.org/trac/bhopal/
http://www.prcentral.com/rmjf95bhop.htm

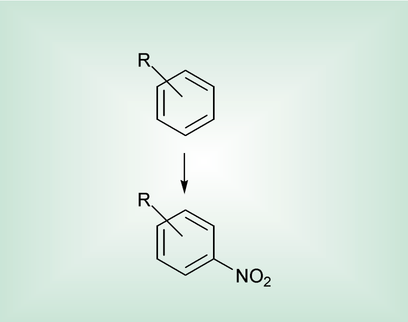
Books

David Weir, The Bhopal Syndrome (1988). ISBN 1 85383 011 9
Paul Shrivastava, Bhopal: Anatomy of a Crisis (1992), Tayler & Francis Inc., (ISBN 1 85396 192 2)
Arthur Diamond, The Bhopal Chemical Leak (1990), Lucent Books (ISBN 1 56006 009 3)
Larry Everest, Behind the Poison Cloud: Union Carbide's Bhopal Massacre (1986), Banner Press (ISBN 0916650251)
The Bhopal Gas Tragedy 1984-? (1988)
The Bhopal Gas Tragedy (recent articles taken from *Pesticides News*) (Pesticides Trust) (in preparation)

Clean nitrations

The nitration of simple aromatics remains, after 150 years, a major challenge in fine chemicals synthesis. Despite the fact that the nitro group is often reduced to an amine (by catalytic hydrogenation—a generally clean process), direct amination of aromatics is not yet generally applicable (although see *Green Chem.*, 1999, **1** G41), and thus clean and regioselective nitration processes are still needed.

The group led by B. M. Choudary, from the Indian Institute of Chemical Technology in Hyderabad has recently published an interesting method for the selective nitration of several simple aromatics (*Chem. Commun.*, 2000, 25). In this work, the researchers have used a zeolite with a high density of Brønsted acid sites, coupled with pore dimensions and connectivity likely to favour para selectivity (demonstrated by computer modelling studies). Normally activity drops rapidly as the reaction proceeds, due to the formation of water diluting the acid—alternative approaches to this problem have included the use of acetic anhydride or the use of acyl nitrate (see references in the paper). This system was coupled with azeotropic water removal to keep the activity of the nitric acid constant. This approach gave excellent reaction rates, improvements in selectivity, and the possibility of recovering the nitric acid not used in the reaction and recycling. While some further enhancements to the para selectivity would be desirable, the approach is attractive from many respects.



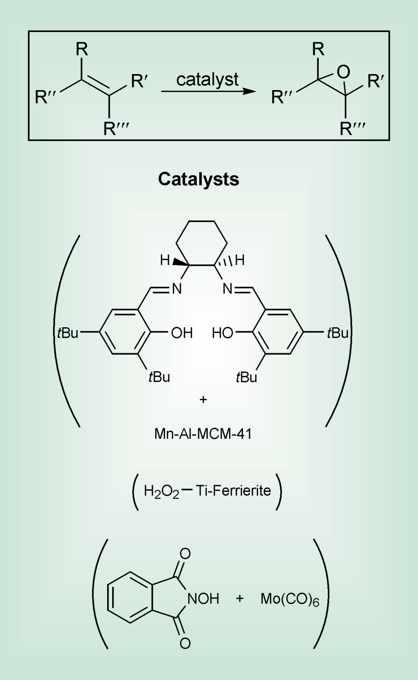
Epoxidations

The epoxidation of alkenes is one of the most important methods of functionalising simple hydrocarbons. Three novel methods have been developed to achieve this:

A group led by Graham Hutchings at Cardiff University has published results on the heterogenisation of Mn salen complexes, and their use in epoxidations (*J. Chem. Soc., Perkin Trans. 2*, 2000, 143). They used Mn-exchanged Al-MCM-41 as support, and adsorbed the chiral complex onto the support. The resultant material was an efficient catalyst for the conversion of (*Z*)-stilbene to the corresponding epoxide. Enantioselectivity under the best conditions was approximately equal to the homogeneous system.

The use of novel Ti-containing zeolites has been described in the epoxidation of alkenes with hydrogen peroxide. Avelino Corma's group in Valencia has described the preparation and use of Ti-ferrierite and TiITQ-6 as catalysts for this transformation (*Chem. Commun.*, 2000, 137). The control of the zeolite structure by delamination processes has been utilised to improve the activity of the catalysts. Conversions of the substrate are excellent (>90%), selectivities to hydrogen peroxide are also impressive at 50-75%. Turnover numbers are reasonable and reuse has been demonstrated.

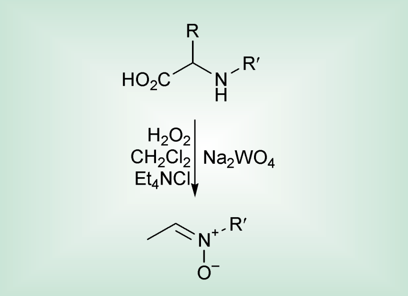
A further example of clean epoxidation is given by the group led by Yasutaka Ishii (*Chem. Commun.*, 2000, 163). The process uses two catalytic cycles; the first involves *N*-hydroxyphthalimide and optionally Co(II) to convert ethylbenzene to the benzylic radical which is trapped by the primary oxidant oxygen. The key advance is the use of molybdenum carbonyl to transfer the peroxy oxygen efficiently to the alkene. High conversions and selectivities were achieved.



Other oxidations

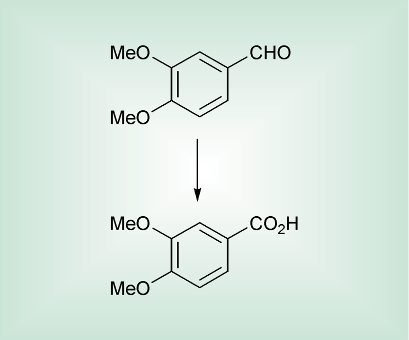
Clean preparation of nitrones

The use of nitrones in organic synthesis is widespread. Unfortunately, most routes to them involve hydroxylamines, the preparation of which is difficult, and subsequent oxidation, which often requires the use of stoichiometric oxidants such as mercury oxide. A group led by Shun-ichi Murahashi at Osaka University has devised a cleaner alternative to these procedures (*Bull. Chem. Soc. Jpn.*, 1999, **72**, 2737). The chemistry involves the use of hydrogen peroxide with sodium tungstate as a catalyst for the oxidation and decarboxylation of amino acid derivatives which leads directly to the nitrone. Yields are generally good.



Clean oxidation of veratraldehyde to veratric acid

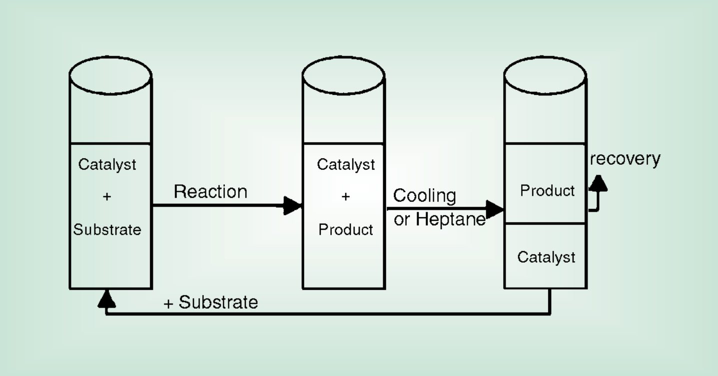
The replacement of highly polluting and toxic heavy metal stoichiometric oxidants such as chromates and manganese species has long been an important goal of green chemistry. Using air as primary oxidant typically requires a catalyst to increase rates and/or control selectivity. A recent contribution to this theme has been published by Sudip Mukhopadhyay of the University of Mumbai in India (*Org. Proc. Res. Develop.*, 1999, **3,** 365). A cobalt catalysed oxidation of the aldehyde was carried out using manganese acetate and lithium bromide as promoters. The reaction was carried out in a bubble column reactor. Complete conversion could be achieved after 3 hours at 130 °C and moderate air pressure. Under these conditions selectivity was excellent at 99%. Recycling and reuse of catalyst was not discussed.



Biphasic hydrogenations

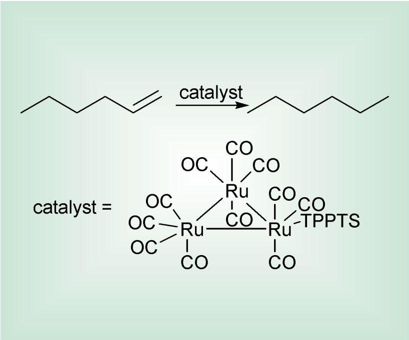
Organic biphase systems for hydrogenation of hexene

The use of many liquid biphase systems has recently been demonstrated. These include ionic liquid biphasic systems, fluorous biphase systems and PTC methodology. Another possibility is the use of a system where both phases are organic. Typically, these systems consist of a polar polymer [*e.g.* a poly(ethylene glycol)], a polar solvent and a non-polar solvent. Two groups from Brazil led by Watson Loh have shown that conventional catalysts can be used without the difficult and costly modifications required for, for example, fluorous or water soluble catalysts (*Chem. Commun.*, 2000, 33). They used Wilkinson’s catalyst and a cationic analogue with a diphosphine ligand to demonstrate the efficient hydrogenation of hexene, and the subsequent separation of the phases. The catalyst was partitioned almost completely into the polymer phase (loss of metal <0.1%) and the product into the nonpolar organic phase. Several reuses of catalyst were successfully carried out.



Water soluble Ru catalysts for biphasic hydrogenation

Paul Dyson and co-workers at the University of York have published results on the use of a water soluble ruthenium carbonyl cluster as an efficient and



reusable hydrogenation catalyst (*J. Mol. Catal.*, 1999, **150,** 71). The cluster is solubilised by replacing some of the CO ligands with a sulfonated phosphine. The resultant catalyst is capable of hydrogenating several alkenes efficiently under mild conditions.

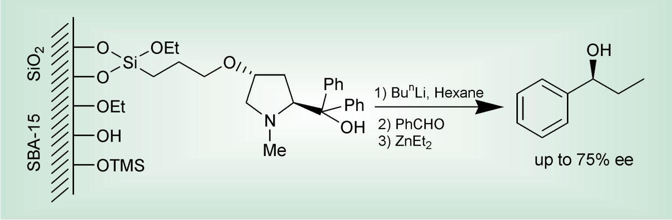
Conversion of CO$_2$ to methanol

The conversion of carbon dioxide to methanol is an interesting potential route for converting the greenhouse gas into a usable feedstock and fuel. Robyn Obert and Bakul Dave of Southern Illinois University at Carbondale have described a silica-entrapped triple enzyme system which does exactly that (*J. Am. Chem. Soc.*, 1999, **121,** 12192). They took formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase, and immobilised them in a silica matrix. Then, using NADH as reductant, they showed that they could reduce carbon dioxide to methanol at ambient temperature over a few hours. Activity was significantly higher than in reactions where the enzymes were not encapsulated. Such a technology may have uses in future as a clean and mild route for the production of methanol from a renewable resource.

Heterogeneous catalysis

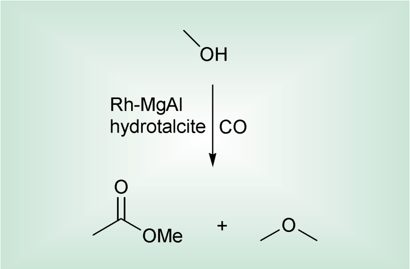
Chiral heterogeneous catalysts

Heterogenisation of chiral catalysts is an area of current interest for many groups. In particular, the advent of highly regular silicas has lent this area of chemistry added impetus. B Moon Kim and co-workers at Seoul National University have applied these novel supports to the anchoring of proline-derived ligand systems to MCM and SBA silicas. (for more detail on these materials, see for example excellent reviews by Ying *et al.* (*Angew. Chem., Int. Ed.*, 1999, **38,** 56) and Scherer *et al.* (*Chem. Mater.*, 1999, **11,** 2633). They found that the resulting materials are promising catalysts for the enantioselective addition of diethyl zinc to benzaldehyde, an important class of C-C bond forming reaction. Enantioselectivities were good, the best cases being >90%. One of the remaining challenges in this chemistry is the ability to completely suppress the ability of the silica surface to cause a background (non-selective) catalysis of the reaction. End-capping of the surface silanols with Me$_3$Si groups was not completely effective. Reuse of the catalysts was not demonstrated (*Chem. Commun.*, 2000, 31).



Heterogeneously catalysed carbonylation

The carbonylation of methanol to make methyl acetate and acetic acid are very successful processes industrially. The low cost of the products compared with the high price of the catalysts (Rh or Ir) makes efficient recovery of the catalyst critical. For this reason immobilised Rh catalysts are being investigated. Kapoor and Matsumura from the Osaka National Research Institute in Japan have recently published details of a nanoparticulate Rh on Mg-Al hydrotalcite which is an active catalyst for this chemistry (*Chem. Commun.*, 2000, 95). Major products were methyl acetate and dimethyl ether, the latter can be carbonylated to give methyl acetate. As is typical for these systems, the presence of a small amount of methyl iodide is essential for



carbonylation to proceed, although dimethyl ether is formed in its absence. No acetic acid is produced, in contrast to the homogeneous system. No leaching of metal could be detected, and the methyl iodide content remained constant throughout the reaction.

New clean route to silica aerogels

Silica aerogels are remarkable materials, which are generating a lot of interest in the electronics industry. They are ultra lightweight, have high thermal stability, and a low thermal expansion coefficient, allowing them to remain the same shape and size over a wide temperature range. These properties make them interesting candidates for applications in electronics.

However, one drawback is the tricky supercritical drying process, which represents a difficult challenge, and loss of the aerogel structure, as well as being expensive. Sheng Dai and co-workers at the Oak Ridge National Laboratory in Tennessee have recently demonstrated that the use of ionic liquids in the preparation of the aerogels avoids the need for the supercritical drying step, making the process simpler (*Chem. Commun.*, 2000, 243). The ionic liquids used during the preparation of the aerogel can be extracted and recovered by refluxing the product in acetonitrile. The products prepared are typical of those formed using the supercritical process.

Water based transformations

Shu Kobayashi and co-workers have developed a polymer-bound scandium catalyst which behaves as an effective Lewis acid in water, and which an be easily recovered after the reaction (*Angew. Chem. Int. Ed.*, 2000, **39** 567). This catalyst is based on a sulfonate-functionalised crosslinked polystyrene, and springs from earlier research on surfactant-based catalysts based on scandium dodecylsulfate. The catalyst is capable of a range of acid catalysed reactions, and can be recovered easily.

A second new catalyst capable of functioning in water has been disclosed by Roger Sheldon and his group in *Science* (3 March 2000). They were looking for a replacement for chromium-based oxidants. and were investigating variants on the known palladium-phenanthroline oxidation catalysts, when they decided to sulfonate the phenanthroline ligand, and came up with not only an alternative for chromium for the oxidation of alcohols, but a catalyst which works well in water too.

Selection of Recent Articles

C. M. Jensen, Iridium PCP pincer complexes: highly active and robust catalysts for novel homogeneous aliphatic dehydrogenations, *Chem. Commun.*, 1999, 2443.

S. Kadi *et al.* Direct synthesis of acetylene from methane by direct current pulse discharge, *Chem. Commun.*, 1999, 2485.

Y. Sun *et al.* Catalytic dehydrogenation of a mixture of C10 - C14 *n*-paraffins to linear C10 - C14 mono-olefins in supercritical phase, *Chem. Commun.*, 1999, 2499.

D. J. Cole-Hamilton, Carbonylation of methanol in supercritical CO_2 catalysed by supported rhodium complex, *Chem. Commun.*, 1999, 2511.

C. M. Wai, Selective extraction of strontium with supercritical CO_2 . *Chem. Commun.*, 1999, 2533.

N. J. Hazel, Environmental Solutions, *Chem. Rev.*, 2000, **9**(3), 13.

H. Carmichael, Making Waves, *Chem. Brit.*, 2000, **36**, 1.

D. Bradley, The ever shrinking laboratory, *Educ. Chem.* 2000, **37**, 1, (*Infochem*, **61**, 2).

W. Kaminski and F. Hartmann, New pathways in plastics recycling, *Angew. Chem., Int. Ed.*, 2000, **39**, 331.

M. Yashida *et al.* Catalytic production of urethanes from amines and alkyl halides in supercritical carbon dioxide, *Chem. Commun.*, 2000, 151.

N. Yashie *et al.*, Effect of low molecular weight additives on enzymatic degradation of poly(3-hydroxybutyrate), *Polymer*, 2000, **41**, 3227.

C. A. Eckert *et al.*, Clean solutions for chemical synthesis, *Chem. Ind.*, 2000, **3**, 94.

J. G. E. Kraute and M. Beller, An easy and practical synthetic route to electron rich water soluble ligands: alpha aminomethylation of trishydroxymethylphosphine, *Tetrahedron*, 2000, **56**, 771.

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

May 2000

Synthetic Methodology and Total Synthesis: New Horizons in Natural Product 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)

CSC2000—Canadian Society of Chemistry National Meeting and Exhibition **May 27–31**
Including symposium on “Green (Sustainable) Chemistry”
Calgary, Alberta, Canada
(http://www.chem.ucalgary.ca/csc2000/welcome.htm)

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)

Green Chemistry Symposium (part of NERM 2000) **June 18–21**
University of Connecticut, Storrs, CT, USA
(http://www.lanl.gov/greenchemistry/conf.html)

Utilisation of Vegetable Oils **June 20–21**
Bonn, Germany
(http://www.dainet.de/fnr/ctvo/final_conference.htm)

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

International Symposium on Ecomaterials **August 20–23**
Ottawa, Canada
(http://www.ecomed.de/journals/espr/)

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Clean and efficient synthesis of azo dyes using polymer-supported reagents

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Summary

The recent technological advancements in polymer-supported reactions have led to the propagation of combinatorial chemistry as a method for the rapid and efficient preparation of novel functionalised molecules. An interesting and fast growing branch of this area is polymer-supported reagents. Here we describe the principles of generating diazonium salts and their coupling using polymer-supported reagents and sequestrating agents, to form azo dyes in a clean manner.

Introduction

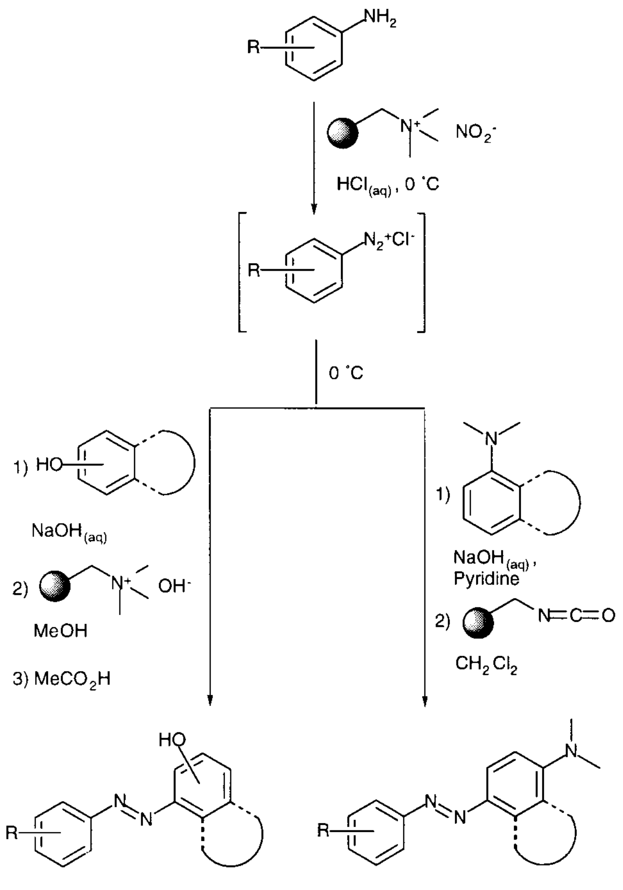
The application of combinatorial methods for the generation of novel chemical libraries, for use in the pharmaceutical and agrochemical industries, is now commonplace.[1] Increasingly, these methods are also being adopted by other sectors of the chemical industry in order to prepare novel materials for application in many diverse areas, especially catalysis.[2]

Many of these chemical libraries are obtained by carrying out linear synthetic sequences on polymer-supported substrates. While this approach has been very successful, there are still many associated problems and limitations which have not been fully addressed. Therefore, we have chosen to adopt a different strategy which allows us to synthesise a large number of compounds in solution, in a linear[3] or convergent fashion,[4] through the sequential use of polymer-supported reagents in a multi-step process. By adopting this approach we have previously been able to prepare a number of heterocyclic systems, including a small library of hydroxamic acid derivatives[5] and some natural products.[6] The advantage of this approach includes the ease of reaction monitoring (*i.e.* TLC, LC-MS) and the fact that with the appropriate design of sequences, clean products may be obtained using only simple filtrations rather than conventional work-up/purification techniques.

As a further demonstration of the potential of this approach we sought to synthesise a library of azo dye substances which are the most prevalent class of synthetic colourants. Although the textile, cosmetic and reprographics industries are by far the largest users of dyes, other applications range from analytical chemistry to the biomedical field in bacteriological work.[7] The most common process for their preparation involves the diazotisation of an aromatic primary amine and the coupling of the resultant diazonium salt with a phenol or an aromatic amine. This is traditionally achieved using conventional wet chemistry which leads to large quantities of down stream waste. With the ever increasing environmental restrictions and control on the release of effluent the ability to effect a clean and efficient synthesis of the azo-compound is of considerable environmental and commercial importance.

Results and discussion

For the generation of the diazonium salts a selection of anilines were reacted with a polymer-supported nitrite (Scheme 1). The preparation of this supported reagent[8] was achieved by ion exchange of the tetraalkylammonium chloride resin (Amberlyst A-26) with an aqueous solution of $NaNO_2$.



Scheme 1 Preparation of the azo dyes.

The generation of the diazonium salts was carried out on four aniline derivatives which were dissolved in HCl (37%), cooled to

Green Context

The clean production of azo dyes is a classical chemistry problem. The manufacture of this industrially important family of compounds is traditionally associated with large volumes of hazardous and coloured waste. The authors of this article have applied modern synthetic methodology to produce a more efficient and cleaner preparation of these compounds. The paper touches on clean synthesis, waste minimisation, the replacement or control of hazardous substances and novel improved separation technologies.

JHC

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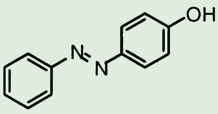
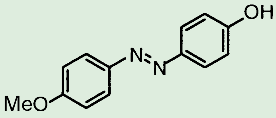
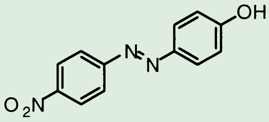
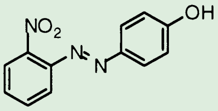
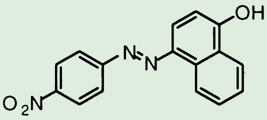
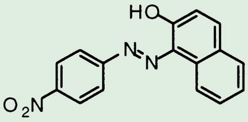
Table 1 Diazo dyes derived from phenolic coupling

Product	Yield[a] (%)	Purity[b] (%)	LC-MS	pH = 0	pH = 14
	90	>98	197.10(−)	Yellow	Yellow
	62	85	229.31(+)	Orange	Orange
	80	>98	224.15(−)	Yellow	Red
	quant.	>98	242.13(−)	Yellow	Orange
	78	80	292.19(−)	Orange	Blue
	quant.	>98	292.16(−)	Yellow	Violet

[a] Yields are based on the amount of phenolic derivative used. [b] Purity was determined by 400 MHz ^{1}H NMR spectroscopy.

0 °C and then the polymer-supported nitrite was added. The suspension was stirred for 5 min before the resin was removed by filtration. The filtrate was added dropwise at 0 °C to a solution of the phenolic derivative in NaOH (10%) with vigorous stirring which produced a coloured solution and a precipitate. The suspension was filtered with the filtrate being discarded and the precipitate then dissolved in MeOH. As the reactions were carried out with an excess of aniline, the methanolic solution contained the azo-derivative and unreacted aniline. In order to obtain the clean final product, the solution was subjected to a catch-and-release work-up which involved shaking the coloured solution with Dowex(OH). This captured only the product leaving a colourless solution after filtration. The isolated resin was subsequently washed with acetic acid releasing the pure product (Table 1). A slightly modified procedure was used for the preparation of the dimethylaniline series (Table 2). The solution of diazonium salt, prepared as described above, was added at 0 °C to a vigorously stirred solution of the dimethylaniline derivative in NaOH (10%) and pyridine.[9] Following the addition, the pyridine was removed *in vacuo* and the resulting precipitate was removed by filtration. The excess of unreacted aniline was selectively removed from the product by dissolving the solid in methylene chloride and shaking the solution with a polymer-supported isocyanate.[10] Filtration of the solution gave, after evaporation, the clean product. An attempt to couple the diazonium salt derived from 4-methoxyaniline with dimethylaniline gave no product. This result is in accordance with data for the relative rates of coupling for diazonium salts of aniline derivatives: 4-NO_2:H:4-CH_3O 1300:1:0.1[11]

As expected the products obtained acted as indicators and showed the characteristic change of colour at extremes of pH. All of the reactions produced essentially clean products as shown by LC-MS and ^{1}H NMR spectroscopy.

Conclusion

In conclusion, we have shown the possibility of using polymer-supported reagents for the generation of dyes without the need for conventional work-up and purification procedures. Moreover, the scheme of reaction demonstrates several different ways in which solid supported reagents can be used; their use as reagents, their use as scavengers in order to remove excess reactants or by-products and their use in catch-and-release procedures for purification. We believe that as the procedure only involves simple filtrations the reaction scheme could also be adopted for use in robotic systems in order to generate a large number of compounds. This would be of value in the generation of novel azo dye substances where rapid optimisation of the desired colour or properties are necessary.

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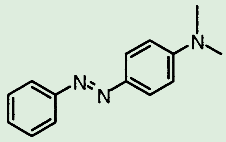
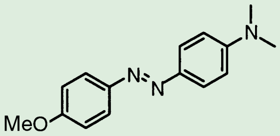
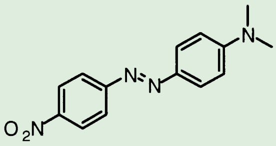
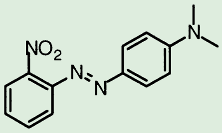
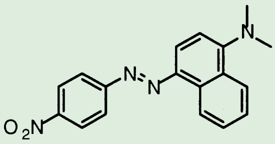
Table 2 Diazo dyes derived from dimethylaniline coupling

Product	Yield[a] (%)	Purity[b] (%)	LC-MS	pH = 0	pH = 14
	92	> 98	226.26(+)	Pink	Yellow
	—	—	—	—	—
	quant.	> 95	271.26(+)	Red	Orange
	quant.	> 98	271.21(+)	Red	Orange
	92	> 92	321.27(+)	Orange	Organge

[a] Yields are based on the amount of dimethylaniline derivative used. [b] Purity was determined by 400 MHz ^{1}H NMR spectroscopy.

1997, 1907; (*b*) B. Hinzen and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1; (*c*) B. Hinzen, R. Lenz and S. V. Ley, *Synthesis*, 1998, 977; (*d*) F. Haunert, M. H. Bolli, B. Hinzen and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2235; (*e*) S. V. Ley, M. H. Bolli, B. Hinzen, A.-G. Gervois and B. J. Hall, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2239; (*f*) M. H. Bolli and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2243; (*g*) J. Habermann, S. V. Ley and J. S. Scott, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3127; (*h*) S. V. Ley, A. W. Thomas and H. Finch, *J. Chem.Soc., Perkin Trans. 1*, 1999, 669; (*i*) J. Habermann, S. V. Ley and R. Smits, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2421; (*j*) J. Habermann, S. V. Ley, J. J. Scicinski, J. S. Scott, R. Smits and A. W. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2425.
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Cyanosilylation of carbonyl compounds catalyzed by a diamino-functionalised mesoporous catalyst†

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Summary

Addition of trimethylsilyl cyanide to carbonyl compounds catalyzed by a diamino-functionalised mesoporous material (MPEDA) as a solid base affords the corresponding cyanohydrin trimethylsilyl ethers in good yields at room temperature. The solid base catalyst can be recycled several times without loss of activity.

Introduction

Cyanohydrin trimethylsilyl ethers are industrially valuable and important intermediates in the synthesis of cyanohydrins, β-aminoalcohols, α-amino acids and other biologically active compounds.[1] These ethers are generally prepared by the reaction of trimethylsilyl cyanide (TMSCN) with carbonyl compounds in the presence of Lewis acid catalysts[2] such as $AlCl_3$, $LaCl_3$ and KCN/18 Crown-6 or $Bu_4N^+CN^-$. This reaction is also catalysed by Lewis bases[3] such as amines, phosphines and arsines and trimethylsilyl triflate[4] at 0 °C. Owing to the increasing environmental pressure, current interest is focused on the development of environmentally friendly solid catalysts for clean processes in the fine chemical industry. Hence, various solid acids[5] and bases[6] such as zeolites, clays, hydrotalcites, hydroxyapatite, calcium fluoride, *etc.* are receiving increased attention for various organic transformations because of their operational simplicity and higher selectivity coupled with the possibility of reusability. The fact that the recently discovered mesoporous materials[7] such as MCM possess conceivable industrial application in fine chemical synthesis is due to their tunable larger pore size. Brunel and co-workers[8] were the first to report the covalent attachment of organoamino groups on MCM-41. The modified mesoporous materials/silica anchored with organic basic moieties are found to be excellent catalysts[8–11] for the Knoevenagel, aldol and Michael reactions. Recently, we reported the synthesis, characterization and application of diamino-functionalised mesoporous material for Knoevenagel and aldol[10] reactions and the one-pot synthesis of nitroalkenes.[11]

Results and discussion

We herein report the use of the diamino-functionalised mesoporous material, a solid base catalyst obtained by functionalising mesoporous material with organic base, 3-trimethoxysilylpropylethylenediamine, for the cyanosilylation of carbonyl compounds to afford cyanohydrin trimethylsilyl ethers in high yields at room temperature (Scheme 1).

Scheme 1 Cyanosilylation of carbonyl compounds.

The diamino-functionalised mesoporous catalyst (MPEDA) was prepared by a two-step process, *viz.*, the preparation of the mesoporous material[12,13] (pure silica MCM-41). 1 g of the calcined MCM-41 (550 °C for 6 h) was added to dry toluene and treated with 0.3 mmol of 3-trimethoxysilylpropylethylenediamine for 24 h under an inert atmosphere. The solid was filtered off, washed with dry toluene, dry diethyl ether and dried under vacuum for 12 h.

In a typical procedure, 0.2 g of catalyst, 0.141 g (1 mmol) of *p*-chlorobenzaldehyde and TMSCN (1.5 mmol) were added to 10 ml of dry toluene and stirred at room temperature. The reaction was monitored by TLC. On completion, the catalyst was filtered off and the filtrate concentrated to obtain the desired product. The product was analysed by ^{1}H NMR and MS. The catalyst was washed with the solvent and reused without any further purification. δ_H 0.1–0.2 (s, 9 H), 5.4 (s, 1 H) and 7.4 (s, 4 H).

The efficacy of this catalyst as a base (0.3 mmol g^{-1} of loading) was tested in the synthesis of cyanohydrin trimethylsilyl ethers (Scheme 1). Various aldehydes and ketones were treated with TMSCN used as a nucleophile to give the corresponding cyanohydrin trimethylsilyl ethers in high yields at room temperature (Table 1). The results are impressive when compared with the other catalysts,[3,5,6] amines, Fe-mont and CaF_2 which require low temperatures and longer reaction times. A plausible mechanism is proposed in Scheme 2, for the addition reaction of trimethylsilyl cyanide with carbonyl compounds under basic conditions. The formation of the hypervalent silicate **1**, reported by Mukaiyama and co-workers[3] also fits in well with present conditions. Thus, hypervalent silicate formed from the interaction of the more basic secondary amine group of the diamino-fuctionalised mesoporous catalyst (MPEDA) and TMSCN is assumed to be an active cyanation intermediate. This silicate **1** readily reacts with a carbonyl compound to produce **2** since the nucleophilicity of the cyano group of **1** is enhanced by electron donation from the pentavalent silicon, followed by immediate silylation to give the corresponding cyanohydrin trimethylsilyl ether and restoring the amine thus regenerating the catalyst.

Green Context

The cyanosilylation of carbonyl compounds is a useful transformation which allows the formation of a C–C bond and the protection of an alcohol function. The products can be further transformed into *e.g.* a range of hydroxy-acid derivatives. The relative lability of the silyl ether, and the subsequent danger of elimination of HCN, means that a simple, mild isolation is necessary. This is provided by the use of a solid base catalyst, which gives good conversions, is easily separated and can be reused many times. *DJM*

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† IICT Communication No. 4442.

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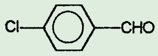
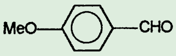
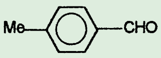
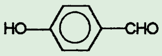
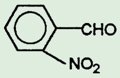
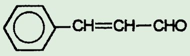
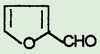
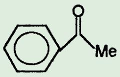
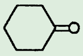
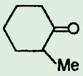
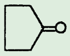
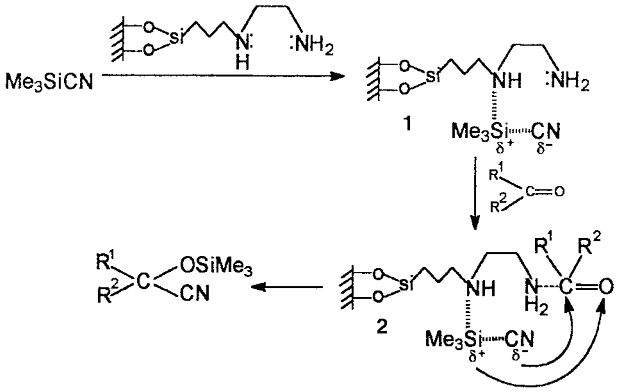
Table 1 Cyanosilylation of carbonyl compounds with TMSCN catalyzed by diamino-functionalised mesoporous material

Carbonyl compound	*t*/h	Yield[a](%)
	12	100 (98)[b]
	12	60
	12	80
	8	80
	12	100 (95)[b]
	12	63
	6	88
	12	28
	2	75
Me_2CHCH_2CHO	6	100
	2	70
	2	80

[a] Determined by ^1H NMR, based on starting material. [b] Isolated pure product.



Scheme 2 A plausible mechanism for the cyanosilylation of carbonyl compounds by the diamino-functionalised mesoporous material.

The reusability of the catalyst was checked over several cycles and shows consistent activity. Thus, the solid base developed by us gives cyanohydrin trimethylsilyl ethers in high yields at room temperature in a quite simple procedure under non-acidic conditions. Easy preparation of the catalyst and reusability by simple filtration for several cycles with consistent activity and without any further reactivation are additional advantages. The application of this methodology to the enantioselective addition reaction of TMSCN with aldehydes is under progress.

Acknowledgements

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Paper a908758c

Chemoselective, solvent-free aldol condensation reaction

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Summary

Aldol reactions may be carried out without use of preformed enolates simply by grinding together solid reagents in the presence of NaOH. No organic solvent (unless product recrystallisation is required) is utilised in the reaction and the only waste produced is a small amount of acidic aqueous waste. Single crossed aldol condensation products are produced in high yields even in reactions where a mixture of products is possible. These reactions are highly atom and energy efficient and are highly chemoselective. An additional advantage is the high stability of the reaction mixture, which may be stored for a lengthy period.

Introduction

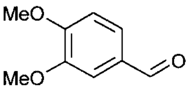
The reaction of a carbonyl compound, acting as a nucleophile (in the form of an enol or enolate derivative) with another, acting as an electrophile, to produce a β-hydroxycarbonyl compound which, on dehydration, becomes an α,β-unsaturated carbonyl compound is commonly referred to as the aldol condensation reaction. Such reactions are widely used in synthetic chemistry and a vast number of methods have been developed to facilitate this reaction.

While the first reports of such reactions utilised underivatised ketones and aldehydes with simple acid[1] or base[2] catalysis, the reaction is usually carried out using preformed enolates which serve both to increase the driving force of the reaction and to ensure that the desired chemoselectivity is achieved. While numerous elegant procedures have been developed to this end[3] these frequently require the use of reagents which are frequently themselves somewhat noxious and result in the generation of significant quantities of waste containing metal salts such as Li salts. The alternative routes to activated preformed enolates using enol esters or silyl enol ethers are poor performers when 'atom afficiency' is taken into account and many of these methods also require the use of potentially polluting solvents and low temperatures.

The perfectly 'green' reaction might be described as one which: proceeds at room temperature, requires no organic solvent, is highly selective and exhibits high atom efficiency yet produces no waste products.[4] Toda *et al.*[5] have reported solvent free aldol condensation reactions of benzaldehyde and acetophenone derivatives. In many of the reactions reported one of the reagents is a liquid at room temperature and in all cases aldehydes without α-hydrogen atoms are used ensuring that only a single aldol condensation product is possible. We now report highly chemoselective aldol condensation reactions between solid aldehydes and ketones as well as between solid ketones under solvent free conditions. These reactions proceed at room temperature and are high yielding and selective yet produce only small quantities of acidic aqueous waste. Interestingly, while the concept of grinding (including ultra high energy grinding) to promote chemical reactions has been known for some time, there have been few reports of application in synthesis.[6,7]

Results and discussion

Veratraldehyde **1**, 4-phenylcyclohexanone **2** and 1-indanone **3** may be reacted in various combinations under appropriate conditions to yield aldol condensation products. In the reaction between **1** and **3** a single condensation product is expected as the aldehyde **1** bears no α-hydrogen atoms and cannot therefore act as a carbon nucleophile. Compounds **1** and **2** may yield two products (a mono and bis adduct). The combination of **2** and **3** is less straightforward and a number of possible products may be envisioned including crossed Aldol products with either ketone acting as nucleophile, self condensation products of the ketones and a mixture of these two as illustrated in Scheme 1.



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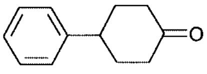

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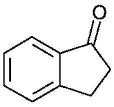

3

Compounds **1**, **2** and **3** are all solids at room temperature yet reaction under solvent free conditions at room temperature proceeds simply on grinding of the solid reagents together with solid NaOH. More remarkably a high degree of conversion is achieved and a single major product results. While a single product would be expected in the reaction of **1** and **3** and (given the correct molar ratio) in the reaction of **1** and **2**, a multiplicity of products, as described above, is possible for the reaction of **2** and **3**. Indeed, if this reaction is carried out in solution,†[8] without the

Green Context

The aldol reaction is widely used in synthetic chemistry. The reaction is usually carried out with preformed enolates so as to ensure high conversions of substrates and good selectivity. Unfortunately this tends to require the use of rather noxious reagents and typically the formation of relatively large amounts of waste. Here the very simple process of grinding together the substrates in the presence of NaOH as catayst is used to effect high yielding and selective aldol reactions. The reactions occur at room temperature and in the absence of solvent. Waste is kept to a low level. This methodology has clear green credentials.

JHC

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† Solid ketones dissolved in absolute ethanol and powdered NaOH added followed by stirring at room temperature.[8] Likely products include self condensation products of both **2** and **3** and both possible crossed aldol products as well as the various intermediate β-hydroxy ketones and multiple condensation products. More than seven spots are noted on TLC.

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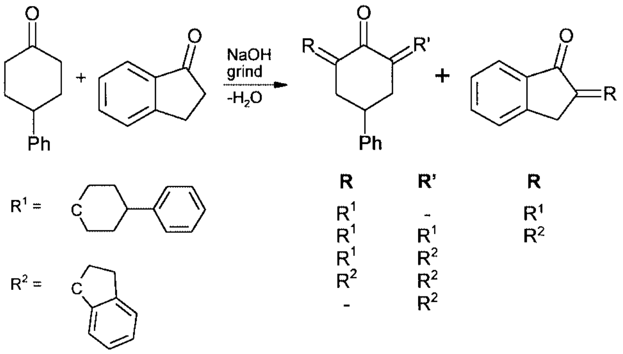


Scheme 1 Possible condensation products of **2** and **3**.

use of preformed enolate methodology a complex mixture of products results yet under the no-solvent conditions described a single crossed aldol product is isolated in excellent yield.

Resultant products and yields are summarised in Table 1. The molecular structures and configuration of the double bonds of products **I** and **H**, along with the molecular structure of **III**, have been established unequivocally by crystal structure determinations (Table 2). It was confirmed that the crystals obtained were representative of the bulk material by NMR spectroscopy and melting point analysis. The molecular structures are presented in Fig. 1. Product **IV** is analogous to that found by Toda *et al.*[5] in the reaction of cyclohexanone with benzaldehyde derivatives.

While the order of mixing of reagents had no discernible effect on the product purity, it should be noted that grinding of carbonyl containing reagents prior to addition of NaOH yielded a viscous, sticky liquid in each case. It appears that a eutectic, with melting point lower than the ambient temperature, exists in each case and that the reaction mixture is in fact a solution of the carbonyl compounds reacting together to yield a solid product which separates from this solution as reaction proceeds. This observation may provide insight into the remarkable selectivity of the ketone/ketone reaction **III** under these conditions. The observed product may be envisaged as the result of attack by a carbanion formed by 1-indanone on the electrophilic carbonyl carbon of 4-phenylcyclohexanone followed by spontaneous dehydration as indicated in Scheme 2.

If dehydration occurs immediately and is irreversible under the conditions of the reaction the product is trapped and no equilibration occurs. The solid product appears to be insoluble in the reaction mixture and is effectively removed by this change in phase driving the reaction rapidly to completion. Stabilisation of the 1-indanonone carbanion intermediate leads to higher acidity of the α-hydrogen atoms and, as no equilibration is possible (as the product is removed from the 'reaction solution'), no products due to attack of 4-phenylcyclohexanone carbanions are noted. Trace amounts of the self-condensation product of 1-indanone **II** are noted but do not increase during the reaction and are readily removed by recrystallisation. The attempted self-condensation of **3** under the same reaction conditions leads to very poor conversion to the condensation product **II**.

This remarkably simple, yet effective methodology is further enhanced by the stability of the powdered intermediate formed after grinding and reaction. The solid material obtained at this stage may be stored, prior to workup, for a lengthy period of time. No deterioration in product quality was noted after storing of the solid reaction mixture, without protection from either light or atmospheric oxygen and water, for 1 month. This advantage

Table 1 Solvent-free aldol reactions

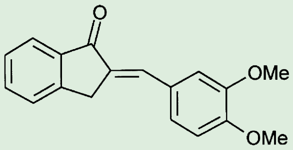
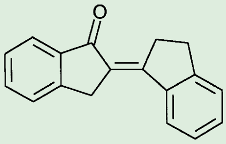
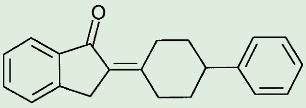
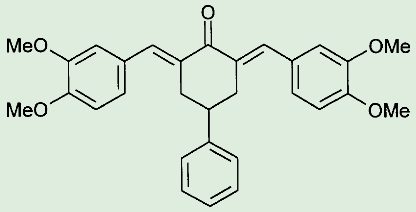
	Reactant mole ratios				Product		
	1	**2**	**3**	NaOH	Yield (%) (post recryst.)	Description, mp	Molecular structure
I	1	1		1	77	Clear pale yellow crystals 183–185 °C	
II		2		1	Trace	Dichromic colourless/orange crystals 140–141 °C	
III		1	1	1	98	Clear colourless crystals 137–139 °C	
IV	2		1	1	81	Bright yellow crystals 145–147 °C	
V			2	1	No reaction		

Table 2 Crystal and refinement data

		I		II		III	
Formula		$C_{18}H_{16}O_3$		$C_{18}H_{14}O$		$C_{21}H_{20}O$	
M		280.31		246.31		288.39	
Crystal system		$P2_1/n$		$P\bar{1}$		$P2_1/c$	
a/Å		6.9104(2)		7.2720(3)		12.2718(2)	
b/Å		15.8694(5)		7.5704(2)		7.8706(1)	
c/Å		13.2342(4)		12.3802(4)		16.1076(3)	
α/°		90.00		77.140(2)		90.00	
β/°		103.601(2)		89.263(2)		102.299(1)	
γ/°		90.00		69.1341(2)		90.00	
V/Å^3		1410.61(7)		619.23(4)		1520.07(4)	
Z		4		2		4	
Refl.$_{tot}$/Refl.$_{indep.}$		22803/3758		8949/3464		33252/4262	
n/restraints		192/0		172/0		199/0	
μ(MoKα)/cm^{-1}		0.089		0.080		0.075	
R indices							
R_1 ($I > 2\ \sigma I$)	R_1 (all data)	0.0492	0.0844	0.0466	0.0707	0.0448	0.0641
wR_2 ($I > 2\ \sigma I$)	wR_2 (all data)	0.1063	0.1163	0.1176	0.1345	0.1089	0.1160
GoF on F^2		1.061		1.078		1.053	

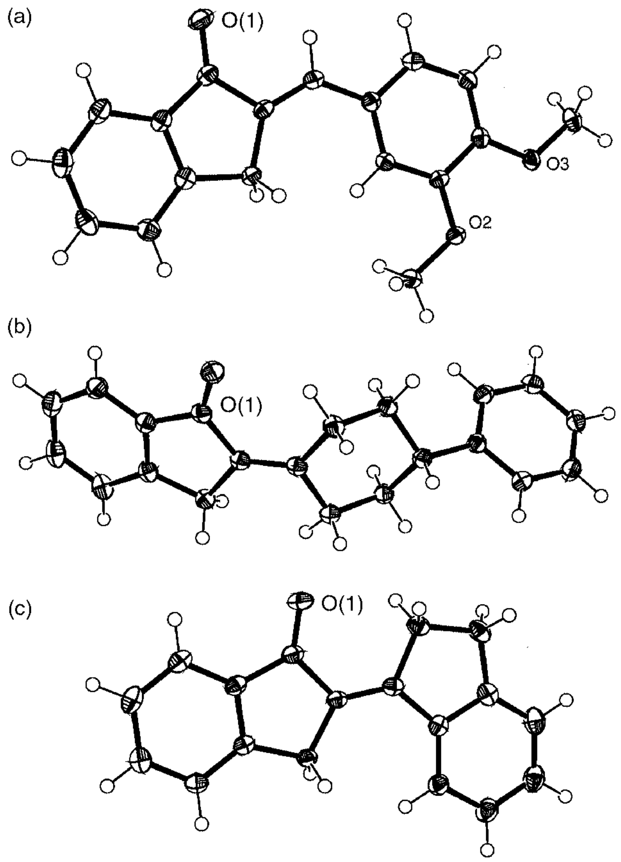
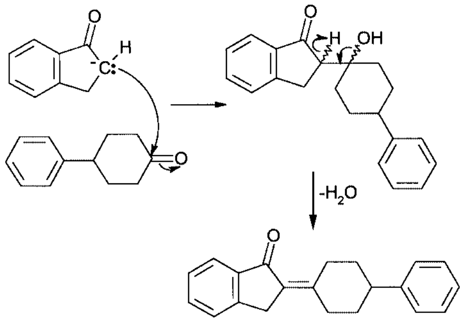


Fig. 1 ORTEP plots of products (*a*) **I**, (*b*) **II** and (*c*) **III** with ellipsoids shown at the 50% probability level. Oxygen atoms are labelled for clarity.

makes this methodology extremely attractive in industrial applications.

Adopting the principles of green chemistry for an important class of reactions, notably Aldol condensation, has resulted in establishing a new benchmark for minimising waste in these reactions while allowing for a greater degree of chemoselectivity than in solution. These are distinct advantages on the classical reactions in organic solvent.



Scheme 2

Experimental

All reagents were used as obtained from the suppliers (98% or better) and AR grade solvents were used without further purification.

Molecular characterisation

^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in $CDCl_3$ with TMS as reference. Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected.

X-Ray diffraction data were collected on an Enraf Nonius CCD diffractometer at 123 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarisation effects. Structures were solved by direct methods using the program SHELXS-97[9] and refined by full matrix least squares refinement on F^2 using the program SHELXL-97.[10] Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted at geometrically determined positions with temperature factors fixed at 1.2 times that of the parent atom except for methyl hydrogen atoms where the temperature factors were constrained to equal 1.5 times that of the parent carbon atom.

CCDC 1048/1. See http://www.rsc.org/suppdata/gc/a9/a907688c/ for crystallographic files in .cif format.

Synthetic procedures

No-solvent reactions

Powdered ketone and aldehyde or ketone and ketone were ground with powdered sodium hydroxide, in the mole ratios indicated in Table 1. Powdered reagents were ground intermittently, over 10 minutes, in a mortar and pestle or in a vibrating ball mill for a total of two minutes over a ten minute period. In many cases reaction was observed to proceed on mixing of powdered reagents but was accelerated by grinding. The sticky solids or viscous liquids so obtained were allowed to stand (unprotected from atmospheric oxygen or water) overnight whereupon the reaction mixtures solidified. TLC of the solids after quenching with 1 M aqueous HCl indicated the presence of a single major product and the solids were worked up by quenching with dilute aqueous HCl followed by filtration of the resultant suspension. The crude product so obtained was washed with water and (if required) recrystallised from an appropriate solvent. Alternately the product could be extracted into an appropriate solvent after quenching as above. Washing of the organic phase with H_2O, drying with $MgSO_4$ followed by filtration and reduction of solvent under vacuum yielded crystalline products of high purity in good yields.

The effect of order of addition of reagents was tested by comparing batches of **III** produced by (*a*) grinding of **2** with NaOH followed by addition and grinding of **3** and (*b*) grinding of **3** with NaOH followed by addition and grinding of **2**. In both of these cases and that of the ground mixture of **2** and **3** to which NaOH was added a single main product is obtained and a trace of **II** detected. Similarly, intermediate produced in the manner described above, stored, unprotected from atmospheric oxygen or water, for 1 month, and worked up by both extractive and aqueous methods was found to have the same product distribution as that worked up within 24 hours.

Reactions in absolute ethanol

For comparison with the solvent free reaction products the reactions were also carried out in absolute ethanol according to the method of Wattanasin and Murphy.[8] Powdered reagents were dissolved in absolute ethanol and powdered sodium hydroxide added. The reaction mixture was stirred overnight during which time products separated from the reaction mixture as solids. 1 M aqueous HCl was added to the slurry to quench the reaction and this led to further precipitation. The precipitate was filtered off and, where necessary, recrystallised from appropriate solvents.

Acknowledgements

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Preparation of a novel silica-supported palladium catalyst and its use in the Heck reaction

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Summary

A novel palladium catalyst supported on a chemically modified mesoporous silica gel has been prepared and exhibits high activity and stability in the Heck reaction of aryl iodides with olefins. The catalysts has been reused several times in reactions without significant loss of activity and selectivity.

Introduction

The palladium catalysed carbon–carbon bond forming reaction between aryl halides and olefins in the presence of a base (Heck reaction) is an excellent method for the synthesis of various organic molecules under mild conditions.[1] Despite the many benefits associated with these reactions including their applicability to unactivated alkenes,[2] tolerance of water and other functional groups in the substrate, interest in the reaction has been sporadic, largely due to the problems of regiocontrol in the case of unsymmetrical alkene substrates leading to low product yields and large volumes of waste, and an incomplete understanding of the reaction mechanism.[2] The reactions have also been of limited industrial use due to low reaction rates along with catalyst instability leading to low turnover numbers and loss of expensive and toxic catalyst. There is also a reluctance to use phosphines which are commonly used as ligands in the catalyst but are unpleasant to work with and are toxic. However, in recent years, there has been a great deal of academic attention paid to the Heck reactions including the advent of an enantioselective variant.[3]

The commonly used palladium species in the Heck reactions are palladium acetate, palladium chloride or preformed triarylphosphine palladium complexes.[1] However, as with all homogeneous catalysts, there are separation, regeneration and reuse problems. These problems are of environmental and economic concern in large scale syntheses where large volumes of hazardous wastes and high production costs are of great importance. These problems can be minimised by carrying out the reactions using heterogeneous catalysts which can be more easily separated from the reaction mixture.[4,5]

The heterogenisation of existing homogeneous palladium catalysts in a way that maintains the advantages of the homogeneous catalyst (activity and selectivity) is an important challenge. In recent years, the development of such catalysts has attracted significant interest.[6–11] These heterogeneous catalysts have been prepared using a range of supports from inorganic solids[6–8] to glass tubing[9] and bead technology.[10,11] However, these entrapped catalysts generally suffer from diffusion limitations while the dissolution of the supported homogeneous catalyst under the reaction conditions can be a major problem for some of these supported catalysts. Herein we report the preparation and application of a stable and active heterogeneous palladium catalyst based on a chemically modified mesoporous silica gel.

Results and discussion

The catalyst is prepared by building up a suitable ligand structure on the surface of a commercial mesoporous silica gel followed by complexation of palladium(II). Thorough conditioning of the catalyst including prolonged treatment with various hot solvents helps to ensure catalyst stability in subsequent reactions. The catalyst pore diameter ranges from 6 to 80 nm with about 71% ranging from 8 to 16 nm. The maximum palladium loading we have been able to achieve is 0.32 mmol g^{-1} with a BET surface area of 248 m^2 g^{-1}. However, catalysts prepared by an alternative route involving templating of preformed metal complexes (the method of choice for some chromium complexes for example[12]) afforded palladium catalysts with loadings less than 0.07 mmol g^{-1}. The infrared spectrum of the chemically modified silica prior to complexation with the metal shows a band at 1647 cm^{-1} attributed to the C=N stretching vibration of the imine. Upon complexation with palladium, the band shifts to 1593 cm^{-1} consistent with strong binding between the metal and the ligand.

The activity of the catalyst was examined in the Heck reaction of aryl iodides with olefins in acetonitrile. After an induction period of about one hour, the conversion rate in the first six hours was about 4% h^{-1} followed by a decrease to about 2% h^{-1}. We cannot rule out a fundamental change in the catalyst sites during this induction period although the material had been thoroughly preconditioned and no changes were evident by IR. It may however, be due to saturation of the product and salt in the catalyst pores which is consistent with the observed drop in

Green Context

Although Heck reactions have been widely studied in academia there are few industrial examples of their exploitation, despite the undoubted widespread potential of these C–C bond-forming reactions. There are several reasons for this, which are concerned with cost, linked to environmental concern; these include high levels of catalyst residue waste, low yield and sometimes poor selectivity. More attention is now being focused on developing selective, highly active heterogeneous catalysts to replace traditional homogeneous catalysts such as palladium chloride. This paper offers an important contribution to this development process. Key Green benefits that these modified mesoporous silica gel heterogeneous catalysts offer include, ready reuse and no leaching of the metal, leading to a significant reduction in the hazardous nature of the waste. Although the yield in model reaction is acceptable high further catalyst development is required to broaden the applicability of the reaction. ***ML***

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surface area of the catalyst from 248 $m^2 g^{-1}$ before use to about 84 $m^2 g^{-1}$ after catalyst use. The decrease in the reaction rate with time may be due to the formation of triethylamine hydroiodide in the reaction which is likely to adsorb on the catalyst surface and block sites. Solvents in which the salt is insoluble (cyclohexane, hexane and toluene) lead to considerably slower reaction rates.

Catalyst reuse studies were carried out by recycling the catalyst without further conditioning or regeneration. This was done by decanting the liquid from the reactor and charging with fresh substrate and then repeating the experiment. The recycled catalyst can be used at least five times (corresponding to a turnover number of > 2000) before there is a significant drop in activity (Fig. 1 shows representative recycle runs). Significantly, there is no induction period on reuse possibly because any changes to the active sites have already occurred or because the catalyst is already saturated with product. The base plays an important role in this reaction[1,13] and when half an equivalent of base was used, the reaction proceeds to only about 50% (Fig. 2).

Analysis of the final reaction mixtures for dissolved palladium showed that no detectable amounts of metal had leached during the reaction (< 0.1 ppm Pd by AAS). Hot filtration of the reaction mixture at 82 °C followed by taking the filtrate back to the reaction showed that the rate of reaction has fallen to almost zero ($< 0.5\%$ h^{-1}). This implies that the transition metal species does not dissociate from the support during the reaction.

The catalyst has also been tested in the Heck reaction of aryl iodides with allylic alcohols to give carbonyl compounds as expected.[1] As shown in Table 1, the catalytic activity and selectivity of this supported palladium catalyst is less than that in the model aryl iodide–methyl acrylate reaction under similar conditions. When 4-iodophenol was treated with but-3-en-2-ol, the yield of a side product was significant. The identity of this side-product is yet to be established but is likely to result from deiodination. The catalyst has been successfully reused in these reactions without noticeable loss of activity. Work on the catalytic reactions of allylic alcohols in a variety of solvents and with different bases is currently being carried out.

Experimental

Catalyst preparation

The catalyst preparation (Scheme 1) involves the grafting of organosilanes onto mesoporous silica gel (either commercial or prepared *via* sol–gel technology) followed by subsequent post modification reactions. Aminopropylsilica [prepared by reacting commercial or synthetic (HMS) silica with aminopropyl-(triethoxy)silane] was reacted with 2-pyridinecarbaldehyde (1 equiv.) in ethanol at room temperature. The modified silica was dried at 90 °C overnight. The surface structure of the material was

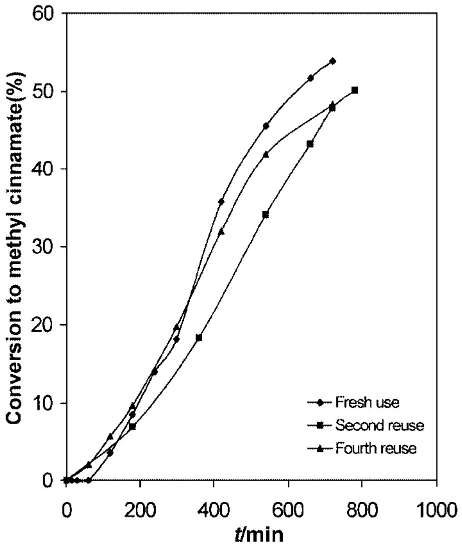


Fig. 1 Reuse of silica supported palladium catalyst for the Heck reaction of 30 mmol iodobenzene and methyl acrylate at 82 °C in acetonitrile with 30 mmol of triethylamine base and 0.2 g of catalyst.

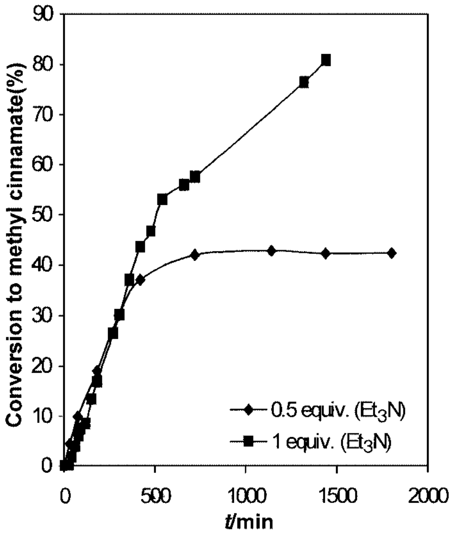
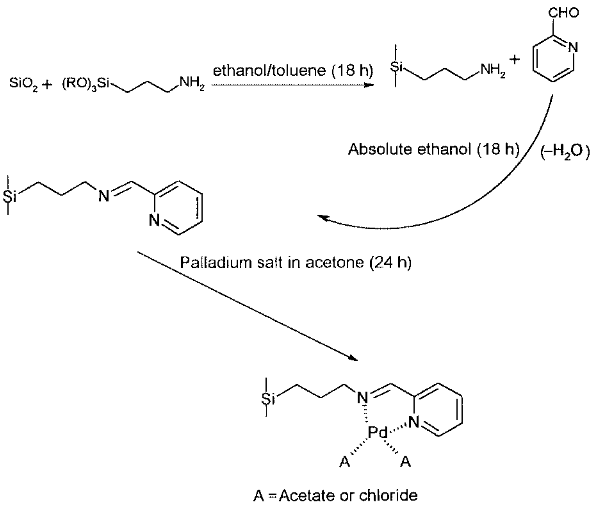


Fig. 2 The effect of the amount of base (NEt_3) in the Heck reaction of iodobenzene and methyl acrylate in acetonitrile solvent at 82 °C.

Table 1 The Heck reaction of aryl iodides with olefins using supported palladium catalyst[a]

Aryl halide	Vinylic substrate	Product(s)	t/h	Conversion (%) to carbonyl compound
Iodobenzene	Allyl alcohol	$PhCH_2CH_2CHO$	24	21
Iodobenzene	Methyl acrylate	$PhCH{=}CHCO_2CH_3$	24	82
Iodobenzene[b]	But-3-en-2-ol	$PhCH{=}CHCOCH_3$	24	41
p-Iodophenol	Allyl alcohol	*p*-$OHC_6H_4CH_2CH_2CHO$	24	15
p-Iodophenol	Methyl acrylate	*p*-$OHC_6H_4CHPh{=}CHCO_2CH_3$	24	31
p-Iodophenol	But-3-en-2-ol	*p*-$OHC_6H_4CH_2CH_2COCH_3$	24	27

[a] Reactions were carried out using 30 mmol of substrate and supported palladium catalyst (0.2 g) with triethylamine base (30 mmol) and 30 ml of acetonitrile solvent at 82 °C. [b] Some biphenyl also formed.



Scheme 1 Preparation of the chemically modified mesoporous silica gel and immobilised palladium catalyst.

confirmed using diffuse reflectance FTIR spectroscopy. It was then reacted with a solution of palladium acetate (or chloride) in acetone. The mixture was stirred for 24 h, and the catalyst was filtered off and washed thoroughly with acetone until the washings were colourless. The catalyst was dried overnight in air at 90 °C. The resulting brown supported catalyst was conditioned for a total of 27 h by refluxing in ethanol, toluene and then acetonitrile so as to remove any surface physisorbed palladium. The conditioned catalyst was dried overnight in air at 90 °C.

Catalyst testing

The conditioned catalysts were tested for activity. In a typical experiment, 30 mmol of each substrate (iodobenzene, methyl acrylate and triethylamine) were charged into a 2-necked round bottomed flask fitted with a condenser. To the magnetically stirred mixture, 30 ml of acetonitrile solvent was added followed by 0.2 g of the catalyst. A small sample was withdrawn through a septum before refluxing. The mixture was then refluxed and small samples were periodically withdrawn by syringe, diluted in dichloromethane and analysed by GC. The conversions were calculated based on dodecane as internal standard.

Conclusion

In conclusion, a novel silica supported palladium catalyst has been successfully prepared through sequential grafting of organic functional groups and thorough preconditioning. The catalyst is active in Heck reactions and more importantly, is stable to the reaction conditions and can be recycled without loss of activity.

Acknowledgements

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Amino-derivatised beaded cellulose gels. Novel accessible and biodegradable scavenger resins for solution phase combinatorial synthesis

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Summary

The synthesis of a derivatised cellulose bead with a high loading of primary amines is reported. This material has proved applicable to the removal of excess electrophiles commonly encountered in solution-phase combinatorial chemistry from organic solvents, thus facilitating a rapid purification method of the desired target. The application of the resin to the preparation of an amide and a urea utilising such methodology is presented, along with data on the biodegradation of the resins using enzymatic approaches. The results indicate that the resin behaves in an identical manner to the more traditionally employed polystyrene/divinylbenzene gels often employed in this field, and yet can be prepared from a renewable resource, and biodegraded after use.

Introduction

The drive to accelerate the drug discovery process has led to continued growth and development in the field of combinatorial chemistry[1] and its associated analytical techniques.[2] This in turn has led to the rapid development of a number of novel resins and associated linker chemistries for the synthesis of molecules on solid supports in so-called solid phase organic Synthesis (SPOS). Recently however, a second complementary and yet conceptually different method has come to the fore; solution phase combinatorial chemistry.[3] The advantages of solution phase chemistry over traditional solid phase methods are potentially manifold, but can be summarised as:

(i) the reaction kinetics are simplified when compared to solid phase methods, thus removing the rate determining diffusion steps encountered in solid phase scenarios.

(ii) The reactions can be readily monitored by standard analytical techniques *i.e.* HPLC, NMR, GC, MS, IR and TLC.

(iii) Standard and thus well-documented organic reactions can be performed without recourse to the use of novel solid phase linker strategies, and without the need for separate attachment and product release steps at either end of the synthetic route.

There is however one major drawback with the solution phase approach, that of rapid product purification. In the vast majority of reactions, a large excess of one reagent is added, in order to drive the reaction to completion, and this must be removed prior to analysis and/or testing. Many solutions to this problem are currently being investigated, and include techniques as diverse as the use of liquid–liquid extraction, particularly using the fluorous phase,[4] solid phase extraction,[5] the precipitation of soluble polymers,[6] and the application of scavenger resins.[7] Of these techniques, those using a solid support to capture either the reaction product or the excess reagent have proved the most widely accepted, presumably since they are easy to perform, and a large number of suitable resins are commercially available. The main drawbacks with the resins currently employed are that they are based on cross-linked polystyrene, and as such are not only hydrophilic, but are also prepared form non-renewable oil resources and are non-biodegradable. We therefore sought an alternative base matrix to produce scavenger resins, which could be prepared from a renewable resource and is biodegradable, whilst retaining the characteristics required in a useful capture resin. We elected to use beaded cellulose,[8] since its activation chemistry, primarily by etherification of the hydroxy moieties, is well documented.[9] The derivatisation of cellulose beads in the development of affinity matrices[10] has also established that the commercially available beads can withstand relatively harsh conditions, whilst retaining a high degree of substitution and porosity.

Results and discussion

Matrix preparation and characterisation

The amine-substituted resin **6** was prepared as detailed in Scheme 1, from commercially available non cross-linked beaded cellulose **1**, with a particle size distribution of 100–250 μm and a mean pore size of 100 Å. Etherification of the hydroxy groups on **1** with allyl bromide **2**, was achieved by a literature procedure,[10b] and gave the highly substituted allyl matrix **3**. Further activation of the allyl groups with bromine-water to afford the bromo-hydroxy resin **4**

Green Context

The field of combinatorial chemistry is the latest area where solid-phase reagents and catalysts are finding application. Solid phase combinatorial methods have many advantages, but also drawbacks. The concept of solution phase combinatorial chemistry solves most of these problems, but at the expense of purification difficulties. Resins can be used to selectively remove excess reagents and by-products, thus helping this process. Generally these resins are based on polystyrene and related systems. This contribution demonstrates that cellulose resins can be employed with equally good results, and can be bio-degraded after their useful lifetime. ***DJM***

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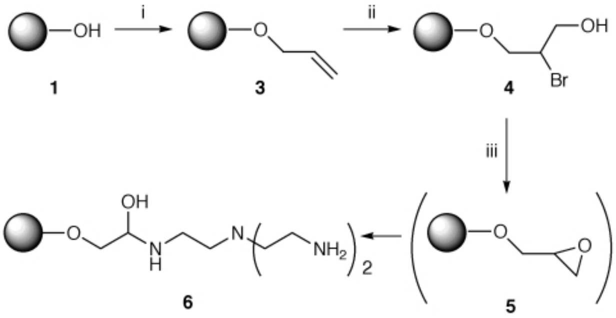


Scheme 1 *Reagents and conditions*: i, NaOH, $BrCH_2CHCH_2$ **2**; ii, HOBr; iii, $(NH_2CH_2CH_2)_3N$ **7**, MeOH.

occurred rapidly, and reaction with tris(2-aminoethyl)amine **7** in methanol, cleanly afforded the target amine resin, presumably *via* the intermediate epoxy resin **5**.[11]

With quantities of the high loading amine resin **6** in hand, we elected to employ the resin as a scavenger of excess electrophiles from solution. Prior to that however, it was decided to examine the swelling properties of the material in a variety of solvents, in order to determine the scope and limitations of cellulose beads in solvents with different properties. The swelling of the matrix was easily determined by washing 10 ml of the resin[12] settled from an aqueous slurry with 1,4-dioxane to remove any water, and then washing the settled resin with the solvent of choice. The solvated resin was then resuspended in *ca.* 10 ml of the desired solvent, thoroughly slurried and allowed to settle in a graduated column, from which the final volume could be read. The results of these experiments are given in Table 1.

Table 1 The swelling properties of resin **6** compared to polystyrene/divinylbenzene resins in a variety of solvents

Solvent	Volume of **6**/ml	Volume of PS DVB/ml
Water	10	2.5
Diethyl ether	10	—
Methanol	9	3.5
1,4-Dioxane	9	—
Tetrahydrofuran	9	9
Dimethylformamide	9	9
Acetonitrile	8.8	—
Ethyl acetate	8.7	—
Dichloromethane	8.4	9.2
Toluene	8	—

As can be seen from Table 1, the resin has a relatively narrow range of swelling volumes, consequently it is applicable for use across a wide range of solvents of different polarities. This is in marked contrast to most commercial polystyrene based resins, which show a broader range of swelling volumes and which do not swell appreciably in water.[13] The fact that the equally highly non-protic solvent diethyl ether gives such a high swelling volume relative to water is interesting, and the reason for this apparently anomalous behaviour has yet to be determined, but may be due to the fact that the solvent is polarised.

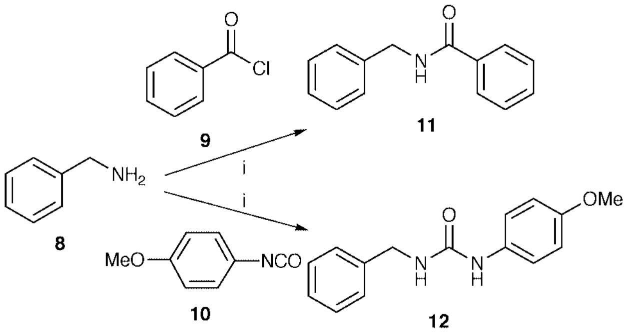
This narrow range of swelling volumes is a great asset when employing **6** as a scavenger resin for two reasons.

(i) Differential swelling in mixed solvent systems can be avoided, thus allowing the use of a different reaction solvent from the wash solvent, allowing a solvent switch to be performed without resin swelling effecting performance.

(ii) An almost constant volume of solvent is present within the pores of the matrix at any time, these thus remain relatively unaffected in various solvents, *i.e.* they do not collapse or over-expand, and are therefore almost equally accessible in all potential environments.

Resin applications

Having determined that the swelling properties of **6** were compatible with a range of solvents, we next sought to demonstrate its synthetic utility. To achieve this, we elected to explore its application as a scavenger resin in the formation of amides and ureas using excess electrophiles in solution. To this end, we chose to perform the reaction of benzylamine **8**, with benzoyl chloride **9** and 4-methoxybenzyl isocyanate **10** to generate amide **11** and urea **12** (Scheme 2). In these two representative examples, 1.5 equivalents of the electrophile was employed relative to the amine, in order to drive the reactions to completion prior to scavenging of the excess electrophile with resin **6**.



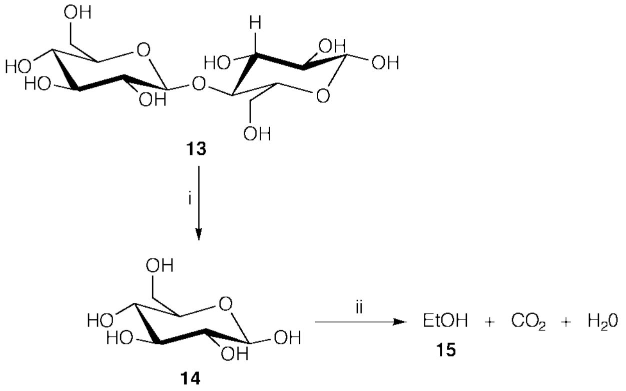
Scheme 2 *Reagents and conditions*: i, CH_2Cl_2 then **6**.

In both cases, the reactions proceeded in $>95\%$ isolated yields, and with product purities determined to be $>95\%$ by HPLC with no further purification being necessary.[14] These results are consistent with those obtained by other workers in this field with traditional polystyrene/divinylbenzene based scavenger resins,[7b] and were achieved utilising similar synthetic steps. The initial aim of the work, namely to synthesize useful scavenger resins having been completed, we now chose to look at the biodegradation of the base matrix, in order to demonstrate the 'Green' nature of the cellulose beads.

Biodegradation studies on the base matrix

In nature, cellulose units are readily broken down by a variety of micro-organisms, which often employ the enzyme cellulase to convert subunits **13** into glucose **14**.[15] Subsequent to this degradation, there exists the potential to metabolise the sugars produced, in order to provide energy for other biological processes within the organism. In our scenario, this last step was to be attempted by the conversion of any glucose units produced into ethanol **15** by a fermentation step, utilising brewers' yeast in conjunction with the cellulase (Scheme 3).[16]

The anaerobic fermentation of hemicellulose sugars to produce ethanol utilising a strain of *bacillus stearothermophilus* has recently been patented,[17] and other reports demonstrate not only the relative ease of this conversion, but also serve to demonstrate its potential economic and environmental benefits.[18] Although this thermophilic fermentation will not proceed when non-digested cellulose is employed as the feedstock, it was hoped that



Scheme 3 *Reagents and conditions*: i, cellulase, pH 5.2, 35 °C 48 h; ii, Brewers' yeast, 48 h.

the use of cellulase would at least demonstrate the biodegradation possibilities of these resins in a laboratory context, without using a bacterial broth, or prior acid digestion of the beads.[19]

It was therefore decided to examine the ability of the enzyme cellulase to degrade the resin. In addition, brewers' yeast was added to selected samples in order to determine whether the reaction outlined in Scheme 3 could be driven across to ethanol by fermentation of the glucose formed in the initial step. In each reaction, cellulase (100 mg) and/or yeast (100 mg) were added to *ca.* 1 ml (aqueous volume) of the cellulose resin in sodium acetate buffer (pH 5.2). The suspensions formed were then incubated at a pre-set temperature for 48 h prior to analysis. Two 'blank' control reactions were also carried out, the first containing no cellulase or yeast, and the second containing only yeast. On completion of the incubation, four parameters were measured in order to ascertain the extent of any reaction. These consisted of:

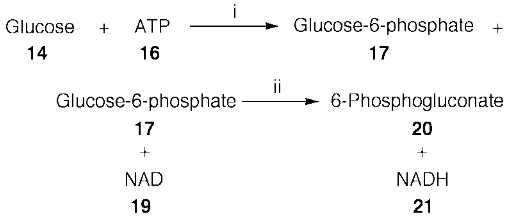
(i) measurement of the final pH of the reaction solution.

(ii) The final settled volume of the resin, measured in millilitres.

(iii) The amount of glucose present as determined by a glucose hexokinase (HK) assay kit.[20]

(iv) The final mass of the recovered resin after washing and drying at 100 °C.

The determination of glucose using the HK assay kit is dependent upon the sequence of enzymatic reactions outlined in Scheme 4. In these reactions, glucose **14** is initially converted to glucose-6-phosphate **17** by hexokinase, with the phosphate group being transferred from adenosine triphosphate (ATP) **16**, generating adenosine diphosphate (ADP) **18** as a by-product. The phosphate **17** is converted to 6-phosphogluconate **20**, with concomitant interconversion of nicotinamide adenine dinucleotide (NAD) **19** present in the mixture into the hydrogenated form NADH **21**. The actual amount of glucose after a pre-set time, can then be quantitatively determined by measurement of the optical density (OD) of the solution at 340 nm, with reference to internal controls.



Scheme 4 *Reagents and conditions*: i, hexokinase; ii, glucose-6-phosphate dehydrogenase.

The amount of glucose present can easily be determined from eqn. (1), where ΔA equals the total test blank OD, V_T is the total assay volume, F is the dilution factor required to obtain a measurable OD, and V_S is the sample volume.

$$\begin{aligned}&\frac{V_T \Delta A F \times \text{mol. wt. glucose}}{V_S dE \times \text{conv. factor mg to mg}}\\ &= \frac{V_T \Delta A F \times 180.2}{V_S \times 6.22 \times 1 \times 1000}\\ &= 0.029\, V_T \Delta A F / V_S\end{aligned} \tag{1}$$

The results of this group of incubation reactions are outlined in Table 2, which shows that the final pH of the reaction mixtures, and the volume of the resin obtained did not alter drastically in any of the reactions. These two factors, although easily and rapidly determined were therefore not employed as measures of reaction efficiency.

The final mass of the recovered resins did however vary markedly from reaction to reaction, except where yeast was employed. In these cases, no final mass was recorded owing to the presence of yeast cells, which could not be removed from the mixture to allow accurate measurements to be made. In all cases, the glucose assay kit proved to be capable of measuring the sugars produced and provided a second measurable factor.[21]

When no cellulase was present (Table 2, entries 1 and 5), no glucose was produced, and the final mass of the resin was identical to that measured for the initial resin (*ca.* 105–110 mg dry). Addition of cellulase alone (Table 2, entries 2, 6 and 7) led to the increasing formation of glucose as measured by assay, and a simultaneous drop in the final mass of resin. Interestingly, the trend towards more glucose and lower resin mass was in line with

Table 2 Results of the biodegradation studies on the cellulose resin utilising cellulase and brewers' yeast

Entry[a]	Cellulase	Yeast	Final pH	Final vol./ml	Glucose[b]/mg	Mass[c]/mg
1	No	No	5.23	1.0	0	105
2	Yes	No	5.23	1.0	36	73
3[d]	Yes	Yes	5.30	1.0	46	nd
4[e]	Yes	Yes	5.27	0.95	44	nd
5	No	Yes	5.30	1.1	0	nd
6	Yes	No	5.21	1.0	64	61
7	Yes	No	5.21	1.0	82	47

nd = Not determined. [a] Experiments run at 35 °C, except for entry 6 (45 °C) and 7 (55 °C). [b] Determined by glucose assay with internal blanks. [c] Final dry mass of residual resin after solvent washing and heating to 100 °C to remove water. [d] Cellulase and yeast added simultaneously. [e] Cellulase added initially, and yeast after 24 h.

an increase in reaction temperature, a fact which was not predicted based on standard non-thermophilic enzyme behaviour. In any case, enzyme inhibition by temperature does not appear to be a problem within the confines of this investigation. Simply heating the resin alone in acetate buffer does not lead to the production of glucose or to a decrease in resin mass, indicating as expected that the enzyme is required for degradation to occur. The mass balance in entries 2, 6 and 7 of Table 2 is, however $> 100\%$ since only 105–110 mg (1 ml) of resin were added to each tube. This is presumably due to inaccuracies in the measurements, and not due to contamination of the reactions by cellulase by-products, since mixing cellulase and acetate buffer with no resin gave a negative result in the subsequent glucose assay.

The addition of yeast to the cellulase reactions either simultaneously as in entry 3, or after a 24 h incubation (entry 4) led to a slight, but measurable increase in the amount of glucose observed. These reactions serve to illustrate two points; first that the presence of yeast at any time does not inhibit the action of cellulase, and secondly that it actually appears to increase the amount of glucose present. This second fact is interesting given that the yeast was added to effectively decrease the amount of glucose present by converting it to ethanol (Scheme 3). The higher level of glucose could be due to a fermentation process producing ethanol, and thus reducing initial inhibition of the cellulase. Such end-product inhibition of the enzyme could potentially be caused by a rapid initial build up of glucose reducing enzymatic activity. Consequently, a reduction in the initial glucose concentration would therefore favour the enzymatic degradation process.

It should be noted that these biodegradation studies were performed on cellulose beads that had not been employed in scavenging reactions. The action of cellulase on resin **6** which has been employed to remove benzoyl chloride from organic solution was attempted, and results similar to those obtained with clean beads were noted provided that the organic solvent was removed by washing with methanol and water prior to degradation. In this case, the enzymatic assay gave slightly lower glucose yields, presumably owing to the fact that any glucose units containing amine chains on the 6-position were not converted into glucose-6-phosphate **17** by hexokinase, and were therefore not detected by the enzyme assay.

Conclusion

We have shown that beaded cellulose can be rapidly and easily converted into a high-loading amine resin which has well defined swelling properties in a range of organic solvents. The resin was successfully employed to remove excess electrophiles from solution, and as such may be employed as a scavenger resin in the field of combinatorial chemistry. Secondly, the resin can be biodegraded by the action of a simple enzyme, and the degree of degradation can be easily quantified either by measurement of the final resin mass, or by enzymatic assay of the glucose produced. Such a degradation makes the resin potentially more benign than the currently employed polystyrene materials, which cannot be biodegraded after use and must therefore either be buried in a landfill, or incinerated, generating waste gases. These two approaches are environmentally less favourable in the long term than a biodegradation step, even if such a step is most efficiently performed at 55 °C as we have described.

The fact that the base material can often be produced from a renewable natural resource such wood pulp, cotton fibres or similar cellulosic materials, which are available as waste products from other industrial processes makes the beads both economically and environmentally attractive. Indeed, although the preparation of beaded cellulose often requires the use of a high boiling organic solvent in the beading step, even this solvent is not consumed in the process and is recovered and recycled. This method of bead preparation is in marked contrast to that employed to prepare traditional polystyrene resins, which are synthesised from non-renewable fossil reserves, and in addition often generate large volumes of solvent and other associated waste.

Currently, the volume of polystyrene resins employed in combinatorial chemistry is low, thus rendering waste management of the spent resin a minor and relatively negligible issue. If however such resins were to be employed on a large scale, their application would rapidly become economically disfavoured, owing not only to the high initial purchase price of the resin, but also in associated disposal costs. Such costs may be minimised by the application of cheaper cellulose beads, which could then be fermented by enzymes or specially designed bio-organisms into harmless waste materials or, in certain cases, into ethanol after use.

Further applications of both resins **3** and **6** in the field of combinatorial chemistry will be reported in due course.[14]

Experimental

General details

Proton NMR spectra were recorder on a Bruker 250 spectrometer at 250.13 MHz with tetramethylsilane as the internal standard. Mass spectra were recorded on a Varian VG7070E spectrometer operating in either electron impact (EI) mode at 70 eV or in chemical ionisation mode (CI) with ammonia as the impingent gas. IR spectra were recorded on a Perkin-Elmer 1615 FTIR operated from a Grams Analyst 1600 package or on a Perkin-Elmer Paragon 1000 using a 'Golden Gate' press. Elemental analyses were performed on a Carlo-Erba Strumentazione instrument. Melting points were obtained using an Electrothermal 9200 instrument, and are uncorrected. High performance liquid chromatography (HPLC) was performed on a Varian 9012 pump utilising a 9050 lamp at 254 nm. The stationary phase employed was a 20 cm Hypersil reverse phase column, with methanol : water (85 : 15) as the mobile phase. The cellulose resin employed was Perloza MT-100, particle size 100–250 μm obtained from Lovochemie (Prague) and was washed with water to remove preservatives prior to derivatisation. All other reagents were of commercial quality, and solvents were dried, where stated, by standard procedures. The rollermixer employed to mix reaction tubes was a Stuart Scientific SRT 2. The glucose (HK) assay kit was purchased from Sigma-Aldrich.

Preparation of allyl resin 3

To a suspension of suction-dried cellulose resin (100 g), in water (50 ml) were added allyl bromide (28 g, 20 ml, 0.23 mol) and 10 M NaOH (10 ml). Water was added, to give a final volume of 200 ml, and the resultant suspension was mixed overnight at 20 °C. The resin was filtered off, washed with water (3 × 100 ml), acetone (3 × 100 ml) and water (3 × 100 ml). Oven dried samples of the allyl matrix were titrated using a standard solution of bromine in water (1% v/v). This gave an average loading of 1.9 mmol g^{-1} of allyl groups.

Preparation of trisamine resin 6

Allyl-activated resin **3** (100 g, 0.19 mol) was brominated by the addition of excess bromine-water (1% v/v). On completion of the reaction (a yellow colour persisted in the supernatant), the resin was washed with water (3 × 100 ml), 1,4-dioxane (3 × 100 ml) and methanol (3 × 100 ml). The volume of the resin was adjusted to 140 ml with methanol, whereupon tris(2-aminoethyl)amine

(29.3 g, 30 ml, 0.20 mol) was added. The mixture was stirred for 16 h at 20 °C, after which time the resin was washed with methanol (3 × 100 ml) and water (3 × 100 ml) and suction dried. Elemental analysis on an oven dried sample: found; C, 42.35; H, 6.37; N, 3.04%. Nitrogen content 2.2 mmol g^{-1}.

Determination of the swelling properties of trisamine resin 6

A slurry of trisamine resin **6** and water (10 ml, 1:1 v/v) was allowed to settle in a graduated column, with the level being adjusted by the addition or removal of slurry, until a resin volume of 10 ml was achieved. The settled bed was then washed with water (10 ml), 1,4-dioxane (2 × 10 ml) and the solvent of choice (3 x 10 ml). Once the final wash was completed, an extra 10 ml of the solvent of choice was added, and the column ends sealed. The column was shaken vigorously to ensure the formation of an even slurry, and allowed to settle for 16 h. On completion of settling, the volume of the resin was recorded.

General procedure for the preparation of amides and ureas using trisamine resin 6

To a mixture of the amine (0.4 mmol, 1 equiv.) and pyridine (95 mg, 97 µl, 1.2 mmol, 3 equiv.) in anhydrous reaction solvent (2 ml) in a glass screw-top vial at 0 °C, was added the electrophile (0.6 mmol, 1.5 equiv.). The vial was sealed, and resultant solution was allowed to warm to 20 °C, and was then mixed on a rollermixer for 2 h. On completion of the mixing, trisamine resin **6** (5 ml aqueous volume, 0.55 mmol NH_2 groups) which had been washed with 1,4 dioxane (3 × 5 ml) and the reaction solvent (2 × 5 ml) was resuspended in 5 ml of solvent and transferred to the reaction vessel. The mixture was roller mixed for 1 h, whereupon the resin was filtered off and washed with dichloromethane (4 × 10 ml). The combined filtrates were evaporated under reduced pressure, and the resulting residue was placed on a freeze dryer for 2 h to afford the desired products.

A representative example of amide formation; *N*-benzylbenzamide 11

Prepared by the standard procedure, using benzylamine (43 mg, 44 µl, 0.4 mmol, 1 equiv.) in dichloromethane and benzoyl chloride (84 mg, 70 µl, 0.6 mmol, 1.5 equiv.) as the electrophile, to afford **11** (84 mg, 99%) as a white solid, mp 104–105 °C. δ_H (250 MHz, $CDCl_3$) 4.50 (2H, d, J = 5 Hz, CH_2Ph), 6.40 (1H, br s, *NH*), 7.2–7.55 (8H, m, aromatic H) and 7.78 (2H, m, aromatic H); *m/z* (EI) 211 (M^+, 73%), 105 (95%) and 77 (100%); HPLC purity >95%.

A representative example of urea formation; 1-benzyl-1-(4-methoxyphenyl)urea 12

Prepared by the standard procedure, utilising acetonitrile as the reaction solvent, with benzylamine (43 mg, 44 µl, 0.4 mmol, 1 equiv.) and 4-methoxybenzyl isocyanate (89 mg, 79 µl, 0.6 mmol, 1.5 equiv.) the product **12** (93 mg, 97%) was obtained as an off white solid mp 160–163 °C. δ_H (250 MHz, $CDCl_3$) 3.8 (3H, s, CH_3O), 4.4 (2H, s, CH_2Ph), 6.1 (1H, br s, NH), 6.8 (2H, d, J = 4.5 Hz, aromatic H), 7.2 (2H, d, J = 4.5 Hz, aromatic H) and 7.3 (5H, m, aromatic H); HPLC purity >95%.

Biodegradation studies on the cellulose resin

Samples of the cellulose bead (1 ml) were settled in graduated columns. The materials were each washed successively with water (2 × 5 ml) and aqueous sodium acetate (50 mM, pH 5.0, 3 × 5 ml). The resins were then transferred into screw-top vials, and sodium acetate buffer (10 ml) was added to each. Cellulase (100 mg) and/or brewers' yeast (100 mg) were then added as detailed in Table 2. The vials were sealed, and the mixtures were incubated at 35–55 °C (Table 2) for 48 h. On completion of the reaction, the pH of the solution was recorded, and the mixture poured into a graduated column, from which the volume of gel was measured. The resin was washed with acetate buffer (10 ml) and the eluted fractions pooled for glucose analysis. The resin was then washed with water (3 × 5 ml), 1,4-dioxane (3 × 5 ml) and diethyl ether (3 × 5 ml) and dried in an oven at 100 °C for 2 h, at which point the dry mass was recorded.

Analysis of cellulase reactions by glucose assay

To a sample of glucose hexokinase (HK) assay kit reagent (1 ml) in a sample tube, was added a sample (10 µl) of the filtrate from the cellulase reaction. The tube was sealed, and mixed at 25 °C for 15 min. After this time, the optical density was recorded at 340 nm, with water used as the blank sample. Two blank samples were also prepared, the first containing water (10 µl) and assay reagent (1 ml) and the second made up from water (1 ml) and glucose standard solution (10 µl) obtained from the assay kit. The optical densities of these solutions were recorded, and combined to give the total blank. The amount of glucose present in each sample was determined by use of eqn. (1).

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11 The actual structure of **6** may not truly be that depicted, and will in fact be a complex number of structures depending on the degree of crosslinking which the tris(2-aminoethyl)amine has performed on epoxide **4**.

12 It should be noted that 10 ml of resin **6** in its aqueous-solvated form has a dry mass of *ca.* 1 g, as determined by residual mass measurements after oven drying at elevated temperatures for 16 h.

13 Information taken from the Argonaut Technologies Inc (San Fransisco , CA) 1998 catalogue and technical data sheets.

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21 The glucose (HK) assay kit is commercially available from Sigma-Aldrich.

Paper a909655h

CO_2/HFC 134a mixtures: alternatives for supercritical fluid extraction

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Summary

The use of CO_2/1,1,1,2-tetrafluoroethane (HFC 134a) mixtures for supercritical fluid extraction is discussed. The utilisation of hydrofluorocarbon solvents significantly increases the polarity of the supercritical medium and significantly increases the solubility of the solute. This means that much less fluid is required for supercritical extraction and because HFC 134a is a gas at ambient pressures it is not left as a residual contaminant in the extract when the cell pressure is reduced.

Introduction

Supercritical (sc) fluids are increasingly used as media for extraction.[1,2] By far the most commonly used fluid is CO_2 because it is inexpensive, non-toxic, environmentally benign and has low critical constants (T_c = 304.2 K; p_c = 72.8 bar). The difficulty which arises with the use of non-polar sc fluids is their poor solubility for polar solutes. For industrial processes this results in the use of large amounts of solvent and the added technical difficulties of using a large volume high pressure plant. Polar modifying fluids are frequently added to CO_2 to increase the solvent polarity and hence improve solubility of polar solutes. Co-solvents such as alcohols and water have limited solubility in $scCO_2$ and are frequently left as residues in the extract when the system is depressurised.

We have recently studied a range of hydrofluorocarbon (HFC) solvents[3,4] which were found to be much more polar than $scCO_2$. Solvents such as 1,1,1,2-tetrafluoroethane (HFC 134a) (T_c = 374.21 K, p_c = 40.56 bar) and difluoromethane (HFC 32) (T_c = 351.26 K, p_c = 57.82 bar) were found to have polarisability/polarity parameters in the supercritical state which were comparable with diethyl ether under ambient conditions. Mixtures of these fluids with CO_2 were also found to be useful solvents. It was shown that a 30 mol% mixture of 1,1,1,2-tetrafluoroethane (HFC 134a) with CO_2 had solvent properties similar to pure HFC 134a at the same reduced temperature.[5] The phase behaviour of CO_2/HFC 134a mixtures has also recently been determined by Poliakoff *et al.*[6] In this work we show how the solubility of salicylic acid is affected by pressure in 5.3 and 30.1 mol% HFC 134a/CO_2 mixtures and these results are compared to those previously reported for unmodified CO_2. It is also shown that the solubility can be related to the polarisability/polarity parameter, π^*.

Experimental

The solubility of salicylic acid [SA] (Fisons, 99.5%) was determined using the dielectric method of Hourri *et al.*[7] The measurement cell and its control system was similar to that reported previously.[8] The electrodes were made of stainless steel with an interelectrode separation of 1 mm and a surface area of 2.5 cm^2. Capacitances were measured *via* an a.c. impedance method using a Solartron 1254 frequency response analyser and a Solartron 1286 potentiostat at a fixed frequency (10 000 Hz). The HFC 134a in CO_2 mixtures (ICI Klea group, 99.99%) were used as received. The polarisability/polarity parameter, π^*, from the theory of Kamlet and Taft was determined by the technique described previously using Nile Red as an indicator solute.[3,4]

Results and discussion

Salicylic acid was chosen as a test solute because it is polar and characteristic of many solutes studied for sc fluid extraction. An interesting phase behaviour was observed upon the dissolution of salicylic acid in a 30.4 mol% HFC 134a in CO_2 mixture at 70 °C. Salicylic acid was initially slow to dissolve but gradually formed a liquid phase which filled approximately two thirds of the cell. It is thought that this was formed from the preferential dissolution of the salicylic acid in HFC 134a. The temperature is below the critical temperature of pure HFC 134a and hence a liquid forms. This phase slowly mixes with the gaseous phase to give a single, homogeneous supercritical phase. It is not thought that the liquid phase is caused by the depression of the melting point of salicylic acid as the temperature is 90 °C below the melting point of the solid. No significant change in temperature was detected during this phase change process. The data obtained for the solubility of salicylic acid in pure CO_2 by Gurdial *et al.*[9] could be reproduced (±20%) using the dielectric method which shows the applicability of this technique for determining solubility. A similar disparity was obtained using a gravimetric method by Ke *et al.*[10] The advantage of using the dielectric method for determining solubility is that the system does not have to be depressurised for each measurement and does not suffer from the problems

Green Context

While the use of supercritical carbon dioxide as a ‘green’ alternative to toxic solvents is rapidly gaining popularity, its very low polarity is proving to be a limiting factor. Polar solutes are often poorly soluble in $scCO_2$ and this can necessitate the use of large volumes of solvent. The common solution to this problem is to add polar co-solutes but these can themselves have limited solubility. In this paper a $scCO_2$-hydrofluorocarbon (HFC) mixed solvent is described which helps to get around these problems. HFCs have themselves been designed as more environmentally acceptable alternatives to CFCs. The solubility of polar solutes in these mixed solvents is significantly improved so that less solvent is required for supercritical extractions.

JHC

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associated with gravimetric analysis *i.e.* inefficient trapping of solute and blocking of the outlet orifice.

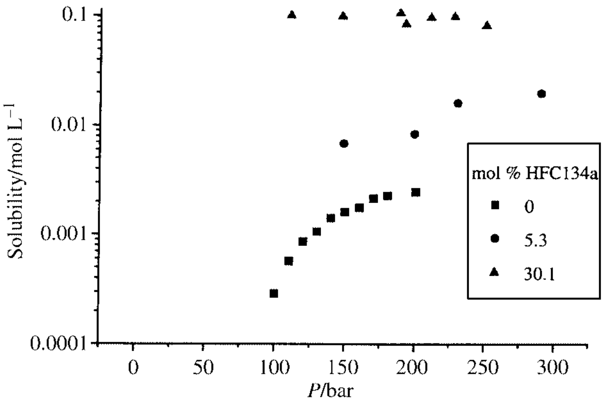

Fig. 1 Solubility of salicylic acid in CO_2/HFC 134a mixtures. ■ pure CO_2[8] at 45 °C, ● 5.3% at 50 °C and ▲ 30.1% HFC 134a at 70 °C.

Table 1 Solubility of salicylic acid in CO_2/HFC 134a mixtures

	P/bar	Solubility/mol L^{-1}
5.3 mol% HFC 134a	149	0.0068
	199	0.0083
	230	0.0161
	290	0.0196
30.4 mol % HFC 134a	121	0.14945
	159	0.11964
	188	0.10808
	210	0.0986
	227	0.1001
	250	0.08297

Fig. 1 shows the solubility of salicylic acid in CO_2/HFC 134a mixtures as a function of pressure. The data are also listed in Table 1. The mixture containing 5.3 mol% of HFC 134a shows a marked increase in the solubility of salicylic acid over pure CO_2. When 30 mol% HFC 134a is added the solubility at low pressures is two orders of magnitude larger than that in unmodified CO_2. Using these fluid mixtures polar solutes can be dissolved in high concentrations under accessible sc conditions. This is extremely important because it means that not only is less fluid required for the sc fluid extraction process but more importantly the size of the sc extraction plant can be reduced. Hence HFC 134a has the potential to become a very useful modifying fluid for use with supercritical extraction.

Gurdial *et al.*[9] showed that temperature only had a small effect on solubility and hence the slight difference in the conditions used for the current study can not account for the large changes in solubility. Ke *et al.*[10] studied the solubility of salicylic acid in $scCO_2$ using ethanol as a modifier. With 6 mol% ethanol in the solution there was an apparent invariance in the solubility of salicylic acid (*ca.* 0.5 mol l^{-1}) with pressure. Such pressure invariance has also been observed with stearic acid in CO_2[11,12] at temperatures close to the critical value. Ke *et al.*[10] measured the effect of dissolved salicylic acid on solution density and noted that although the density increased it could not account for the observed changes in solubility. Hydrogen bonding between the ethanol and carboxylic acid was highlighted as a cause of the increased solubility.

In an attempt to explain the solvent effect on solubility it is important to quantify the solvent–solute interactions in terms of the hydrogen bonding as well as the polarisability/dipolarity properties of the solvent. Using spectroscopic methods, we have recently shown that in HFC 134a/CO_2 mixtures preferential solvation of the solute by the polar HFC component occurs and HFC 134a has a high dipolarity, polarisability parameter, π^*. Lagalante *et al.*[13] recently showed that the hydrogen bond acceptor parameter, β, for HFC 134a was insignificant (*ca.* −0.1) in the temperature range 105–130 °C and was relatively unaffected by pressure. Using the raw spectral shift data from Lagalante *et al.*[13] and the data recently published using Nile red as an indicator solute[3] it was also recently shown that the hydrogen bond donor parameter, α, was insignificant and was also largely unaffected by pressure.[14] This suggests that in these mixtures hydrogen bonding between the solvent and solute does not account for the solubility of the solute. The dipole–dipole interactions between the solute and HFC 134a/CO_2 mixtures have recently been shown to be significantly affected by pressure.[5] It is interesting therefore that this and other work has shown an invariance in solubility with pressure for solutes such as carboxylic acids.

Fig. 2 shows the correlation between the solubility of salicylic acid and the π^* parameter for the HFC 134a/CO_2 mixtures. A good correlation is obtained for pure CO_2 and the 5.3 mol% HFC 134a mixture showing that the solubility is governed by the dipole–dipole and dipole–induced dipole interactions. However for the 30 mol% mixture the π^* values of the bulk solvent can not account for the invariance in solubility with pressure. In relatively concentrated solutions the solute–solute interactions can not be neglected and it is therefore imperative to measure the effect of the solute on π^*. Fig. 3 shows the π^* parameter as a function of pressure for a 30 mol% HFC 134a in CO_2 mixture at 70 °C with and without 1 wt% salicylic acid. The solution to which the acid was added showed a much higher π^* value showing that the solute is solvating the indicator solute. This suggests that when salicylic acid dissolves in the mixed sc fluid it tends to form clusters which makes solubilisation easier.

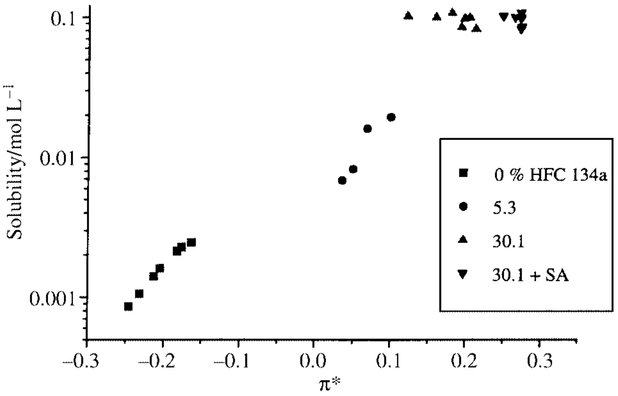

Fig. 2 The solubility of salicylic acid as a function of the π^* parameter for the HFC 134a/CO_2 mixtures.

Conclusions

This work has shown that mixtures of HFC 134a and CO_2 are potentially useful for supercritical fluid extraction. There is a two order of magnitude increase in the solubility of salicylic acid in a

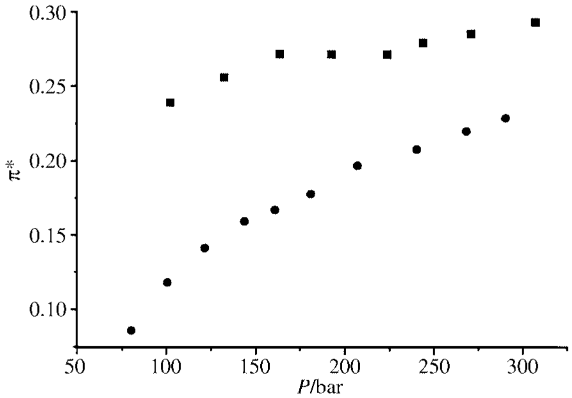

Fig. 3 The π* parameter as a function of pressure for a 30 mol% HFC 134a in CO_2 mixture at 70°C with ■ and without ● 1 wt% salicylic acid.

30.1 mol% mixture of HFC 134a in CO_2 with respect to pure CO_2. The solubility can be modelled using solvent polarity parameters and the work has shown that as the salicylic acid concentration increases it forms clusters which increase the solubility.

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Paper a907683b

Acylation of alcohols with carboxylic acids *via* the evolution of compatible acidic sites in montmorillonites†

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Summary

An efficient and selective acylation of alcohols employing carboxylic acids as acylating agents is realized, for the first time, through the tuning of acidic sites of montmorillonite achieved by incorporation of the appropriate exchangeable cations.

Introduction

Organic esters represent an important family of intermediates widely employed in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, solvents and chiral auxiliaries. Acylation of alcohols is usually performed employing acid anhydrides or acyl chlorides in the presence of stoichiometric amounts of amine bases such as tertiary amines,[1] 4-(dimethylamino)pyridine or 4–pyrrolidinopyridine[2] and tributylphosphine[3] to afford excellent yields. On the other hand protic acids such as *p*-toluenesulfonic acid[4] and Lewis acids, such as scandium trifluoromethanesulfonate,[5] trimethylsilyl trifluoromethanesulfonate,[6] zinc chloride[7] and cobalt chloride[8] are well known to catalyze the acylation of alcohols and phenols in the presence of acetic anhydride. The above options employing acetic anhydride as acetylating agent and soluble bases or acids as reagents/catalysts present problems in the recovery of large amounts of soluble bases or acids and achieve less than 50% atom economy in the consumption of acetic anhydride by utilising only the acetyl group. These disadvantages have a negative impact on the environment. Recently research directed to overcome the above problems culminated in the development of solid acids in the form of modified clays, montmorillonite K10 and KSF as catalysts[9] and soluble Sc and La triflates.[10] Previous reports using clay catalysts still utilized acetic anhydride as the acetylating agent while metal triflates are expensive and difficult to recover and reuse in the process although acetic acid is used as the acylating agent. Therefore, there is a need to develop a reusable and economic solid catalyst for acylation of alcohols using carboxylic acids so as to achieve high atom energy.

We herein report the high-yielding acylation of alcohols with carboxylic acids in the presence of the natural and Na$^+$-exchanged form of montmorillonite catalysts sourced from natural montmorillonite and montmorillonite K10[11] with high atom economy for the first time. Ion exchanged clays are prepared adopting literature methods.[12]

Experimental

In a typical procedure, 1-phenylethanol (5 mmol) and glacial acetic acid (50 mmol) corresponding to a 1:10 molar ratio (1:3 alcohol:carboxylic acid ratio for other solvent systems) were refluxed under stirring for 15 min in the presence of montmorillonite catalyst (100 mg). After completion of the reaction, monitored by TLC or GC, the reaction mixture was filtered and the filtrate was concentrated to obtain the pure product. The product was analyzed by ^{1}H NMR, while the catalyst was washed with ethyl acetate and dried in an oven at 120 °C for 1 h and then reused. δ_H 0.5–0.6 (d, 3H), 2.1 (s, 3H), 5.8–5.95 (q, 1H), 7.25–7.4 (m, 5H).

Results and discussion

This present methodology illustrates a simple esterification procedure and has wide applicability, extending the scope to benzylic, primary, secondary, allylic, cyclic and heterocyclic alcohols (Table 1). Exclusive formation of acylated product in quantitative yield was observed with most of the substrates used, when natural montmorillonite (nat.mont) (M/S. Neelkant Chemical Works, Jodhpur, India), or Na$^+$-mont (Kunipia G) (M/S. Kunimine Industries Co., Ltd, Tokyo, Japan) are used as catalysts. It is very interesting that even at elevated temperatures no olefin, ether or polymeric products were found in the acylation of alcohols using carboxylic acids. These results indicate that the process of acylation affords excellent possible atom economy when accounted for with respect to substrate, product and acylating reagent.

Increasing the fatty chain length of the alcohols or acids increases the rate of the acylation reaction (Table 1, entries 4, 5, 8, 9 and 13a,b). This may be ascribed to the hydrophobic chain of the higher homologue of either reactant that drives away water formed during the reaction from the active site more effectively than the hydrophilic lower alcohols or acids. The rate of the acylation reaction of cyclohexanol employing nat.mont, is much faster than with the expensive solid acid catalyst, Amberlyst-15, a synthetic resin or the homogeneous catalyst, dodecatungstophosphoric acid.[13] Impressive selectivity is achieved in the acylation of allylic alcohols in the present liquid phase reaction (Table 1, entries 1a, b and 3). Phenolic hydroxy groups could not be acylated under similar conditions. This inertness has been exploited in the selective acylation of alcoholic hydroxy groups in phenols (Table 1, entries 2a,b). Chiral menthol is acylated without any racemisation (Table 1, entry 12). However, the acylation of

Green Context

Organic esters are versatile compounds and have many applications in areas including cosmetics, pharmaceuticals, perfumes and as solvents. There are many possible synthetic routes to esters but one of the most attractive from environmental and economic standpoints is *via* the direct reaction of a carboxylic acid with an alcohol especially if it avoids the use of a non-reusable catalyst. Here the effective use of a small amount of an ion-exchanged clay in this reaction is demonstrated. It is important to note how the choice of cation in the clay and the origin of the clay can have such a large effect on the efficiency of the reaction. This helps to demonstrate the importance of fine-tuning the properties of clays in order to achieve maximum benefit. ***JHC***

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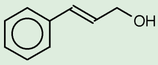
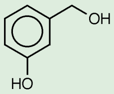
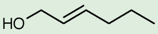
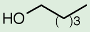
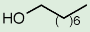
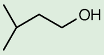
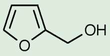
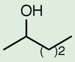
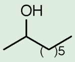
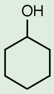
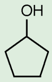
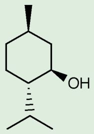
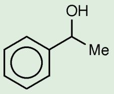
Table 1 Acylation of alcohols with carboxylic acids as acylating agent catalysed by montmorillonite clays

$$R{-}OH + R^1CO_2H \xrightarrow{\text{Natural montmorillonite}} R^1CO_2R + H_2O$$

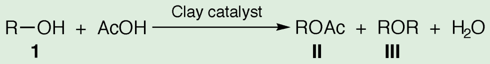
Entry	Alcohol[a]	Acid	Catalyst	T/°C	t/h	Yield[b] (%)
1a		Acetic	nat. mont	116	0.2	98 (98)[c]
1b		Acetic	Na^+.-mont	116	0.75	98
2a		Acetic	nat. mont	116	2.0	98
2b		Acetic	Na^+.-mont	116	3.5	98
3		Acetic	nat. mont	116	0.15	98
4		Acetic	nat. mont	116	2.5	99[d]
5		Acetic	nat. mont	116	1.0	98
6		Acetic	nat. mont	116	2.5	99[d]
7		Acetic	nat. mont	116	0.25	65[e,f]
8		Acetic	nat. mont	116	2.5	77[d,e]
9		Acetic	nat. mont	116	1.5	96
10		Acetic	nat. mont	116	0.5	97
11		Acetic	nat. mont	116	1.0	98
12		Acetic	Na^+.-mont	116	3.5	99 (98)[c]
13a		Acetic	Na^+.-mont	110	0.4	97
13b		Acetic	Na^+.-mont	110	0.3	98

[a] Alcohol : acid molar ratio = 1 : 10. [b] Isolated yield. [c] Isolated yield after fifth cycle. [d] Based on GC analysis. [e] Remainder is by-product. [f] Based on ^1H NMR nat.mont (Indian natural montmorillonite). Na^+-mont (Kunipia G, Japanese natural montmorillonite).

tertiary alcohols afforded olefins, rearranged and polymeric products. The activity of the nat.mont was found to be superior to Na^+-mont, but the selectivity of the products was similar (Table 1, entries 1a,b and 2a,b).

In the course of development of the catalyst, we have explored a variety of montmorillonite catalysts with varied acidities. Influence of the acidic sites on the activity and selectivity of the acylation reaction has been investigated (Table 2) The activity and the selectivity of the acylation of alcohols are in the order: Na^+-mont K10 ⩾ nat. mont. ⩾ Na^+-nat. mont > Na^+-mont ⩾ Cu^{2+}-mont > Ce^{3+}-mont > Zn^{2+}-mont ⩾ Al^{3+}-mont > Fe^{3+}-mont ⩾ K10. The hydrated cations, in montmorillonite are more acidic than their corresponding homogeneous analogues. The enhanced Bronsted acidity is ascribed to the polarising influence of the cation on hydrated water molecules in the spatially restricted interlayers. The interlayer acidity increases with increasing ratio of charge to ionic radius of the cation.[14,15] NH_3-temperature programmed desorption (TDP) reults obtained are in agreement with the above observations and the weakly adsorbed NH_3 is desorbed in the range 120–320 °C from the Bronsted acidic sites, whereas desorbed NH_3 at higher temperatures in the range 320–450 °C is due to Lewis acidic sites. Exchange of trivalent and divalent metal ions such as Fe^{3+}, Ce^{3+}, Al^{3+}, Cu^{2+} and Zn^{2+} on natural or acid treated K10 mont, affects the selectivity of the reaction. Increasing the acidity of the Bronsted acidic sites changes the course of the reaction to facilitate the

Table 2 Direct acetylation of alcohols with acetic acid catalysed by montmorillonite clays



$$\underset{\mathbf{1}}{\text{R–OH}} + \text{AcOH} \xrightarrow{\text{Clay catalyst}} \underset{\mathbf{II}}{\text{ROAc}} + \underset{\mathbf{III}}{\text{ROR}} + H_2O$$

Entry	Alcohol[a]	Catalyst	Treatment range/°C	NH_3 adsorption/ mmol (g cat)$^{-1}$	Total acidity/mmol (g cat)$^{-1}$	t[b]	Selectivity[c] (%)	
							II	**III**
1a	1-Phenylethanol	nat. mont	120–320	0.0037	1.462	20	100	—
			320–450	1.425				
1b		Na$^+$-mont	120–320	0.000	0.000	45	100	—
			320–450	0.000				
1c		Na$^+$-mont K10	120–320	0.027	0.027	20	100	—
			320–450	0.000				
1d		Na$^+$- nat. mont	120–320	0.018	0.018	25	100	—
			320–450	0.000				
1e		mont K10	120–320	0.047	0.047	15	Polymer	
			320–450	0.000				
1f		Fe^{3+}-mont K10	120–320	0.056	1.029	15	Polymer	
			320–450	0.973				
1g		Cu^{2+}-mont K10	—	—	0.311	15	70[d]	—
2a	Benzyl alcohol	Cu^{2+}-mont K10				30	100	—
						15	~ 15[e]	—
2b		nat. mont				30	100	—
2c		Fe^{3+}-mont K10				15	70	30
2d		mont K10				20	72	28
3	l-(*p*-Methylphenyl) ethanol	nat. mont				10	100	—

[a] Alcohol : acetic acid molar ratio = 1 : 10. [b] Acetic acid reflux temperature was maintained. [c] Based on ^{1}H NMR. **III** = 1,l-diether. [d] Remainder is self alkylated product (Polymer). [e] Remainder is monoalkylated product (*o*- and *p*-mixture) when toluene used as solvent.

dehydration of alcohol that results in the formation of ether as a by-product. The formation of dibenzyl ether from benzyl alcohol (Table 2, entries 2c,d) in sizeable quantities with Fe^{3+}-mont and mont K-10 catalysts containing highly acid Bronsted sites, is in accord with this.[15,16] It is significant that the selectivity towards acylated product is higher with primary alcohol, *e.g.* benzyl alcohol (Table 2, entry 2a) than for secondary alcohols *e.g.* 1-phenylethanol using Cu^{2+}-mont (Table 2, entry 1g). The selectivity of the nat.mont towards the acetylation of primary and secondary alcohols with acetic acid is found to be similar with sodium exchanged montmorillonite catalysts (Table 2, entries 1a-d, 2b and 3), but Na$^+$-mont showed lower activity towards 1-phenylethanol. Acid treated montmorillonite, commercially known as K10 montmorillonite, which has Bronsted acid sites predominantly on broken edges also affords ether in large quantities.[15,17] Therefore it is necessary to suppress the Bronsted acidity to attain higher selectivity towards acylated product. The exclusive selectivity obtained employing Na$^+$ exchanged mont sourced from natural mont or acid treated mont in all the examples (Tables 1 and 2) indicates that weakly acidic Bronsted sites are adequate to promote the acylation reaction. The nat.mont (Indian clay) employed by us showed higher activity than the Na$^+$-mont (Japanese) used as such, although the selectivity is same. It is observed that the nat.mont has a pH of 10.2, whereas the pH of Na$^+$-mont and Na$^+$-nat.mont sourced from India as well as Japan are 10.8. In the nat.mont, a mixture of cations (Na, K, Ca and Fe) have been found to be exchangeable ions. Although NH_3 adsorption is very high on the dried sample of nat mont (Table 2) the Na, K and Ca ions reduce the number of available protons generated by hydrated Fe^{3+} cations in the interlayers due to formation of water during the reaction as a consequence of the antagonistic effect of alkali and alkaline earth metals which are inherently basic in nature. Therefore, increased activity without sacrificing selectivity is attributed to the compatible number of acid sites of nat.mont in acylation reactions. However, it is difficult to obtain natural montmorillonite, having identical sites and Fe, Na, K and Ca ratios during mining processes at different locations. It is thus imperative to develop a reproducible clay catalyst possibly by an exchange process of montmorillonites. It is found that the Na$^+$-mont K10 is the best catalyst for our purposes, since it has sufficient Bronsted acidity to promote the acylation of alcohol. Further the pH of this clay is 6.8 and it is significant that Na$^+$ exchanged clay sourced from nat.mont displayed similar activity and identical selectivity to that of Na$^+$-mont K10. All the reactions proceeded smoothly using acetic acid as solvent, however when toluene or chlorobenzene is used as solvent the corresponding Freidel–Crafts alkylated product and dehydrated olefinic products are obtained in large quantities (Table 2, entry 2a). The catalyst acts as a bifunctional catalyst serving as a molecular sieve to absorb water formed during the reaction to shift the equilibrium and force the reaction with the solid acid possessing compatible acidic sites towards ester formation.

Conclusion

We have described a mild, highly efficient and extremely fast and selective acylation procedure for various functionalized primary and secondary alcohols using acetic, propionic and butyric acids as acylating agents in the presence of catalytic amounts of clay catalyst. Tuning the acidic sites of montmorillonite by introducing suitable exchangeable cations, enables the optimum selectivity and activity from the acylation of alcohols by carboxylic acid. This method can be adapted to large scale commercial processes and offers an environmentally safer alternative to the existing methods.

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Selective synthesis of perfumery grade cyclohexyl esters from cyclohexene and carboxylic acids over ion exchange resins: an example of 100% atom economy

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Summary

Esterification is important in the perfumery and flavour chemical industry, wherein, both homogeneous and heterogeneous catalysts have been widely used. The use of solid acid catalysts can be effective from the view of activity, selectivity, reusability and economy in the manufacture of perfumery esters. This paper delineates a 100% atom economical process for the preparation of cyclohexyl esters from carboxylic acids and cyclohexene over ion exchange resin catalysts where all the reactant atoms are utilised without any by-product formation. The preparation of perfumery esters such as cyclohexylphenyl acetate, cyclohexyl acetate, cyclohexyl anthranilate, cyclohexyl benzoate, cyclohexyl butyrate, cyclohexyl *iso*-butyrate, cyclohexyl heptanoate and cyclohexyl propionate is covered. A complete theoretical and experimental analysis is presented for the model studies with phenylacetic acid and cyclohexene.

Introduction

Organic esters are a very important class of chemicals having a variety of applications in perfumery, flavours, pharmaceuticals, plasticizers and intermediates industries. Esters are typically synthesised by:[1,2] (*a*) solvolytic reactions (direct esterification of acids, alkylation of carboxylic salts, alcoholyses of acyl halides, alcoholyses of anhydrides, alcoholyses of nitriles and amides, alcoholyses of ketenes, transesterification); (*b*) condensation reactions (Knoevenagel reaction, Darzens reaction, Wittig type reactions, Reformatsky reaction, acetoacetic ester synthesis, malonic ester synthesis, Michael reaction, Claisen condensation); (*c*) free radical processes (radical addition and substitution reactions, acyloxylation reactions, anodic dimerisation); (*d*) other miscellaneous routes (from organoboranes, from acetylenes, from diazo esters, by carbonylation of alcohols, by phase transfer catalysed reaction of aryl or alkyl halide with inorganic carboxylic acid salt).

For the preparation of perfumery and flavour grade esters, only a few of the above mentioned routes can be considered due to the stringent specifications of the final product. The most widely employed and supposedly cleaner production technique for such esters involves the reaction of the appropriate carboxylic acid with an alcohol in the presence of a mineral acid catalyst or a heterogeneous catalyst under reflux conditions, followed by separation of the ester by distillation.

However, the direct addition reaction between carboxylic acid and olefin over a solid acid catalyst would be the most atom economical and ecofriendly process. For instance, cyclohexyl carboxylates are very important perfumery and flavour esters. The direct esterification of cyclohexene with carboxylic acids is advantageous due to the availability of cyclohexene on a large scale at attractive prices.

Cyclohexylphenyl acetate has a herbaceous green odour with a hint of sweet honey and chrysanthemum. It is used as a fixative for rose, chypre, oriental fragrances, *etc.* Cyclohexyl acetate has a sharp sweet-fruity odour and is used in flavour composition mainly for imitation apple, blackberry, banana, raspberry and tutti-fruity flavours. It is also used in masking odours for industrial purposes. Cyclohexyl anthranilate has a faint, fruity-orange blossom type odour of good tenacity with a sweet-fruity, grape-like taste. It is used in flavour compositions for imitation grape, banana, apple *etc.* Cyclohexyl benzoate has a mild, faint, warm-balsamic, floral and herbaceous odour of good tenacity. Cyclohexyl butyrate has an overall fruity, but a nondescript floral note and used in flavour compositions for imitation apricot, banana, apple, peach, strawberry, *etc.* Cyclohexyl *iso*-butyrate, having a powerful sweet-fruity odour, finds applications in flavour compositions mainly for imitation apple, pineapple, peach, *etc.* Cyclohexyl heptanoate has an oily-herbaceous, grassy but overall not pleasant odour. It is used in perfume compositions, mainly as part of citrus topnote compositions or bases for lemon and bergamot. Cyclohexyl propionate has an intensely fruity and sweet odour, somewhat reminiscent of banana, pineapple and peach. It is occasionally used in flavour compositions, mainly for pineapple imitation and similar fruit flavours.[3]

There is practically no literature on the esterification of cyclohexene with phenylacetic acid, acetic acid, anthranilic acid, benzoic acid, butyric acid, heptanoic acid, *iso*-butyric acid and propionic acid, using solid acids as catalysts. However, there is some information on the esterification of cyclohexene with formic acid, acrylic and methacrylic acids.[4] There is a report on the reaction between phenylacetic acid and cyclohexyl bromide in the presence of mercury oxide and tetrafluoroboric acid to produce the target compound.[5]

It thus appeared that the preparation of cyclohexyl esters is important from the view point of green chemistry and that the

Green Context

Esters are widely used as fragrances in perfumery and other areas. Their synthesis is however, not always straightforward or efficient. Strong acid conditions may be required to achieve good reaction rates and common synthetic routes can have low atom efficiencies. In this article the use of environmentally acceptable solid acids is investigated in highly atom-efficient processes. The results are very encouraging and demonstrate that atom economical processes are viable for the synthesis of perfumery-grade cyclohexyl esters. ***JHC***

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efficacy of some commercial as well as cheap solid acids should be evaluated, including ion exchange resins, acid treated clays and metal oxides. Some solid acid catalysts such as, Amberlyst-15, Indion-130, Amberlite IR-120, Dowex 50W (all cation exchange resins), Filtrol-44, sulfated zirconia, and dodecatungstophosphoric acid (DTPA) supported on K-10 clay were chosen.

Experimental

Chemicals and catalysts

Indion-130, an ion exchange resin, was obtained from M/S Ion Exchange (India) Ltd. Heptanoic acid, K-10 and Filtrol-44 were obtained from Fluka. Amberlyst-15 and Amberlite IR-129, both ion exchange resins, are from Rohm and Hass. Dowex 50W is a product of Dow Chemicals. Zirconium oxychloride, dodecatungstophosphoric acid, phenylacetic acid, acetic acid, butyric acid, benzoic acid, propionic acid, cyclohexane and cyclohexene were obtained from M/S s.d. Fine Chemical Ltd., Mumbai, India. Anthranilic acid was procured from Loba Chemie, Mimbai, *iso*-Butyric acid was obtained from Sisco Research Laboratory, Mumbai. All chemicals were analytical grade reagents and were used without further purification. The catalysts used for the reaction were dried at 110 °C for 6 h before use. Dodecatungstophosphoric acid (DTPA)/K-10 was prepared by a well established procedure in our laboratory.[6] Sulfated zirconia was also prepared by an established procedure in our laboratory.[7]

Reaction procedure and analysis

The reaction was carried out in a Parr autoclave (100 ml capacity) with an internal diameter of 0.05 m. The temperature was maintained at ±1 °C of the desired value with the help of an in-built proportional-integral-derivative (PID) controller. A four bladed pitched turbine impeller was employed for agitation. In a typical experiment, 0.026 mole of acid, 0.078 mole of cyclohexene, 39 ml of cyclohexane and 0.75 g of catalyst were charged to the autoclave. The reaction mixture was then allowed to reach the desired temperature and the initial/zero time sample was collected. Agitation was then commenced at a particular speed. Samples were withdrawn periodically for analysis.

After filtration of the catalyst the sample was monitored by chemical as well as instrumental analysis. In chemical analysis, the reaction samples were titrated against alcoholic KOH solution. The instrumental analysis was done on a gas chromatograph (Chemito 8510) equipped with a flame ionisation detector. A 2.5 m long stainless steel column packed with 10% OV-17 supported on chromosorb-WHP was used for the analysis. The injector and detector were kept at 300 °C. The oven temperature was programmed from 130 °C (0.5 min) up to 280 °C with a ramp rate of 20 °C min^{-1}. Nitrogen was used as the carrier gas and its flow rate was 30 ml min^{-1}. Calibrations were done with synthetic mixtures for quantification of data.

Identification and isolation of product

For isolation of the ester, the catalyst was filtered off. The filtrate was neutralised with excess sodium hydrogencarbonate wash to remove unreacted acid. The ester remained in the organic layer which was then dried with anhydrous sodium sulfate, purified by column chromatography to remove the impurities and tested by thin layer chromatography (TLC). Hexane and ethyl acetate (90:10) and silica were used for column chromatography and TLC. Eluent containing pure ester was evaporated by rotary vacuum evaporator to remove the solvent. The isolated product was confirmed by ^{1}H NMR, IR and boiling point determination.

Results and discussion

The esterification of cyclohexene with phenylacetic acid was taken as the model system and the effect of various parameters was evaluated on the conversion and selectivity.

Effect of various catalysts

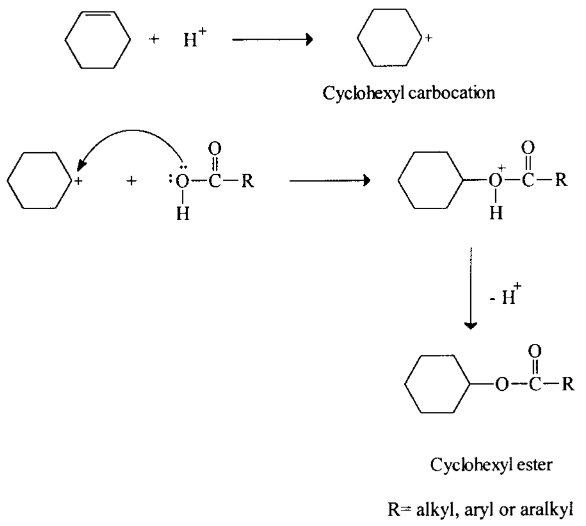
Different solid acid catalysts were used to assess their efficacy in this reaction. A 0.015 g cm^{-3} loading of catalyst based on the organic volume of the reaction mixture was employed at a mole ratio of phenylacetic acid to cyclohexene of 1:3 at 100 °C and an agitational speed of 1000 rpm. The catalysts used were Amberlyst-15, Indion-130, Amberlite IR-120, Dowex 50 W, Filtrol-44, sulfated zirconia, 20% w/w DTPA/K10. It was found that cation-exchange resins Amberlyst-15 and Indion-130 showed higher conversions compared to other catalysts. Table 1 shows the conversion of phenylacetic acid, the limiting reactant, for the various catalysts. The esterification with ion exchange resins Amberlyst-15 and Indion-130 was quantitative. S-ZrO_2 offered very poor conversion, whereas others were totally ineffective. It appears that there is a strong adsorption of cyclohexene on these catalysts. However, no oligomers of cyclohexene were formed with Amberlyst-15, the most efficient catalyst. Further experiments were conducted with Amberlyst-15 as the catalyst. A possible reaction mechanism explaining the efficacy of this catalyst is shown below.

Table 1 Effect of various catalysts on the conversion of phenylacetic acid

Catalyst	Conversion (%)
Amberlyst-15	74
Indion-130	58
Sulfated zirconia	6
Amberlite IR-120	0
Filtrol-44	0
Dowex 50 W	0
20% DTPA/K10	0

Phenylacetic acid:cyclohexene = 1:3; t = 6 h; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

In order to assess the role of external mass transfer, the effect of the speed of agitation was studied. Since the selectivity to the



desired product was 100% at all conversions, these conversions are also the yields of the product based on initial amount of phenylacetic acid.

In order to ascertain whether any oligomer of cyclohexene could be formed, a blank experiment was conducted by taking the same concentration of cyclohexene (1.56×10^{-3} gmol cm^{-3}) in cyclohexane (7.81×10^{-3} gmol cm^{-3}) at the same catalyst loading (0.015 g cm^{-3}) for 6 h at 100 °C. The conversion to the dimer was only 0.035% which was negligible. Thus, in the presence of the carboxylic acid, the reaction of cyclohexene would be almost 100% selective to the ester formation and hence no dimer of cyclohexene was detected.

Assessment of external and internal resistance to mass transfer

This is a typical solid–liquid slurry reaction involving the transfer of phenylacetic acid (A) and cyclohexene (B) from the bulk liquid phase to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intra-particle diffusion, adsorption, surface reactions and desorption take place. The influence of external solid–liquid mass transfer resistance must be ascertained before a true kinetic model could be developed.

The overall reaction can be presented as follows:

$$A + B \xrightarrow{\text{solid catalyst}} E \tag{1}$$

Where A and B are the reactants and E is the product ester.

At steady state, the rate of mass transfer per unit volume of the liquid phase (gmol cm^{-3} s^{-1}) is given by:

$$R_A = k_{SL\text{-}A}a_p\{[A_0] - [A_s]\} \tag{2}$$

(rate of transfer of A from bulk liquid to external surface of the catalyst particle)

$$= k_{SL\text{-}B}a_p\{[B_0] - [B_s]\} \tag{3}$$

(rate of transfer of B from the bulk liquid phase to the external surface of the catalyst particle)

$$= r_{obs} \tag{4}$$

= rate of reaction within the catalyst particle.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward.[8] When the external mass transfer resistance is small, then the following inequality holds

$$1/r_{obs} >> \frac{1}{k_{SL-A}a_a[A_0]} \text{and} \frac{1}{k_{SL-B}a_p[B_0]} \tag{5}$$

The observed rate r_{obs} could be given by three types of models wherein the contribution of intra-particle diffusional resistance could be accounted for by incorporating the effectiveness factor η. These models are (*a*) the power law model if there is very weak adsorption of reactant species; (*b*) Langmuir–Hinselwood–Hougen–Watson model; (*c*) Eley–Rideal model.

It is therefore necessary to study the effects of speed of agitation, catalyst loading and particle size to ascertain the absence of external and intra-particle resistance so that a true intrinsic kinetic equation could be used. It is seen that the conversion remains practically the same at and beyond a speed of 1000 rpm, which indicates the absence of external solid–liquid mass transfer resistance. Theoretical analysis was also done to ensure that the external mass transfer resistance was indeed absent as delineated below.

Effect of speed of agitation

The effect of speed of agitation on the rate of reaction was studied over 800–1200 rpm for average particle size of 200 μm. The conversion of phenylacetic acid, the limiting reactant, at different intervals of time is shown in Fig. 1. There was no significant change in the conversion patterns beyond 1000 rpm. This implies that there was no resistance to the transfer of phenylacetic acid from bulk liquid phase to the outer surface of the catalyst. Theoretical analysis was also done as given below to confirm that there was no external mass transfer resistance.

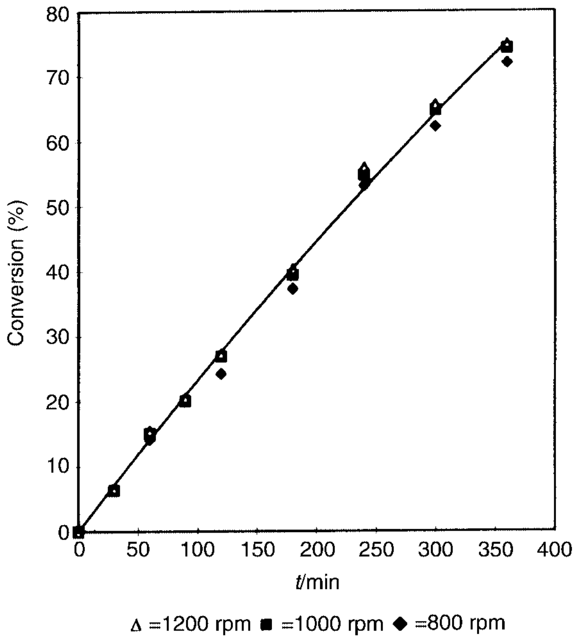


Fig. 1 Effect of speed of agitation. Phenylacetic acid : cyclohexene = 1 : 3; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C.

According to eqn. (5), it is necessary to calculate the rates of external mass transfer of both phenylacetic acid (A) and cyclohexene (B) and compare them with the rate of reaction.

For a typical spherical particle, the particle surface area per unit liquid volume is given by

$$a_p = \frac{6w}{(\rho_p d_p)} \tag{6}$$

where w = catalyst loading g cm^{-3} of liquid phase, ρ_p = density of particle g cm^{-3} and d_p = particle diameter, cm.

For the maximum catalyst loading used in the current studies, a_p = 4.73 cm^2 cm^{-3} liquid phase. The solid–liquid mass transfer coefficient, k_{SL}, for the two reactants was calculated by using the correlations of Sano *et al.*[9] which have been developed for ion-exchange resin type catalyst and take into account the effects of Reynolds number and Schmidt number.

$$\frac{k_{SL}d_p}{D\Psi} = 2 + 0.4\left(\frac{ed_p^4\rho_L^3}{\mu_L^3}\right)^{1/4}\left(\frac{\mu_L}{\rho_L D}\right)^{1/3} \tag{7}$$

where D is bulk diffusivity of the species (A or B), (in cm^2 s^{-1}), Ψ is shape factor, μ_L = viscosity of liquid phase, ρ_L = liquid density, g cm^{-3}, e = power consumption in ergs s^{-1}

$$= p/(\rho_L V_L) \tag{8}$$

where the power

$$p = N_P N^3 d_I^5 \rho_L \qquad (9)$$

N_P = power number, N = speed of agitation, rps; d_I = impeller diameter, cm; V_L = volume of liquid phase, cm^3; ρ_L = liquid density, g cm^{-3}.

The diffusivity values (D) were calculated by using the Wilke–Chang equation[10] and these values are as follows: $D_{AB} = 2.237 \times 10^{-5}$ cm^2 s^{-1} and $D_{BA} = 1.761 \times 10^{-5}$ at 100 °C. Thus the corresponding values of the solid-liquid mass transfer coefficients for both of the reactants were obtained as follows: $k_{SL\text{-}A}$ for phenylacetic acid = 5.5×10^{-2} cm^2 s^{-1}, $k_{SL\text{-}B}$ for cyclohexene = 4.69×10^{-2} cm^2 s^{-1}.

Thus, it was possible to calculate various resistances. A typical initial rate of reaction was calculated as 3.75×10^{-8} gmol cm^{-3} s^{-1}.Therefore, putting the appropriate values in eqn. (5):

$$2.66 \times 10^7 >> 7.39 \times 10^3 \text{ and } 2.88 \times 10^3 \qquad (10)$$

The above inequality demonstrates that there is an absence of resistances due to the solid–liquid external mass transfer for both the species A and B and the rate may be either surface reaction controlled or intraparticle diffusion controlled. Therefore, the effect of catalyst loading and particle size was studied to ascertain the influence of intraparticle resistance.

Effect of catalyst loading

In the absence of mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume.

The catalyst loading was varied over a range of 0.01–0.03 g cm^{-3} on the basis of total volume of the reaction mixture. Fig. 2 shows the effect of catalyst loading on the conversion of phenylacetic acid. The conversion increases with increasing catalyst loading, which is obviously due to the proportional increase in the number of active sites. At higher catalyst loading the rate of mass transfer is excessively high and therefore there is no more increase in the rate.

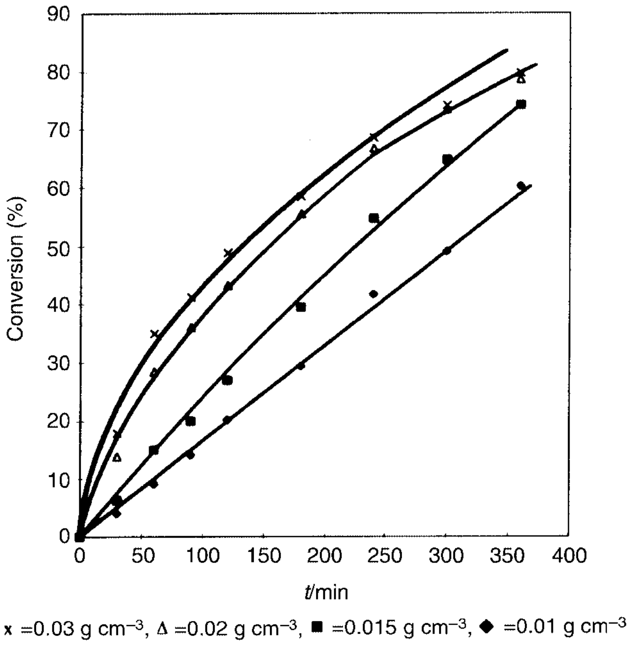


Fig. 2 Effect of catalyst loading. Phenylacetic acid : cyclohexene = 1 : 3; catalyst = Amberlyst-15; solvent = cyclohexane; T = 100 °C; speed of agitation = 1000 rpm.

As shown by eqns. (1) and (2), at steady state, the rate of external mass transfer (*i.e.* from the bulk liquid phase in which A and B are located with concentration [A_0] and [B_0], respectively) to the exterior surface of the catalyst is proportional to a_P, the exterior surface area of the catalyst where the concentrations of A and B are [A_S] and [B_S], respectively. For a spherical particle, a_P is also proportional to w, the catalyst loading per unit liquid volume as shown by eqn. (6). It is possible to calculate the values of [A_S] and [B_S]. For instance,

$$\begin{aligned} k_{SL\text{-}A}a_p \{[A_0] - [A_S]\} &= r_{obs.} \text{ at steady state} \qquad (11) \\ &= 3.75 \times 10^{-8} \text{ gmol cm}^{-3} \text{ s}^{-1} \end{aligned}$$

Thus putting the appropriate values, it is seen that $[A_S \approx [A_0]$, similarly $[B_S] \approx [B_0]$. Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer. The experimental observation is consistent.

Since the reaction could be limited by either intraparticle diffusion or by reaction on the pore walls within catalyst particle (intrinsic reaction), for which the effect of particle size needs to be considered.

Effect of particle size

In order to assess the role of intra-particle resistance, the effect of particle size of the catalyst on the reaction rate was studied by taking four different particle size ranges under otherwise similar conditions as shown in Fig. 3.

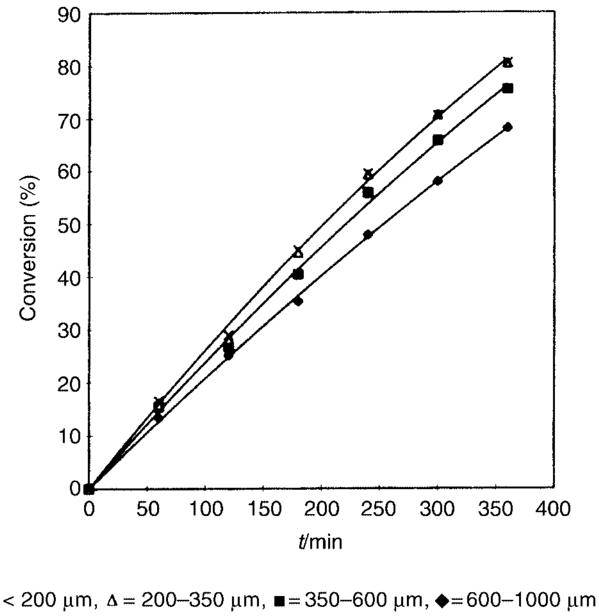


Fig. 3 Effect of particle size. Phenylacetic acid : cyclohexene = 1 : 3; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

It is seen that for the particle size below 200 μm the reaction rates were independent of the size, which in turn supports that the intra-particle diffusional resistance was absent, and the reaction is intrinsically kinetically controlled. This was further confirmed by invoking the Wietz–Prater criterion.[11] According to the Wietz–Prater criterion (C_{WP}), if (i) $C_{wp} = -r_{obs}\rho_p R^2/\{D_e[A_S]\} \gg 1$, then the reaction is limited by severe internal diffusional resistance; (ii) $C_{wp} \ll 1$, then the reaction is intrinsically kinetically controlled.

In the present case, the value of effective diffusivity for A (D_e) was calculated as 2.82×10^{-6} from the value of the bulk diffusivity D_{AB}, tortuosity τ, and porosity of the particle ε ($D_e = D_{AB}\varepsilon/\tau$). Thus by substituting the appropriate values, for a particle radius R of 100 μm, C_{wp} is calculated as 2.43×10^{-3} which is much less than unity and hence the reaction is intrinsically kinetically controlled. A further proof of the absence of the intra-particle diffusion resistance was obtained by studying the effect of temperature and it will be discussed later.

Effect of concentration of phenylacetic acid

The effect of concentration of phenylacetic acid was studied at 7 different initial concentrations from 1.3×10^{-4} gmol cm^{-3} to 1.56×10^{-3} gmol cm^{-3} for a fixed concentration of cyclohexene of 1.56×10^{-3} gmol cm^{-3} at a catalyst loading of 0.015 g cm^{-3}. Complete concentration profiles were measured for 4 different initial concentrations of phenylacetic acid as shown in Fig. 4. The initial rates of reactions were measured for 7 different concentrations of phenylacetic acid and are plotted against its concentrations to observe that they are linear, which suggested a first order dependence on concentration of phenylacetic acid. The data fit gave R^2 value of 0.978 from which the coefficient of linear correlation (R) was calculated as 0.988. Thus the linear relationship is appropriate (Fig. 5).

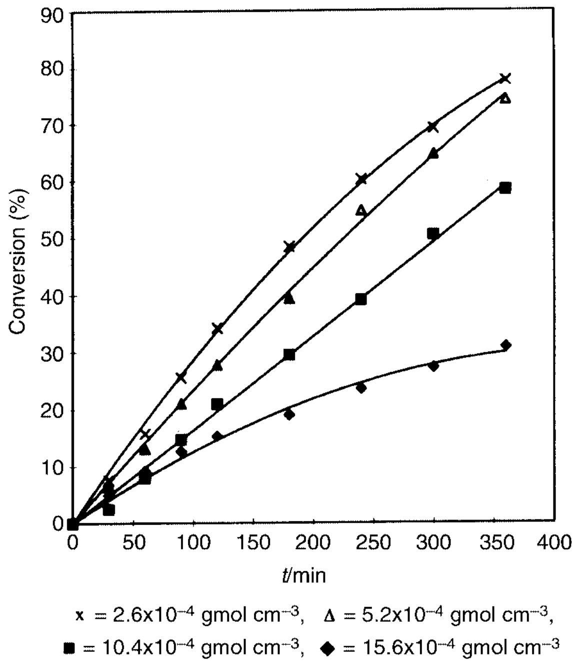


Fig. 4 Effect of concentration of phenylacetic acid. Cyclohexene = 1.56×10^{-3} gmol cm^{-3}; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

Effect of concentration of cyclohexene

The concentration of phenylacetic acid was maintained at 2.6×10^{-4} gmol cm^{-3} and that of cyclohexene was varied from 7.8×10^{-4} to 2.34×10^{-3} gmol cm^{-3} under otherwise similar conditions (Fig. 6). It is clearly seen that the conversion of phenylacetic acid is independent of the concentration of cyclohexene.

Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the temperature range of 90–110 °C as shown in Fig. 7. The conversion of phenylacetic acid was found to increase substantially with increasing temperature up to 100 °C. At 110 °C conversion had decreased due to the formation of dimer of cyclohexene. Therefore, all reactions were carried out at 100 °C.

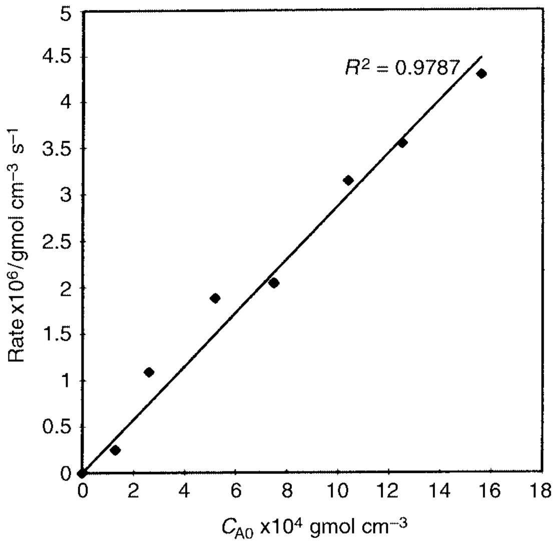


Fig. 5 Plot of initial rate *vs.* concentration of phenylacetic acid.

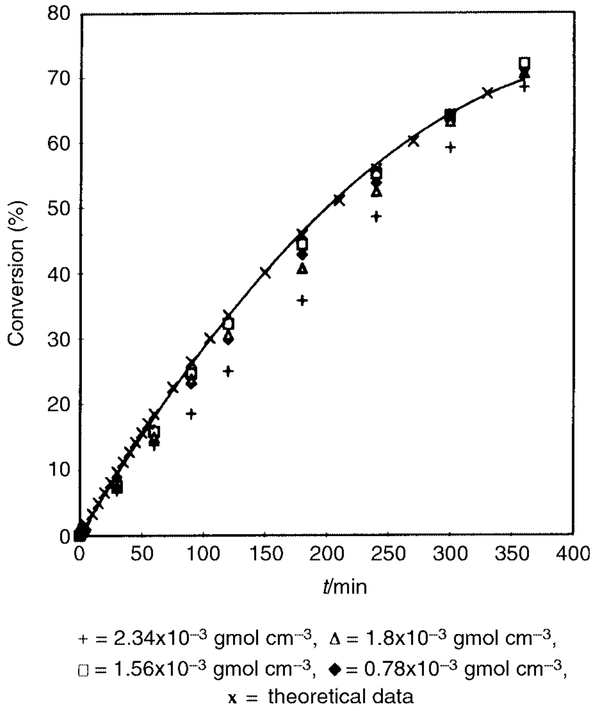


Fig. 6 Effect of concentration of cyclohexene. Phenylacetic acid = 2.6×10^{-4} gmol cm^{-3}; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

Kinetics of the reaction

The initial rate data were analysed to find that cyclohexene (B) gets adsorbed on the catalyst site to form the surface carbocation, which reacts with the acid (A) from the liquid phase and the following rate equation holds

$$-r_A = \frac{-dC_A}{dt} = \frac{k_R K_B C_A C_B w}{1 + K_B C_B} \qquad (12)$$

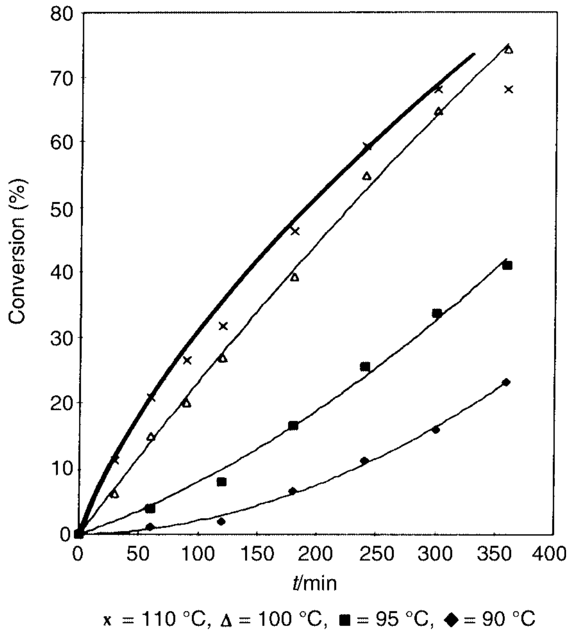


Fig. 7 Effect of temperature. Phenylacetic acid : cyclohexene = 1 : 3; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; speed of agitation = 1000 rpm.

where $-r_A$ is the rate of reaction (mol cm^{-3} s^{-1}), k_R is the rate constant, K_B the adsorption equilibrium constant of B, w the catalyst loading in g cm^{-3}. At higher concentrations of B, $K_BC_B \gg 1$, and thus eqn. (12) reduces to

$$-r_A = k_RC_Aw \tag{13}$$

Thus the reaction is zero order in cyclohexene and first order in the acid. This behaviour was observed as shown in Fig. 5. There is a mention in literature by Guenzet *et al.*[12] that reaction of cyclohexene with acetic acid is first order in acetic acid. Our studies have also shown similar behaviour. Eqn. (13) can be integrated to get eqn. (14):

$$-\ln(1 - X_A) = k_Rwt \tag{14}$$

As explained earlier, at a fixed concentration of phenylacetic acid and varying concentrations of cyclohexene it was observed that the conversion of phenylacetic acid practically remained the same; thereby suggesting that the rate of reaction is independent of the concentration of B. This is due to the fact that cyclohexene gets strongly adsorbed over A and hence, the reaction becomes zero order in B and first order in A (Fig. 5). Thus, it is seen that practically the same conversions of phenylacetic acid are obtained although the concentration of cyclohexene was changed over three fold.

However, at low concentrations of cyclohexene, $K_BC_B << 1$, eqn. (12) leads to a typical second order rate equation given by:

$$-r_A = k_RK_BC_AC_Bw \tag{15}$$

Eqn. (15) can be integrated for equimolar quantities of A and B to get the following:

$$\frac{X_A}{1-X_A} = k_RK_BC_{A0}wt = k_1wt \tag{16}$$

Thus, experiments were conducted at low equimolar concentrations of phenylacetic acid and cyclohexene to observe that eqn. (16) holds (Fig. 8). The goodness of the fit is very good (R^2 = 0.9607; R = 0.98).

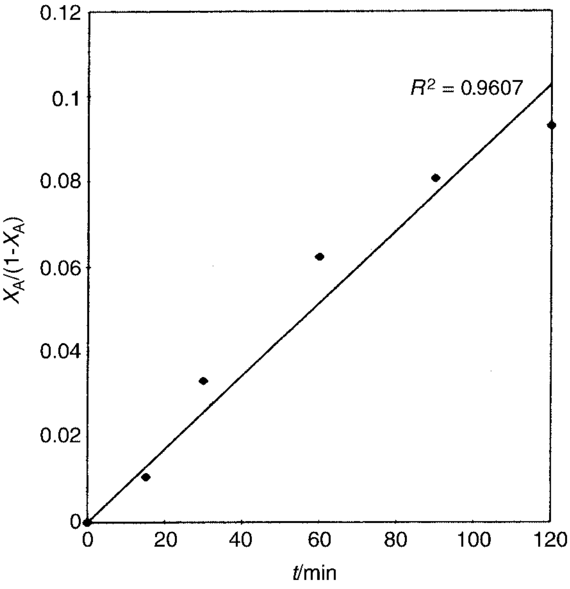


Fig. 8 Plot of $X_A/(1 - X_A)$ *vs.* t.

Energy of activation

The concentration profiles of phenylacetic acid at different temperatures were used to fit the first order rate equations and the rate constants were evaluated. Arrhenius plot of ln k_1 *vs.* T^{-1} (K^{-1}) was made to determine the activation energy value as 48.9 kcal mol^{-1} (Fig. 9). Again the goodness of the fit is very good (R^2 = 0.979, R = 0.989).

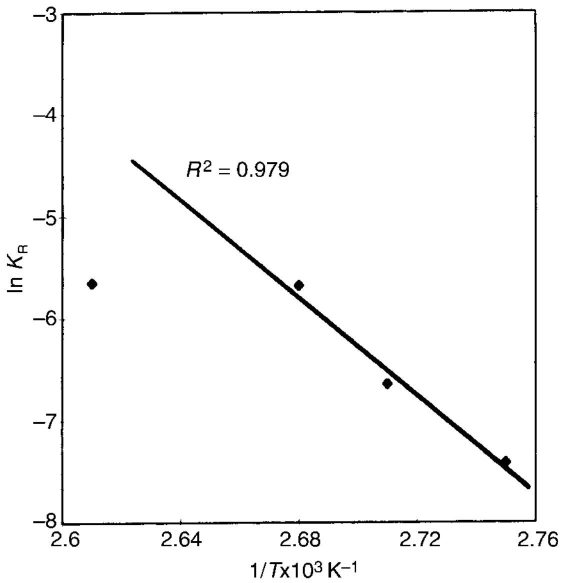


Fig. 9 Arrhenius plot.

Reusability of the catalyst

The catalyst was filtered and dried at 110 °C overnight and was employed without any post-treatment or washing for subsequent runs as shown in Fig. 10. It was found that the activity had decreased appreciably with each use. Therefore, a fresh set of experiments were conducted, wherein the catalyst was washed for 15 min with cyclohexene in order to remove any adsorbed material from the catalyst surface and pores and dried at 110 °C after every use. Fig. 10 shows the results. The reduction in activity of the catalyst was marginal as compared to the catalyst without

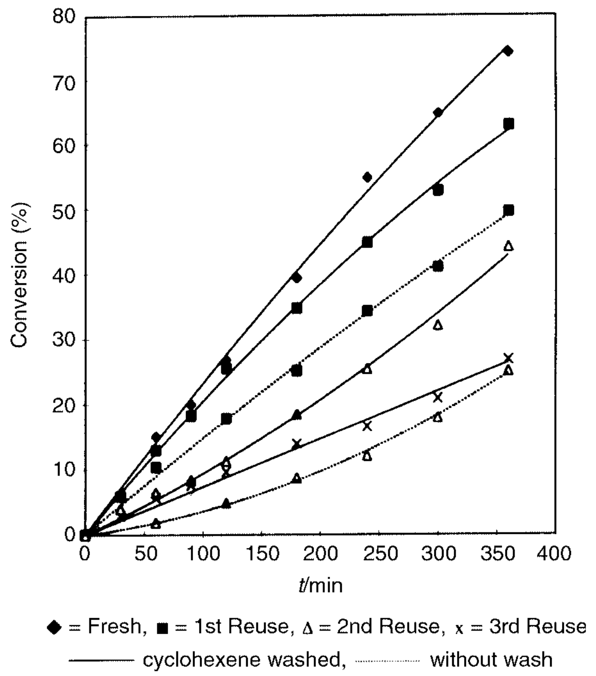


Fig. 10 Effect of reusability of catalyst. Phenylacetic acid: cyclohexene = 1:3; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

post-treatment. In fact, conversion obtained in the third run with post-treated catalyst was comparable to that obtained in the second run in the case of catalyst, which was used without any treatment.

Validity of the model

In order to assess the validity of the model, the rate constant values were calculated and theoretical conversions were calculated using eqn. (14) and a curve was plotted in Fig. 6 (shown by '*x*' points). The model fits the experimental data well.

Effect of different substrates

Different carboxylic acids were treated with cyclohexene under otherwise similar conditions at 100 °C. The results for esterification of phenylacetic acid, benzoic acid, acetic acid, propionic acid, butyric acid, *iso*-butyric acid, anthranilic acid and heptanoic acid are shown in Table 2. Amongst all acids, the conversion of phenylacetic acid was highest due to the active methylene group.

Table 2 Conversion of different substrates

Acid	Conversion (%)
Phenylacetic acid	74
Benzoic acid	39
Butyric acid	11
iso-Butyric acid	10
Anthranilic acid	15
Acetic acid	30
Propionic acid	21
Heptanoic acid	11

Acid: cyclohexene = 1:3; t = 6 h; catalyst = Amberlyst-15; solvent = cyclohexane; catalyst loading = 0.015 g cm^{-3}; T = 100 °C; speed of agitation = 1000 rpm.

The conversion of benzoic acid was lower than that of phenylacetic acid as expected. The conversions of other aliphatic acids were still lower due to the aliphatic chain that they contain.

Conclusions

The current work has addressed the use of ion exchange resins in the synthesis of cyclohexyl esters from carboxylic acids and cyclohexene. The ion exchange resins, Amberlyst-15 and Indion-130, were found to be effective and highly selective. Filtrol-44 and DTPA/K10 did not show any activity to the model reaction of phenylacetic acid and cyclohexene. The reaction was 100% selective towards cyclohexylphenyl acetate and hence the process is 100% atom economical. A mathematical model was built to suggest stronger adsorption of cyclohexene *vis-à-vis* phenylacetic acid.

Acknowledgements

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Paper a908035j

Developing environmentally benign routes for semiconductor synthesis: improved approaches to the solution deposition of cadmium sulfide for solar cell applications

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Summary

Chemical Bath Deposition (CBD) is a useful method for the deposition of thin films of semiconductors such as CdS, which are important components of polycrystalline solar cells. Such devices potentially offer low cost solar energy conversion which are interesting sustainable energy sources. We are attempting to reduce the environmental impact on the fabrication of such devices by developing routes in which cadmium is used efficiently in the deposition of films. At present the fabrication of CdS window layers by CBD generates considerable quantities of cadmium-containing waste and the incorporation of cadmium into the films accounts for only a small fraction of the total used in the process. The use and disposal of cadmium-containing compounds is highly regulated in the EU and elsewhere. In CBD, the extent of the heterogeneous film formation process is limited by two major factors: homogeneous reaction in solution (precipitation) and the deposition of material on to the reactor walls. In this paper we describe the development of a novel high-efficiency CdS CBD system, using concentrations of cadmium orders of magnitude lower than in previously reported methods. The modelling of chemical equilibria have enabled us to develop this method which also offers the potential to eliminate ammonia (which is volatile and undesirable for large-scale CBD operations). Films have been characterized as good quality CdS by spectroscopic methods (UV–VIS, PL and XPS), microscopy (SEM and TEM) and powder XRD.

Introduction

The conversion of sunlight into electricity, by exploiting the photovoltaic properties of a semiconductor material, is both an environmentally benign and technologically interesting process. Although the photovoltaic effect was discovered by Becquerel in 1839 the forerunner to contemporary silicon solar cell technology, the diffused silicon p–n homojunction, was only developed in 1954.[1] The invention of the CdS:CuS heterojunction solar cell,[2] the antecedent of CdS:CdTe based devices, led to intense research on thin film solar cell devices.

Semiconductor materials can absorb light (photons of energy greater or equal to the bandgap of the material) and generate electron–hole pairs. Normally these charged species would recombine with each other after some finite period, however if they can be separated and collected at two externally connected contacts a photocurrent can be produced. Efficient photovoltaic energy conversion requires a high probability of photon absorption, efficient separation and effective transport of the charge carriers. The most widely employed device principle for solar energy conversion is the p–n semiconductor junction. The configuration provides an intrinsic electric field that facilitates the separation of photogenerated charge carriers. The principles of solar energy conversion and the material aspects of photovoltaic technology have been reviewed in many papers and books.[3]

In 1990, a review of photovoltaic technology by the then UK Department of Energy was undertaken by ETSU. The main conclusion of the exercise was an acknowledgement that PV systems, integrated into the fabric of UK buildings, could provide an environmentally benign power source at a cost competitive with conventional sources.[4] Although there have been both academic advances and market growth in photovoltaic technology in recent years, there remains a need for increased efficiency of the cells, lower cost processing and increased process yields. Photovoltaic energy generation is currently dominated by bulk crystalline silicon cell technology. The widespread utilisation of the product is problematic due to the high production cost of these cells. Thin film polycrystalline solar cells, such as the BP Solar 'Apollo' CdS:CdTe heterojunction device,[5] offer the potential for lower cost solar energy conversion. The large-scale exploitation of these devices is partly dependent on a reduction of the potential environmental impact of the technology. There is considerable potential for the development of cheaper and safer processes for their manufacture. Cadmium-containing compounds and wastes are highly regulated in the EU and elsewhere and the associated environmental legislation is subject to

Green Context

While the conversion of sunlight into electricity using semiconductors is fundamentally an environmentally benign process the manufacture of the solar cells can involve environmentally damaging chemistry. The deposition of thin films of cadmium sulfide using chemical bath deposition is currently very inefficient and leads to considerable quantities of cadmium waste. The use and disposal of cadmium compounds is highly regulated and it seems unlikely that processes of this type will be acceptable in the future. Here a new process is described which uses much lower concentrations of cadmium in the preparation of the film, is highly efficient in cadmium use, and also offers the potential to eliminate volatile ammonia from the process. ***JHC***

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continuous review; trends for regulatory limits are increasing downwards.[6]

Although the electrodeposition of CdTe on CdS layers (on tin oxide glass) has been developed to contain Cd in a safe manner, the fabrication of CdS window layers by Chemical Bath Deposition (CBD) generates considerable Cd-containing waste. We have and others recently reviewed some of the chemistry underlying CBD processes.[7] Typical CBD processes for sulfides employ an aqueous alkaline solution (*ca.* 60–90 °C) containing the chalcogenide source, the metal ion and added base. A chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. The technique under these conditions relies on the slow release of S^{2-} ions, *via* thermal decomposition of an organic precursor, into an alkaline solution in which the free metal ion is buffered at a low concentration. The deposition of cadmium sulfide by CBD is particularly straightforward and well-studied with notable contributions from the Lincot group.[7] However, minimising the environmental impact of the process presents a considerable challenge.

A major limitation of current CBD methods is the inefficiency of batch processing techniques, in terms of the utilisation of starting materials and their conversion to thin films. Typically 2% of the cadmium source in CdS CBD is deposited in the thin film. Significant volumes of Cd-contaminated water and precipitates are generated. In addition the process employs high concentrations of ammonia which is volatile and detrimental to the environment. An efficient system for recovering and recycling cadmium and other chemicals would place a much lower burden on the environment. It would also ensure that the process will be able to comply more easily with regulatory requirements on emission. The quantity of chemicals to be disposed of in landfill sites will be reduced as will the quantities of cadmium compounds that have to be stored in a production facility (which will reduce the environmental risk of accidental release).

The extent of the heterogeneous reaction on the substrate surface is limited by two major factors; the competing homogeneous reaction in solution (which is autocatalytic and results in massive precipitation in solution) and deposition of material on the CBD reactor walls. There are analogies here with the problems encountered in Chemical Vapor Deposition (CVD), where the use of ‘cold wall’ (in preference to ‘hot wall’) configurations can suppress the undesirable reactor wall reactions. The lower thermal energy input of the system also increases the relative importance of surface reactions on the heated substrate.[8]

In general the controlling physiochemical factors for successful CBD are the supersaturation of the solution and the kinetics of the growth process (*e.g.* the catalytic activity of the deposition surface).[7] Supersaturation is defined as the metastable condition whereby the concentration of a substance in solution exceeds the equilibrium concentration with respect to its solid phase. As cadmium ions are labile in aqueous media and equilibria are rapidly established in stirred solutions, thermodynamic equilibria models are useful in assessing the initial stages of these chemically reactive baths. Studies of the speciation of cadmium in chemical baths (*i.e.* calculation of distributions and concentrations of metal and metal-ligand species) allow us to determine the initial supersaturation of the system.

Here we demonstrate the application of equilibrium and speciation calculations for CBD systems. The results of these studies have provided a rational framework for the development of high-efficiency CdS CBD systems that use cadmium and ethylenediamine at low concentrations. It is desirable to eliminate ammonia from the process (which is commonly employed in CdS CBD) as it is volatile and undesirable in larger scale CBD operations. We have successfully performed CBD in optically clear solutions under conditions of low temperature with direct heating of the target substrate.

Experimental

Deposition of thin films

CdS thin films were grown on glass microscope slides or tin oxide (TO) coated glass (Tec 10, LOF) from solutions containing cadmium chloride (0.01–0.001 mol dm^{-3}), an amine ligand (ammonia or ethylenediamine; 5–0.001 mol dm^{-3}), thiourea (0.01 mol dm^{-3}) and sodium hydroxide (0.01 mol dm^{-3}) to obtain a solution of final pH 12.5 (adjusted by dropwise addition of 5 mol dm^{-3} HCl or NaOH or the use of a PC-controlled automatic titrator). Deposition baths containing ammonia were prepared according to a formulation described elsewhere.[5] An EIL 7000 pH meter with temperature compensation and Russell glass electrode (calibrated against standard pH 4.00 and 10.00 buffers) were used to record solution pH. Substrates were degreased and cleaned thoroughly by ultrasonication using a standard procedure, before immersion in the chemical bath. The essential features of the modified CBD process (Fig. 1) are the incorporation of a filtration unit (to remove homogeneously generated precipitates) and the potential for continuous reaction by replenishment, treatment and purification of reagents within a recirculating closed-loop CBD reactor. We have used direct heating of the CBD substrate, the configuration limits the undesirable homogeneous reaction. Precipitation and deposition of CdS on the walls of the reactor vessel limit the effectiveness of *in situ* strategies for cadmium recovery. The CBD solution was maintained at moderate temperature (*ca.* 300 K) for deposition. Films were deposited on resistively heated substrates (*ca.* 350 K) and removed from the bath after the desired period of time (*ca.* 45 min), washed with de-ionised water and any adherent particulate matter removed by ultrasonic agitation. Film thicknesses (*ca.* 40–60 nm) were determined by Quartz Crystal Microbalance (QCM) measurements. Throughout the deposition process the chemical bath remained optically clear and no deposition on the CBD reactor was observed to occur. The substrates were allowed to dry under ambient conditions (*ca.* 0.5 h) before film characterisation or a further annealing step in air.

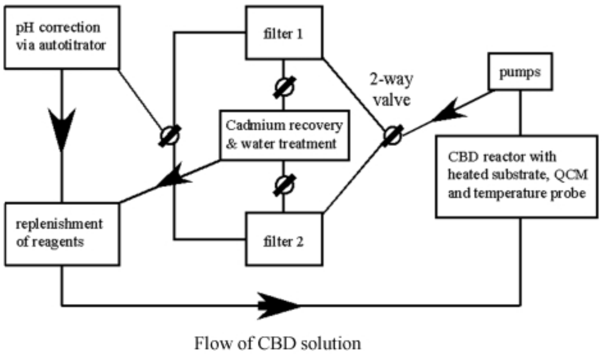

Fig. 1 Schematic representation of a high-efficiency CdS CBD system. Potential for continuous operation is achieved *via* alternate use of filters 1 and 2 (polypropylene 200 nm mesh) to facilitate recovery of particulate cadmium compounds. Organic by-products of the CdS CBD process are also removed during water treatment.

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Characterisation of thin films

Electronic absorption spectra were recorded with a Philips PU 8710 spectrophotometer. Photoluminescence (PL) measurements were obtained at 10 K using the 457.9 nm line of an Ar-laser and excitation density of 3.0 mW mm^{-2} (spectral resolution of 2 nm), with a 495 nm long wavelength pass filter in front of the monochromator. X-Ray diffraction studies were performed using secondary graphite monochromated Cu-Kα radiation (40 kV) on a Philips X'Pert Materials Research Diffractometer (MRD). Measurements were taken using a glancing angle incidence detector at an angle of 3°, for 2θ values over 20–60° in steps of 0.04° with a count time of 1 s. Scanning electron microscopy (SEM) and EDAX were carried out on a JEOL J535CM instrument with a LINK QX2000 unit. Samples were carbon coated before analysis. A JEOL-JEM 2010 transmission electron microscope operating at 200 kV was used for TEM studies and to obtain electron diffraction patterns. Wide scan XPS measurements were performed in the ultra-high vacuum chamber (base pressure 10^{-8} Pa) of a VG ESCALAB-Mk II (VG Scientific) using Al-Kα excitation (analyser pass energy of 50 eV). The energy scale was calibrated using trace carbon (C_{1s} 284.8 eV) as a reference.

Modelling and speciation

All calculations were carried out using microcomputers either in EXCEL or using the program SPECIES.[9]

Results and discussion

Minimizing cadmium concentration in solution: modelling and speciation studies

A number of reports in the literature suggest that good quality, specular and adherent films of CdS are only obtained, from alkaline solutions, when the solution used for deposition is formally supersaturated with respect to the precipitation of hydroxy-cadmium species. We have sought to generalize this condition and have now defined the concept of an equivalent solution. The idea can be simply stated as follows; if an alkaline bath successfully deposits a thin film of CdS it can be characterized in terms of a free cadmium ion concentration and its pH. It is a simple matter to define solutions that provide this same level of supersaturation either for the same or a different ligand.

The calculations for CBD solutions are quite straightforward, for in general we are working with a substantial excess of the ligand and at elevated values of pH, such that $[L] \gg [M]$ and therefore we can write:

$$M_T = M_F \{1 + \beta_1[L]_T + \beta_2[L]_T^2 + \beta_3[L]_T^3 + \ldots\ldots\ldots\ldots\} \quad (1)$$

where M_T and L_T are the total metal and ligand concentrations respectively, M_F is the free metal ion concentration and β_n the n^{th} overall thermodynamic formation constant. For CdS CBD from basic solutions we employ amine ligands and the free ligand concentrations are dependent upon pH (a minor correction for conditions of pH > pK_a + 1)

$$M_F = M_T \{1 + \beta_1(K_A[L]_T/[H^+] + K_A) + \beta_2(K_A[L]_T/[H^+] + K_A)^2 + \ldots\ldots\}^{-1} \quad (2)$$

where K_A is the relevant acid dissociation constant.

We can hence establish conditions for which pM (the negative logarithm of free metal ion concentration M_F) and hence the concentration of hydroxy-cadmium species is the same for different solutions at a fixed solution pH.

Calculations were carried out using either equations of type (1) or (2) in EXCEL spreadsheets or by modelling with the program SPECIES. The latter program uses a precise algorithm to calculate pM and pL, from input data defining total concentrations for the metal and ligand.The input parameters for SPECIES are the stability constants for the homogeneous and heterogeneous equilibria being modelled and their stoichiometric coefficients. The calculated speciation curves are displayed as a function of pH. Identical results were obtained by either method of calculation, which served to confirm the approximations detailed above.

The results of these calculations can best be presented in terms of contour lines defining a constant pM (determined for the onset of supersaturation *i.e.* $[Cd]_F = K_{sp}/[OH]^2$), on a plot of total metal M_T against total ligand L_T, for different conditions for a single metal–ligand combination or alternatively, on a different line for a new metal–ligand combination. The approach provides a more precise definition of the concept of a critical metal–ligand ratio for CBD as outlined by Hodes *et al.*[10] In this study we have modelled ethylenediamine, 1,2-diaminopropane, ammonia, ethanolamine, triethanolamine and hydrazine as representative ligands for the cadmium system. Equivalence plots are shown in Fig. 2 for which all the contour lines correspond to $-\log[Cd]_F$ = pM = 10.61, conditions for which good films of CdS are deposited from a commercial CBD system defined in ref. 11. The contours reflect the tendency of metal complexes to dissociate on dilution. The positions of the contour lines provide an indication of the thermodynamic stability of the complexes formed, for example, ethylenediamine (en) is a stronger ligand than ammonia and is hence needed at lower concentrations.

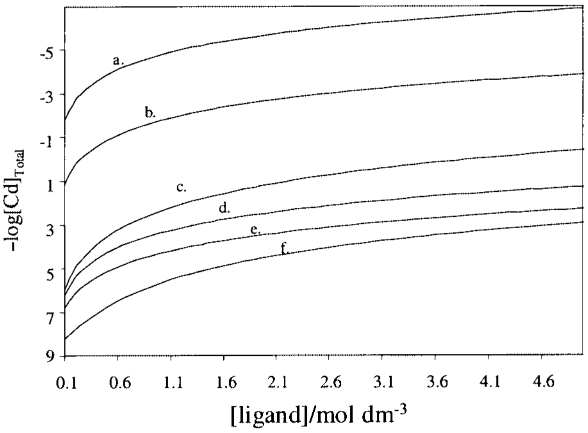
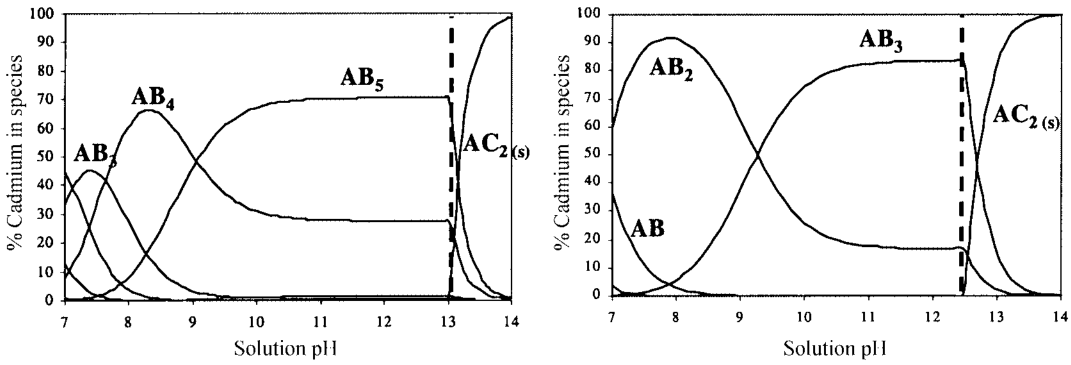


Fig. 2 The concept of chemical equivalence for different CdS CBD systems. Ligands represented in this study are (*a*) ethylenediamine; (*b*) 1,2-diaminopropane; (*c*) ammonia; (*d*) ethanolamine; (*e*) triethanolamine and (*f*) hydrazine. Contour lines represent conditions of $[Cd^{2+}]_F = 2.44 \times 10^{-11}$ mol dm^{-3} at pH = 12.5.

In terms of developing new regimes for deposition, the concept of chemical equivalence is very useful. The calculations suggest that CBD solutions (Bath B) of solution pH = 12.5, containing lower concentrations of cadmium (0.001 mol dm^{-3}) and en (0.012 mol dm^{-3}), are equivalent in terms of cadmium supersaturation to the much stronger solutions of cadmium and ammonia (Bath A) typically used for the growth of solar cell window layers.[11] Speciation profiles of both systems are shown in Fig. 3.

Deposition of CdS from conventional baths

Thin films of CBD CdS have been deposited from 3 different CdS CBD solutions which provide similar levels of supersaturation (Table 1). The films were characterized by spectroscopic methods



Bath A

Bath B

Fig. 3 Speciation diagrams of high cadmium/high ammonia (Bath A; solution pH = 13) and low cadmium/low ethylenediamine (Bath B; solution pH = 12.5) CBD solutions used to deposit CdS thin films. The baths are defined in terms of cadmium supersaturation. Precipitation points for hydroxy-cadmium species are indicated by the vertical dashed lines. Good quality CdS films are deposited from baths of solution pH values greater or equal to those corresponding to the precipitation points: A = Cd^{2+}, B = NH_3 or en, C = OH^-

Table 1 CdS CBD solutions of similar hydroxy-cadmium supersaturation used to deposit thin films. All concentrations in mol dm^{-3}. Solution pH values adjusted by dropwise addition of 5 mol dm^{-3} $NaOH_{(aq)}$

CBD solution	[Cd^{2+}]	[Ammonia]	[Ethylenediamine]	[Thiourea]	pH
Bath A	0.01	5.028		0.01	13
Bath B	0.001		0.012	0.01	12.5
Bath C	0.001	2.8		0.01	12.5

(UV–VIS, PL and XPS) and XRD. The as-deposited films were optically transparent, specular and ranged in colour from yellow (Baths A and C films) to orange–red (Bath B films). The colour of films changed to pale yellow (Bath B) or brick-red (Bath A and C films) after annealing in air at air (673 K for 15–30 min). Bandgaps of the films were determined from UV–VIS spectroscopic measurements before and after annealing. The linear dependence of α^2 with $h\nu$ indicated a direct bandgap. Extrapolation of the linear region of the absorption profile from plots of α^2 *vs.* eV provided data on the change in bandgap energy upon annealing in air. Representative spectra are shown in Fig. 4 and data are presented in Table 2. Preliminary PL measurements on films indicated that there were notable differences in emission spectra of films, obtained from baths containing either ammonia or ethylenediamine. It was interesting therefore to compare the PL emission spectra of films obtained from Baths A and C (that contained lower concentrations of cadmium and ammonia) which were identical in terms of hydroxy-cadmium supersaturation (*i.e.* chemically equivalent in our model). No significant differences were observed. PL spectra of films obtained from Baths A (ammonia bath) and B (ethylenediamine bath) are presented in Fig. 5. In all cases these spectra consisted of a broad, complex low energy band. No convincing evidence for (near) bandgap emission was obtained. The observation was ascribed to the polycrystalline nature of the films which would be expected to contain many defects (both structural and impurity based), leading to sub-bandgap emission(s) at lower energies. PL spectra of as-deposited films from Baths A and C were identical in all major features, these consisted of a broad low energy emission which could be deconvoluted into three components with peak maxima at 1.47, 1.58 and 1.68 eV; PL bands of films from Bath B (*cf.* Bath A and C) were similar in their features but broader and displaced to higher energy by *ca.* 0.05 eV. Annealing in air has a marked effect on the PL emission spectra of films. PL spectra obtained for all annealed films presented a change in relative intensities of the three components of the broad emission band.

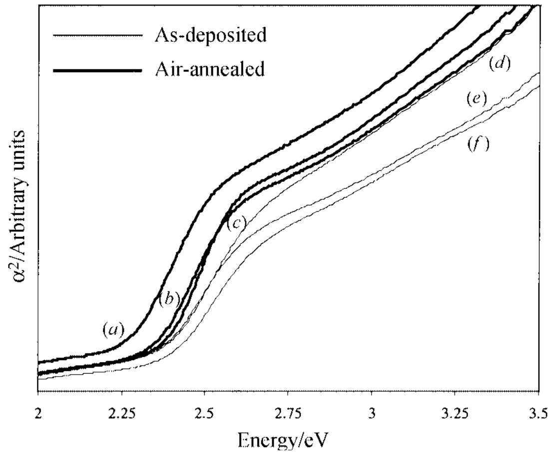


Fig. 4 Determination of bandgaps of CdS CBD films from UV–VIS measurements. Data recorded for films before and after annealing in air.

Table 2 Bandgap measurements as determined from UV–VIS measurements on CdS CBD films before and after annealing in air. Data reported in eV

CBD solution	Air-annealed	As deposited
Bath A	2.21	2.36
Bath B	2.31	2.36
Bach C	2.35	2.37

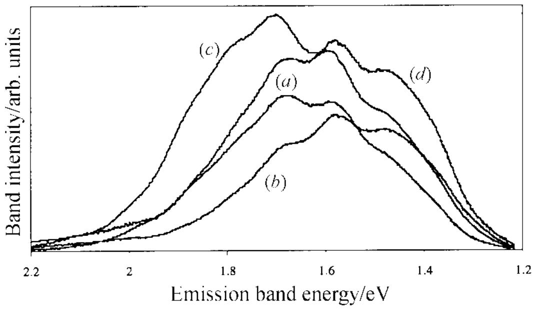


Fig. 5 Low temperature photoluminescence (PL) spectra of as-deposited (*a* and *c*) and annealed (*b* and *d*) CdS CBD films. Films deposited from high cadmium/high ammonia (Bath A, films *a* and *b*) and low cadmium/ethylenediamine (Bath B, films *c* and *d*) exhibit similar characteristics in PL spectra. The absence of band edge emission and the broad nature and low energy of the PL response are typical for small grained CBD CdS films.

No change in band positions were recorded for the films from Baths A and C, films derived from Bath B displayed a hypsochromic shift of the band at 1.595–1.600 eV. For all films the highest energy band ($E_{\max}$ = *ca.* 1.68–1.7 eV) diminished in intensity and for films from Baths A and C, the lowest energy band ($E_{\max}$ = 1.47 eV) greatly increased in intensity and extended the entire broad emission band into the lower energy region. Two tentative conclusions can be made from these observations. Films deposited from CBD solutions of identical formulation chemistry (more simply, the same ligand) and cadmium speciation have been shown to yield CdS films of very similar optical and electronic properties. Minor differences are observed for films derived from baths containing a different ligand to ammonia (*i.e.* ethylenediamine) but similar cadmium supersaturation, although the differences are only in detail.

Glancing angle XRD measurements were recorded [Fig. 6(*a*) and (*b*)] and the diffraction patterns compared with standards in the JCPDS data files. As-deposited films were composed of a mixture of cubic and hexagonal phases of CdS, annealing in air for 30 min at 673 K improved crystallinity and effected conversion to the hexagonal modification.[12] The effect was more pronounced for films deposited from baths containing ethylenediamine, in general these films exhibited superior crystallinity to those deposited from ammoniacal solutions, which are polytypical and often ill-defined.[11] Wide-scan XPS measurements of films were performed, photoelectron binding energies of 405.6 eV (Cd $3d_{5/2}$), 411.2 eV (Cd $3d_{3/2}$) and 162.4 eV (S 2p) were recorded for the major XPS peaks of the CBD CdS films (Fig. 7). Similar values have been reported for good quality CBD CdS films deposited from acidic solutions containing no added ligand.[13] No significant differences between films were observed for films deposited using different baths.

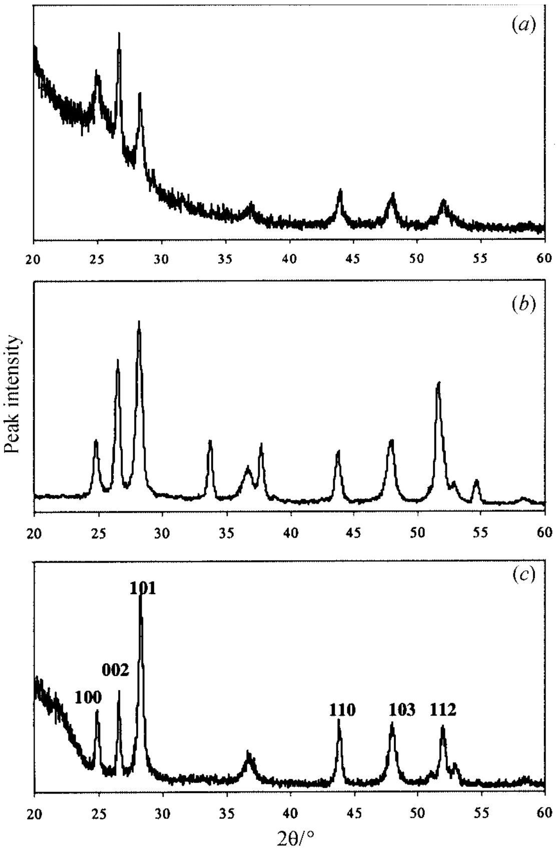


Fig. 6 X-Ray diffraction spectra of air-annealed CdS thin films on TO-glass deposited from different chemical bath solutions. Films grown from (*a*) high cadmium-high ammonia baths ([Cd^{2+}] = 0.01 mol dm^{-3}, [ammonia] = 5.02 mol dm^{-3}, pH = 13); (*b*) low cadmium-low ethylenediamine baths ([Cd^{2+}] = 0.001 mol dm^{-3}, [en] = 0.012 mol dm^{-3}, pH = 12.5); (*c*) film deposited on heated TO-glass substrate from recirculating CBD solution as used for (*b*). Films deposited from baths containing ammonia appear to have a preferred [002] orientation, ethylenediamine baths deposit films that are in general more crystalline with alignment in the [101] direction.

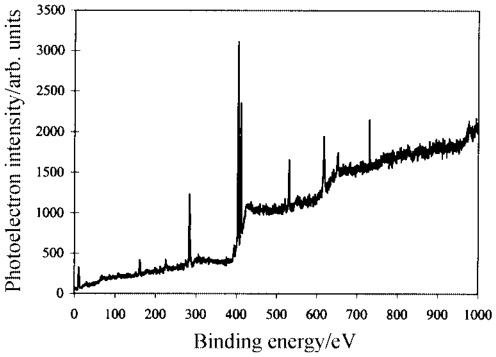


Fig. 7 Wide scan XPS spectrum of CdS CBD film on TO-glass deposited from low cadmium-low ethylenediamine solution (Bath B).

Deposition of CdS on heated substrates in circulating systems

One major problem in the CBD of films of CdS and related materials is that the efficiency of the process is low due to homogeneous precipitation and deposition on the reactor walls. We have now sought to combine the use of dilute solutions as described above with a novel approach to the heating of the substrate. Typical CBD experiments involve the heating of the whole deposition bath, we have modified the deposition system in such a way that the dilute deposition solution is continuously circulated over a TO-glass substrate, in contact to a resistively heated immersion apparatus. In some ways this approach is analogous to the difference between a hot walled and a cold walled CVD reactor. A schematic representation of our simple design is shown in Fig. 1.

The deposition of good quality CdS films on heated glass substrates was carried out using the low cadmium–ethylenediamine CBD solution (Bath B). Throughout the deposition process the CBD solution remained optically clear and pale yellow in colour, there was an absence of CdS formation on reactor walls or as homogeneous precipitate over 10 h. Films were removed and replaced periodically with fresh TO-glass substrates. The films were characterized by spectroscopic methods (UV–VIS and XPS), microscopy (TEM) and XRD. The as-deposited films were optically transparent, specular and yellow–orange in colour. The colour changed to pale yellow after annealing in air at 673 K. The bandgaps of the films were determined before and after annealing. Annealing produced a shift in the bandgap from 2.38 to 2.31 eV (Fig. 8). The values were comparable to those obtained for conventional CBD films. Glancing angle XRD measurements were recorded [Fig. 6(*c*)] and the diffraction patterns compared with standards in the JCPDS data files. Similar to observations made for conventonal CBD films, the as-deposited films were composed of a mixture of cubic and hexagonal phases of CdS. Films were annealed in air for 30 min at 673 K, the process improved crystallinity and effected conversion to the hexagonal modification. The effect of air-annealing was further investigated by TEM. The as-deposited films on heated substrates appeared to be composed of dense, asymmetric grains of diameter in the range 80–120 nm, no compelling evidence for grain growth with annealing was obtained (Fig. 9). We have reported similar observations for conventional CBD of CdS from ethylenediamine-buffered solutions.[14] An approximate elemental ratio of Cd:S 1:1 was determined from EDAX measurements. No significant differences in XPS data were recorded for films from heated substrates in comparison with those obtained by conventional CBD. Photoelectron binding energies of 405.9 eV (Cd 3d$_{5/2}$), 411.5 eV (Cd 3d$_{5/2}$) and 162.5 eV (S 2p) were recorded for the major XPS peaks of our CBD CdS films. An important conclusion was the impurities in the as-deposited films did not increase for films grown from replenished baths (Fig. 10). Minor concentrations of impurities assigned to carbon (C 1s 284.8 eV), nitrogen (N 1s 396.0 eV) and oxygen O 1s 532.1 eV) were present in all CBD films. These contaminants have been identified in CdS CBD films by other workers.[15] Annealing of films in air reduced the nitrogenous contaminant to a concentration below the detection limit of the instrument.

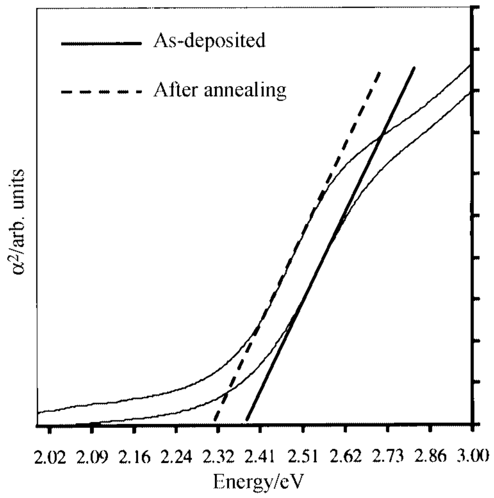


Fig. 8 The effect of annealing on the bandgap of CdS CBD films grown from a continuous flow reactor on heated TO-glass substrates.

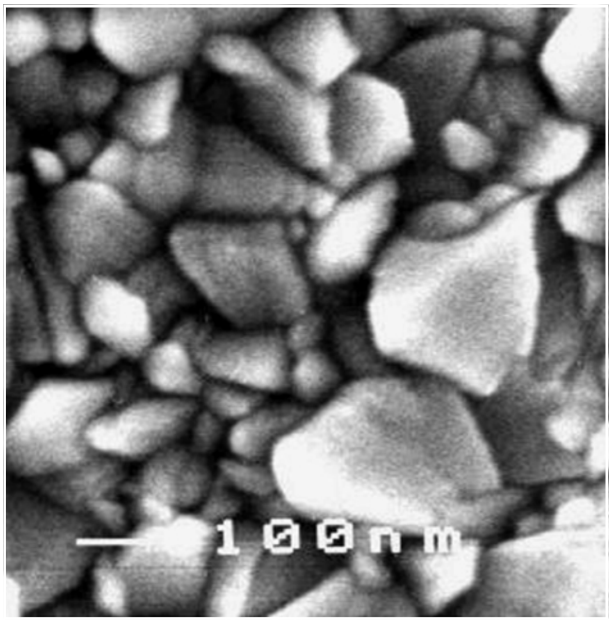


Fig. 9 Transmission electron micrograph of an as-deposited CdS CBD film obtained from a high-efficiency reactor. Films grown on heated TO-glass substrates from low cadmium-low ethylenediamine solutions (Bath B). Deposition time of 45 min. Annealing of films in air (673 K for 30 min) does not result in significant grain growth.

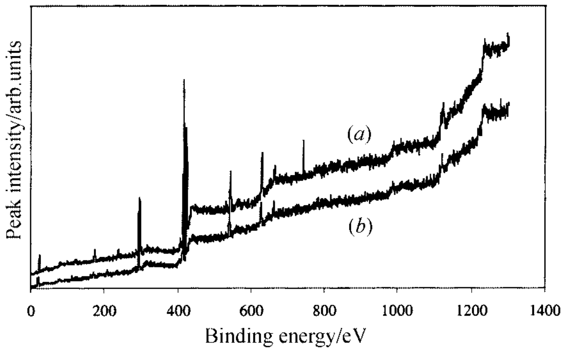


Fig. 10 Wide scan XPS of CdS CBD films acquired from a high efficiency reactor. Films grown from (*b*) replenished baths after 6 h possess very similar photoelectron spectra to those obtained from fresh baths (*a*) (45 min).

Conclusions

Chemical modelling and speciation studies have enabled us to develop a novel high-efficiency CdS CBD process that utilises low cadmium concentrations and provides a viable alternative to the use of volatile solutions of ammonia. Films have been deposited by conventional CBD from heated solutions and also in a novel reactor with a heated substrate. The films obtained from the new reactor have been characterised as good quality CdS by spectroscopic methods (UV–VIS and XPS), microscopy (SEM and TEM) and powder XRD. No significant differences in the chemical or physical nature of films have been observed for films deposited from fresh and replenished baths. This suggests that continuous recycling may be possible. Our initial successful and reproducible attempts to lessen the environmental impact of CBD appear to be successful. These efforts have involved the design of deposition solutions by modelling and the development of a new geometry for deposition. The approach may offer a viable route towards the high efficiency production of CdS layers for solar cell applications. Further investigations to determine the long-term stability of these new systems are in progress.

Acknowledgements

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Paper a909257i

Catalytic reduction in subcritical water

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Summary

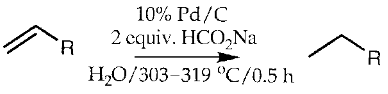
Palladium on carbon in subcritical water employing sodium formate as a hydrogen source provides a green procedure for the catalytic reduction or hydrogenation of olefins and acetylenes.

Introduction

Recently, great attention has been drawn to the use of supercritical fluids for organic syntheses. Supercritical carbon dioxide has played an important role as a reaction medium and/or reactant. In the past supercritical water has been deemed destructive,[1] yet supercritical water has been proven to be a synthetically useful tool.[2] Under sub-[3] to super-critical conditions, organic materials have greatly enhanced solubility in water[4] and the hydrogen boding network of water is minimized.[5] The weakening of the hydrogen bonding is thought to induce the evolution of protons, further increasing its acidity.[6] Palladium on carbon is a long standing, dependable heterogeneous catalyst for the saturation of olefins and acetylenes.[7] More recently, palladium on carbon and formate has further expanded the utility of this catalyst.[8] We present a novel green use of Pd/C with formate to saturate olefins and acetylenes.

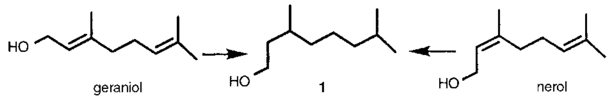
Results and discussion

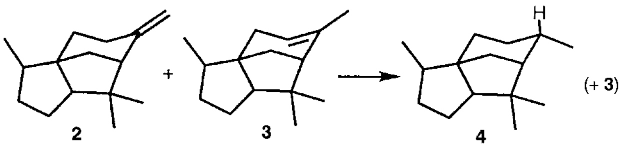
Generally, unsaturated organic materials with 2–3 equivalents of sodium formate, a catalytic amount of 10% Pd/C in a 316 stainless steel pressure reactor[9] with water at approximately 300 °C and 1200–1300 psi[10] affords the saturated hydrocarbon in good yield.[11,12] The conditions we have employed are below the critical point (374 °C and 218 atm), but appear to be within range of good organic miscibility in water. However pre- and post-reaction the hydrocarbons are immiscible, thus facilitating product recovery and purification. Olefins or partial reduction products have been detected when acetylenes are treated with Pd/C and formate using shorter reaction times. In the absence of either formate or Pd/C, reduction fails.



Formate appears to serve a dual role in the reduction process as a hydrogen source and as a weak base or buffer. In general, under acid to neutral hydrothermal conditions alcohols are prone to dehydration. However, geraniol and nerol have been reduced to the primary alcohol **1** with sodium formate with little detectable hydrocarbon by-product (dehydration-reduction).

In further investigations, the aspect of stereoselectivity was addressed in the case of the *exo* and *endo* olefins of α-cedrene and β-cedrene. The mixture of cedrenes was treated under hydrothermal conditions in the presence of Pd/C and sodium formate. The recovered materials (96%) proved to be hyrogenation products **4** (cedrane : isocedrane = 1 : 24)[13] contaminated with 3% α-cedrene **3**. Hydrothermal conditions appear to be more selective for isocedrane than using standard hydrogenation conditions.[14] Incomplete reduction may be due to a slower rate of reduction of the more sterically hindered trisubstituted double bond in **3**.[15] Under these conditions it is also possible that the exocyclic olefin migrates into the ring before reduction occurs, but it has been our experience that base (NaO_2CH, $NaHCO_3$) usually minimizes double bond migration under hydrothermal conditions.





Sodium formate under hydrothermal conditions can be an effective carbonyl reducing agent.[16] Therefore, keto olefin **5** was treated with limited amounts of sodium formate in the presence of Pd/C in order to discover the olefin to carbonyl selectivity. Depending on conditions, 50 to almost 70% of the product was 2-propylcyclohexenone (Table 1, entries 8–10). Lower temperatures clearly disfavor ketone reduction; this is a trend noticed in other carbonyl–sodium formate studies.[16] Similarly the production of phenol **9**, that was probably formed from olefin migration and *dehydrogenation*, decreased with temperature (14 to 7%). The amounts of alcohols **7** and **8** also decreased with temperature, but the *cis* to *trans* ratio seemed constant.

Green Context

When a solvent is needed water will often be the greenest choice. It is renewable, in good supply, non-toxic and environmentally compatible (though it can be difficult to clean up water to the extent that it can be safely returned to the environment). A major drawback with using water in organic sytems is the poor solubility of many organic compounds. In, *e.g.*, reactions of simple olefins, immiscibility under normal conditions makes aqueous conditions inappropriate. However, at high temperatures and pressures, water loses much of the hydrogen bonding structure that effectively inhibits organic compound solubility, and even non-polar organics are soluble. This dramatic change in behaviour can occur below the critical point beyond which water can be destructive towards organic compounds. Here we see a demonstration of this effect at work. The solubility of olefins and superhot water enables their very effective reduction of acetylenes using palladium catalysis. Furthermore, the complete separation of the organic and aqueous phases on cooling the system post-reaction facilitates product recovery and purification. ***JHC***

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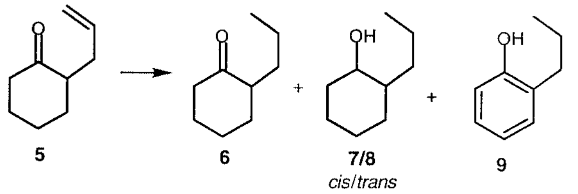
Table 1 Reductions using 10% Pd/C and sodium formate

Entry	Substrate	Product(s)	Amount of formate equiv.	T/°C	Yield[f] (%)
1	1-Decene	Decane	2	303–319	74
2	1-Decyne	Decane	3	304–315	78
3	5-Decyne[12]	Decane	3	302–308	89
4	2-Decanone	Decane	3	305–320	30
5	Geraniol	**1**	3	325–331	93
6	Nerol	**1**	3	328–333	75
7	Cedrene[a]	**3**,**4**	3	327–342	96[b]
8	2-Allylcyclohexanone	**6**–**9**	2	307–326	95[c]
9	2-Allylcyclohexanone	**6**–**9**	2	250–301	80[d]
10	2-Allylcyclohexanone	**6**–**9**	2	201–223	82[e]

[a] Mixture of α-cedrene : β-cedrene = 4.2 : 1; [b] **3** : **4** = 1 : 32; [c] 53% of **6**; [d] 59% of **6**; [e] 69% of **6**; [f] Yields are calculated from NMR and GC analysis.



Conclusions

These simple, green, reaction conditions[17] provide an alternative to typical catalytic hydrogenation of olefins and acetylenes. Studies are continuing with other catalysts, hydride sources and conditions. With these variables it may be possible to generate selectivities that will afford a range of products from the same polyfunctional starting material.

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12 Samples of 50 mg to 2 g of alkene or alkyne have been hydrogenated. The following represents a typical reaction affording the data of Table 1: Hydrogenation of 5-decyne (0.371 g) to decane (89%) uses sodium formate (0.476 g) and 10% Pd/C (0.052 g) with 3.6 ml of water in a 10 ml pressure reactor. The temperature was brought to and maintained at *ca.* 308 °C for 0.5 h. The organics were separated from the salted water layer and analyzed by GC.

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17 See http://www.epa.gov/opptintr/greenchemistry/whatis.htm for green chemistry concepts and goals.

Paper b000231n

Starch-derived polyols for polymer technologies: preparation by hydrogenolysis on metal catalysts

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Summary

Aqueous solutions of sorbitol derived from biosustainable resources are converted by catalytic hydrogenolysis to a mixture of C_4–C_6 polyols for the synthesis of alkyds† employed in paint manufacture. Copper catalysts were selected because of their larger activity in the dehydroxylation reaction than in C–C bond breakage. Reactions at 180 °C under H_2-pressure in the presence of CuO–ZnO catalyst gave a 73% yield of C_{4+} polyols, and more specifically, 63% of deoxyhexitols. The mixture of polyols was effectively employed as a substitute for hydrocarbon-derived polyols in the synthesis of alkyd polymers.

Introduction

This study, performed in the framework of the EC programme FAIR,[1] was aimed at converting starch, derived from biosustainable resources, into mixtures of polyols that could be used to manufacture polyesters, alkyd resins and polyurethanes employed in paints, powder coatings and construction materials. Mixtures of polyols can be used for these applications, but small diols (ethylene and propylene glycols) are not suitable for paints because of the poor drying properties of the final products. In addition, hexitols (*e.g.* sorbitol and mannitol) that are easily obtained by hydrogenating starch hydrolysates or inverted sucrose give coloured products when used in large amounts in the polyol blend. Deoxyhexitols consisting of C_6 diols, triols and tetrols, obtained by partial dehydroxylation of hexitols would be well adapted for the targeted applications. So far, these molecules have not been used for polymer manufacture because they are not available commercially at a reasonable price.

Starch can be hydrolysed by well known acidic or enzymatic processes into glucose, which is easily converted to sorbitol by catalytic hydrogenation.[2] Therefore, sorbitol was used as the starting feedstock for the hydrogenolysis studies on metal catalysts. Comparatively few investigations on catalytic hydrogenolysis of carbohydrates were performed,[3–21] and most of them were designed to produce C_2–C_3 polyols, particularly glycerol, rather than higher molecular weight polyols. The best yields of C_{4+} products were reported in a BASF patent[19] claiming that aqueous solutions of sucrose can be converted in the presence multimetallic, mixed oxide catalysts to solutions containing 5–7 wt% of butane-1,2-diol and 3–10 wt% of hexane-1,2,5,6-tetrol.

Results and discussion

Preliminary experiments performed with ruthenium and nickel catalysts yielded mainly C_1–C_3 hydrogenolysis products with a high fraction of hydrocarbons. Thus, after hydrogenolysis of a 20 wt% sorbitol solution at 240 °C in the presence of Ru–C catalyst, the total organic carbon (TOC) in the solution was only 57% of the initial amount, which means that 43 wt% of the feedstock was converted into volatile hydrocarbons. Conducting the reaction at lower temperatures decreased the rate of sorbitol conversion without significantly improving the selectivity. In contrast platinum and palladium catalysts exhibited too weak hydrogenolysis properties and yielded mainly C_6 cyclic ethers by internal dehydrocyclisation reactions.

To improve the selectivity of sorbitol hydrogenolysis towards deoxyhexitols, the catalyst and reaction temperature were optimised to favour the breakage of C–OH bonds (dehydroxylation reactions) rather than C–C bond breakage. Copper-based catalysts, which have a low activity for hydrogenolysis of C–C bonds, were employed in subsequent experiments. Reactions were performed on a CuO–ZnO (33 : 65) catalyst primarily designed for alcohol synthesis from syngas. Reactions were conducted at 240, 220, 200 and 180 °C. Table 1 gives the products detected in the solutions after the reactions.

The reaction data given in Table 2 show that at 240 °C the rate of sorbitol conversion was high, but the selectivity to deoxyhexitols was poor. Volatile hydrocarbons were formed because the TOC in the final solution was only 85% of the initial amount of carbon in solution. Upon decreasing the reaction temperature, the selectivity to deoxyhexitol increased; the best yields were obtained at 200 and 180 °C where the selectivity attained 61.6 and 63.1%, respectively (Table 2). The distribution of products obtained after reaction at 180 °C is given in Fig. 1. The TOC value

Green Context

We are now in the century when it is widely accepted that hydrocarbon resources will become in very short supply. It is vital that we develop chemical processes and chemical products on alternative feedstocks and especially renewable crops. Starch is the second largest biomass on the earth and is a potentially rich source of many useful chemical intermediates especially highly oxygenated compounds. In this paper a novel route to polyols from sorbitol is described. Apart from the obvious green chemistry significance of the use of a renewable starting material, the process itself which is carried out in water has green credentials. ***JHC***

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† Alkyds are polyesters, formed by repeated esterification reactions (polycondensation) between polyhydric alcohols and di- or poly-basic carboxylic acids or their anhydrides, with fatty acid residues attached along their backbone.

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Table 1 Polyols obtained by hydrogenolysis of sorbitol solutions on metal catalysts (see also Fig. 1)

Entry	Products	Composition
1	Cyclic ethers	Isosorbide; 2,5-anhydromannitol; 2,5-anhydroiditol; 1,4-anhydrosorbitol
2	C_2	Ethylene glycol
3	C_3	Propane-1,2-diol
4	C_3	Glycerol
5	Deoxytetritols	Butane-1,2-diol; butane-1,3-diol; butane-1,4-diol; butane-2,3-diol; butane-1,2,3-triol
6	Tetritols	Threitol, erythritol
7	Deoxypentitols	Pentane-2,4-diol; pentane-1,2-diol; pentane-1,4-diol
8	Pentitols	Xylitol, arabitol, ribitol
9	Deoxyhexitols	Hexane-1,2-diol; hexane-1,6-diol; hexane-1,2,3-triol; hexane-1,2,6-triol; hexane-1,2,4,6-tetrol; unassigned polyol[a]
10	Hexitols	Unconverted sorbitol, mannitol, iditol

[a] GC peaks with retention times close to those of deoxyhexitols

Table 2 Reaction data on CuO–ZnO catalysts

T/°C	Sorbitol (wt%)	Conversion(%)	Mass balance(%)	TOC balance(%)	Activity/g_{sorbit} h^{-1} g^{-1}	Selectivity, S^a (%)
240	22.5	98.4	71	85	6.3	35.4
220	22.1	93.5	76	95	2.4	53.0
200	21.9	96.8	83	97	0.5	61.6
180	21.3	92.0	81	100	0.1	63.1

[a] *S* = [deoxyhexitol weight%]/Σ [products weight%]. All reactions were conducted on CuO–ZnO (33:65) catalyst under 130 bar hydrogen pressure.

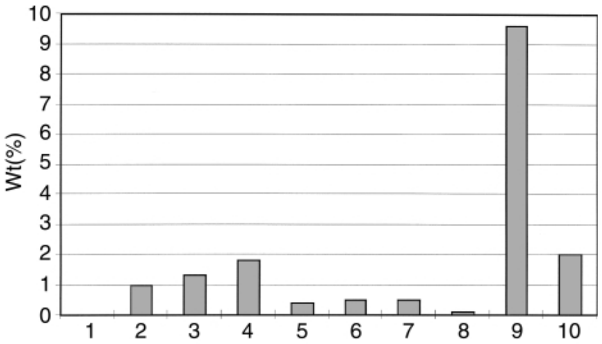

Fig. 1 Distribution of polyols obtained by hydrogenolysis of 21.3 wt% sorbitol solution (see Table 1 for polyol description).

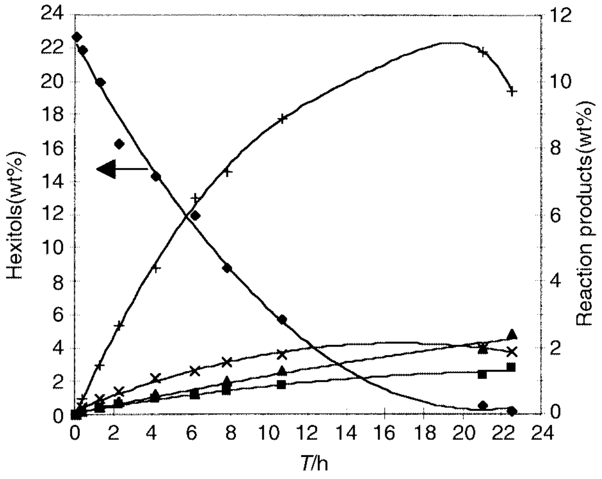

Fig. 2 Distribution of ethylene glycol, propane-1,2-diol, glycerol and deoxyhexitols as a function of time for the hydrogenolysis reaction at 200 °C. ◆ = sorbitol; ■ = ethylene glycol; ▲ = propane-1,2-diol; X = glycerol; + = deoxyhexitols.

was close to 100%, indicating that there was no loss of carbon-containing molecules. The mass balance obtained by comparing the sum of the weights of all the compounds in the final solution with the initial sorbitol amount was 83 and 81% after reaction at 200 and 180 °C, respectively (Table 2). The deficit in the mass balance (*ca.* 20%) can be attributed to dehydroxylation reactions leading to the loss of two or more oxygen atoms per molecule or sorbitol.

Measurement by ICP-AES of the metal concentration indicated that there was no leaching of copper, within the accuracy limit of 0.1 ppm, whatever the temperature of reaction. The concentration of Zn^{2+} ions in the solution after reaction at 180 °C was 30 ppm. This moderate leaching was further decreased to 13 ppm by conducting the reaction at basic pH.

Fig. 2 gives the distribution of C_2, C_3 and C_6 products as a function of time for the reaction conducted at 200 °C. The conversion of sorbitol was completed after 22 h and the specific reaction rate, calculated from the initial slope of the conversion curve, was 0.5 $g_{sorbitol}$ h^{-1} g^{-1}. All the reaction products appeared at the beginning of the reaction (Fig. 2), which means that they were formed directly by sorbitol hydrogenolysis. Nevertheless, the amount of deoxyhexitols and glycerol decreased at high conversion, which indicates that these molecules underwent further hydrogenolysis reactions.

In an attempt to decrease the amount of C_2 and C_3 diols in the final solution, the reaction medium obtained after reaction at

180 °C was filtered, weighed, heated at 180 °C for 3 h under reduced pressure, and then restarted to the weight by adding water. The amount of ethylene glycol and propanediol in the mixture decreased by 20 and 35%, respectively, whereas the concentration of C_{3+} products remained constant. This simple experiment indicates that C_2 and C_3 diols can be recovered by distillation and removed from the reaction mixture if required by the application, *e.g.* for paint manufacture.

Experimental

Sorbitol from ACROS ORGANICS (D-sorbit, P.A., purity > 99%) in powder form was dissolved in permuted water to obtain a 21 wt% solution (concentration: 1.3 mol l^{-1}, total organic carbon: 91 g_C l^{-1}). The reactions were conducted in the presence of CuO–ZnO (33 : 65, powder) (C61-1, lot RAO 4/98) obtained from United Catalysts, Inc. Reactions were conducted in a 300 ml autoclave built in Inox 316L, which was equipped with a motor driven turbine (1600 rpm), pressure and temperature control devices, and the necessary inlets (argon and hydrogen lines, dropping funnel for liquid) and outlets (gas exhaust, safety head, liquid sampling tube). Graphitized Teflon seals allowed sustained temperatures up to 260 °C.

The standard procedure for sorbitol hydrogenolysis involved the following steps to avoid caramelizing the carbohydrate. The reactor was loaded with 60 ml of water and 2–8 g of catalyst. The reactor was purged with argon, pressurized under 40 bar of hydrogen and heated to the reaction temperature under continuous stirring. Simultaneously, 23 g of sorbitol and 25 g of water (total volume 40 ml) were introduced by dropping funnel and the mixture heated to 100 °C. As the temperatures in the reactor and dropping funnel were stabilized, the sorbitol solution was dropped under H_2-pressure into the reactor. The hydrogenation of the 100 ml, 21 wt% sorbitol solution thus obtained started immediately and the slurry was maintained at the reaction temperature (180–240 °C) under a constant 130 bar H_2-pressure.

Samples of the reaction medium were taken at various time intervals to measure the product distribution. Polyols were analyzed by GC with a capillary/column (J&W DB 5, 30 m × 0.32 mm) after derivation by silylation with hexamethyldisilazane (HMDS) and trifluoroacetic acid in dimethylformamide (DMF). The C_6 polyols were also analyzed by HPLC (HPX-87C column at 85 °C, eluent: water, RID detector). GC peaks were attributed to specific polyols by comparison with reference compounds. A few weak peaks were not identified because of the lack of reference compounds (because their retention times were close to those of deoxyhexitols, their concentrations were measured using the same response coefficient). For the best description of the results, the polyols were grouped as shown in Table 1. The concentrations of the polyols in solution were given in weight percent (wt%). The total organic carbon (TOC) in solution, expressed in g l^{-1}, was measured with a Shimatsu 5050A TOC-meter. The concentration of copper and zinc in the solution after reaction was measured by ICP-AES.

Conclusions

This preliminary investigation has shown that treatment of aqueous sorbitol solutions on CuO–ZnO catalyst under hydrogen pressure at 180 °C gives a high yield of C_{4+} polyols (73%), particularly deoxyhexitols (63.1%). The mixture of polyols obtained was employed to prepare alkyd polymers, which were used to manufacture gloss paint. The final product showed satisfactory specifications, except for a low viscosity and long drying time; these specifications could be improved by distillation of ethylene and propylene glycol from the mixture. This investigation provides an interesting example of clean catalytic conversion of a cheap and abundant biosustainable resource into oxygenates, which could be used as a substitute for alcohols derived from fossil feedstocks. More basic research is needed in the future to establish the complex mechanism of the hydrogenolysis reactions, which could help to design more selective and active catalysts for preparing polyols for this, or other applications.

Acknowledgements

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