Putting Things in Perspective

The 2000 Royal Society of Chemistry Annual Congress took place from 17–20 April 2000 in Manchester, UK, at UMIST (University of Manchester Institute of Science & Technology). One of the major themes of the meeting was entitled ‘Towards Sustainability’, and included a symposium with a wide range of presentations on many aspects of the subject. This was a timely reminder to the delegates that the subject of sustainability, and green chemistry, must be considered and evaluated in context. Talks from several experts in the field of sustainable development and life cycle analysis made that point very clearly. While their talks ranged from the strategic/political to technical to tools for evaluation, it was clear that defining sustainability and measuring it is by no means a straightforward task. It is vital, however, to continue to have this perspective inherent in our work.

Within this framework, it is important that we continue to strive to work towards resource-efficient and safe processes and products, and that we try to utilise renewable resources. The message from the symposium made it plain that this goal will best be achieved by multidisciplinary approaches.

Applying this concept to green chemistry, it becomes clear that we must consider not only the reaction (chemists often concentrate only on parameters such as selectivity, rate of conversion, activity of catalysts *etc*.), but green approaches should also include feasible and efficient methods for the isolation of product and recovery of auxiliaries such as solvent and catalyst. Only when all this has been achieved can the new method genuinely be considered green. The input of engineers is often vital in this regard, as the traditional stirred batch reactor can often be the root of many difficult problems. Articles which have already appeared in *Green Chemistry* have highlighted some of the possibilities available for carrying out reactions, but many others exist. My personal experience of working with engineers (both as an industrial chemist, and in academia) has been very positive, and has simplified many processes and solved many problems. It is certainly one instance where learning another language is very advantageous.

A further element of perspective was introduced in the Annual Congress through the session on ‘The History of Green Chemistry’. While it might be surprising that a subject as new as green chemistry could have a history worth discussing, the session managed to put many elements into perspective. The history of catalysis was presented, which indicated the enormous cost and energy savings made in *e.g.* the synthesis of ammonia over the course of a century. The changing nature and levels of pollution was also discussed by a series of speakers, making clear that things may not be perfect, but in some respects at least things have improved massively (*e.g.* air quality in London, where 5000 people died due to the smogs of the 1950s, leading to the Clean Air Act, which was an early and very successful example of legislative control of the use of one class of chemicals—fuels). This historical perspective was not only interesting from an academic point of view, but helped to put into context some of the emotive issues which hit the headlines. A recent example of this is the debate over chlorine and organochlorine chemicals, which has led to calls for a complete ban on the uses of the entire class of compounds. The next issue of *Green Chemistry* will contain a major, detailed overview of the entire area, which hopefully will help to put these claims into a proper and serious scientific context.

Duncan Macquarrie,
University of York, UK.

Lean, mean and green chemistry—can we have it all?

This article is based on a presentation given by Mike Lancaster, Manager of the Green Chemistry Network, to the British Association for Chemical Specialities (BACS) annual forum in March 2000

Can a modern speciality chemical business be successfully run on the principles of the triple bottom line? Are green chemistry and increased profitability happy bedfellows? These are questions many people are starting to ask. As a concept the triple bottom line is difficult to argue against. However, those of you who have had to sign on the bottom line for some new environmental technology equipment may have come to the conclusion that protecting the environment costs money. But many companies that have invested in clean process technologies have also seen the cost benefits.

Cost of environmental technology

Industry does not need to look on environmental protection as an additional burden imposed by Governments and society; it should look at it as an additional opportunity to develop more cost effective processes and products. With a little thought, and perhaps a culture change, chemical industry can be competitive *and* environmentally benign.

Fig. 1 shows UK chemical industry expenditure on environmental technology during 1997. It is divided into three—by far the largest is operating expenditure, some 65% of the total of over £1000 million. The rest is capital expenditure—some 26% on end-of-pipe technology with only 9% on what might be considered integrated process clean technology.

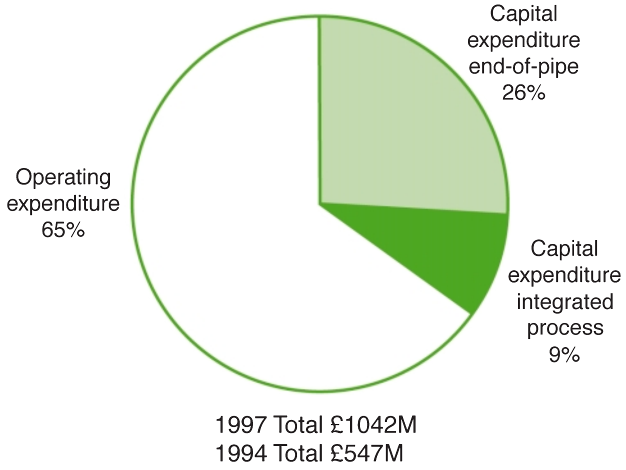


Fig. 1. Chemicals sector expenditure on environmental control (1997).

Mike Lancaster, Manager of the Green Chemistry Network.

The chemical industry accounts for 24% of the total spend but, for industry as a whole, the ratios are fairly similar, with more being spent on end-of-pipe than clean technologies. Spending on environmental technology almost doubled between 1994 and 1997. It is little wonder looking at these figures that industry believes that protecting the environment is adding to its uncompetitiveness, since the figure spent is over 5% of revenue generated by sales.

However, these figures should be seen as an opportunity, not a threat. Only £100 million is currently spent on what may be considered the most valuable area—integrated process clean technology. The real opportunity lies in increasing this expenditure by a factor of 2 or 3 and eliminating a significant part of end-of-pipe and operating costs.

One of the real issues behind these figures is that, when asked why the expenditure occurred, by far the top answer from industry was "To comply with legislation". The time has surely come for industry to be more proactive rather than reactive. Again, this is part of the culture change process of green chemistry. In an ever-busier industry it is too easy to wait until legislation is put in place and react by buying some end-of-pipe treatment kit, or paying increasing amounts for the safe disposal of waste. With a little thought and investment in process development significant savings on end-of-pipe equipment and associated operating costs could be made.

Wasted money

The root cause of this vast sum spent on environmental technology is waste, and Sheldon has pointed out[1] it is the fine, speciality and pharmaceutical sectors which have more of a problem with waste than the bulk chemicals industry. Looking closely at the cost of waste within the speciality chemicals sector is a little more difficult. For many smaller companies working with multi-purpose plants the true breakdown of manufacturing costs is still often unknown—overheads can be used to hide a multitude of sins! With the rapid development in IT and sophisticated process monitoring equipment the true production cost is slowly becoming evident. The most important information coming out of this analysis is that the cost of waste, (including effluent treatment, waste disposal, loss of raw materials *etc.*) often amounts to some

40% of the overall production costs (Fig. 2).

Armed with this information it is becoming much easier to justify work on cleaner process technologies. By eliminating waste, not only will the environmental impact be reduced, but the process economics are likely to improve. When margins get reduced through competition and production costs become a significant part of the product's selling price, it is important to know how the process costs can be cut. In recent years these efficiency gains have largely come at the expense of employment and improved technology; IT in particular has enabled this to happen. Many industries have now gone as far as they can down this route, so what next—look at the waste. If waste accounts for 40% of production costs and production costs are 70% of the product's selling price there is almost 30% of selling price available as a potential saving.

Case studies

Turning to a real example, over the last 6 years or so process development chemists at Zeneca realised that they could both improve the environmental friendliness of their processes and add profit to the bottom line. The drive to waste minimisation came in a very enlightened move from the top of the then ICI. After the demerger senior managers at Zeneca pursued the idea with even more vigour. When a study of the cost of waste was undertaken at the Huddersfield site, the results showed that 10 processes accounted for 90% of the waste to landfill, water and air. The associated waste cost of these processes averaged 44% of production costs. For each individual case the process development team had to justify waste minimisation expenditure on a cost–benefit basis and it was soon realised that the least expensive form of waste disposal is not to produce it in the first place.

Over a period of years progress was monitored and, as can be seen from Fig. 3, waste produced was reduced by about 25% and over 4 years and savings of over £12 million were achieved. These savings are real savings with all the development costs being taken out.

Another excellent example is optical brightener production at Hickson & Welch.[2] The company had been making stilbene-type optical brighteners for over 50 years and until recently the technology had hardly changed. Each of the seven steps involved had some environmental problems which were increasingly making the process uneconomic. The biggest problem with this process was the VOC emissions; it was estimated that some £300,000 would need to be spent in installation of new equipment to comply with future legislation.

It would have been easy to spend this money on end-of-pipe technology and carry on with the same proven process. In an enlightened move they decided to invest in R&D, some £250,000, and green the complete process. In general, existing equipment and proven technology was used and savings of £300,000 pa on chemical and effluent costs were achieved. The clear message from this example is that green chemistry need not be rocket science—the process modifications could have been done much earlier—the technology was available. The driving force for change was the threat of legislation, but this was seized as an opportunity to cut costs.

New technologies

Existing processes can be greened with existing technologies—it is the culture and philosophy that needs to change, since most green chemistry is evolutionary not revolutionary. However when developing a new process or a product it is always worth considering leading edge developments. Some of the leading green technologies that will become increasingly used in the manufacture of speciality chemicals during the next 10 years are:

- Process intensification
- Ionic liquids
- Catalysis
- Energy sources
- Supercritical fluids

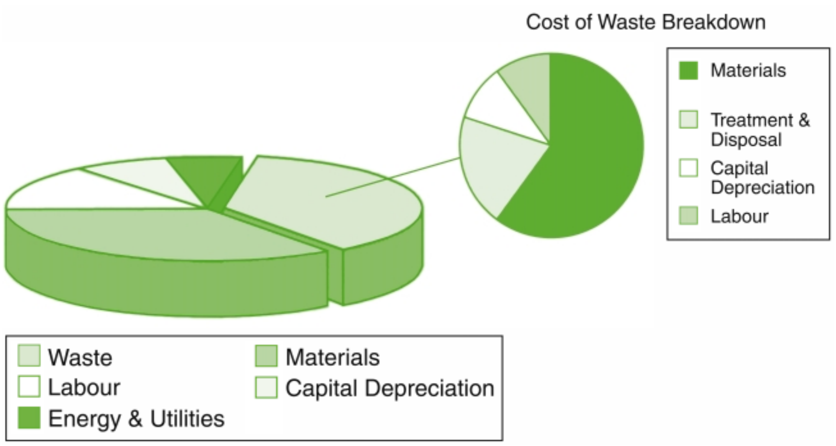


Fig. 2. Breakdown of typical speciality chemical manufacturing cost.

Catalysis has revolutionised the bulk chemicals industry over the last 25 years. Today there are around 130 chemical manufacturing processes, such as alkylation, isomerisation, amination and etherification using catalysts such as zeolites, ion exchange resins, clays and complex oxides. This technology has largely been developed to maintain competitiveness, improve product quality and improve process efficiency. For example, when the waste produced from the large-scale use of aluminium chloride in alkylation reactions started to make the process uneconomic, introduction of zeolites and other heterogeneous catalysts brought significant cost and environmental benefits. It is untrue to say that catalysts are not used in the speciality chemicals industry, but their use is not as widespread as it could be. Potential cost benefits result from faster processes, higher selectivities and lower energy use. The catalyst market is estimated at $10 billion or less than 1% of the products they help to produce. The market is growing at 5% pa and a lot of this growth is starting to be outside the bulk chemicals industries.

Supercritical fluid technology has been around for many years but, largely due to the relatively high pressures involved, remained a laboratory curiosity. Supercritical carbon dioxide is commercially used for extraction processes and the technology is now being looked at seriously for chemicals manufacture. The reasons for this are that improvements in engineering mean that the equipment is more affordable and when combined with modern catalyst technology the rates of some reactions are very fast. Hence for true low-volume specialities there is the potential for producing requirements from a small relatively low-cost plant. Companies such as Thomas Swan and Hoffman La Roche are now looking to commercialise the

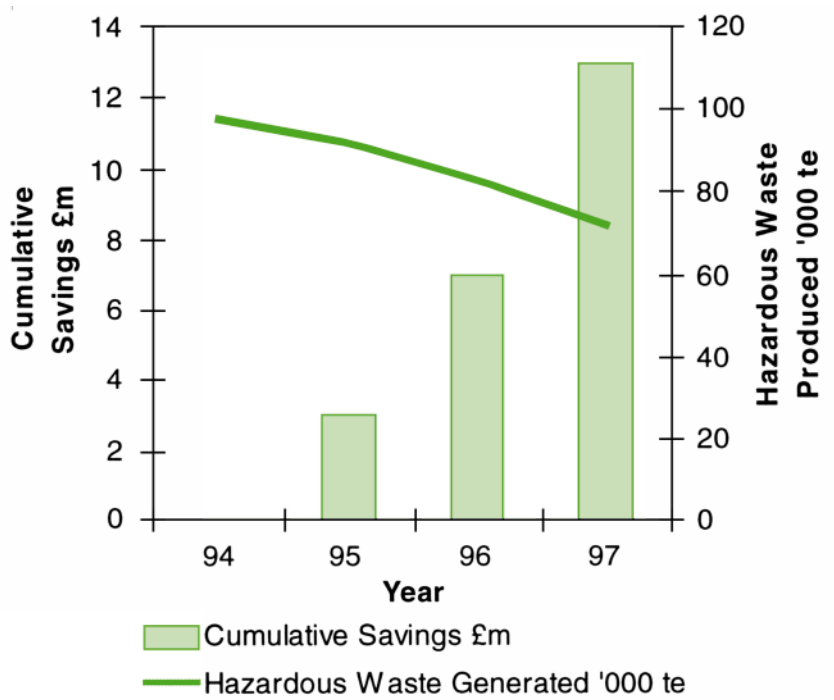


Fig. 3. Waste minimisation savings from process development at Zeneca.

technology for reactions like continuous hydrogenation and alkylation. It is not a universal answer, but is likely to provide true competitive advantage in a niche market.

Ionic liquids are another emerging technology which may avoid the use of organic solvents. Although these materials are strong acids and may not be particularly environmentally friendly in their own right, they can be readily recycled due to their immiscibility with most organics. They are being studied particularly for reactions which require highly acidic conditions such as alkylation, where they act as both a solvent and a catalyst.

Process intensification is the one of the chemical engineering solutions to clean technology. The main benefits are often lower energy uses, lower capital costs and increased throughput from a smaller plant derived from different engineering conceptual designs. The next generation of plants will be smaller, cheaper and more environmentally friendly to run.

As the energy intensity of a process becomes more of an issue on cost and environmental grounds, we shall start to see processes being developed using microwave, ultrasonic, electrochemical and photochemical reactors. For some reactions these techniques will not only deliver energy efficiency but may also lead to higher selectivities and atom efficiencies.

Conclusions

Environmental concerns are here to stay. They can be viewed as a threat requiring ever-increasing expenditure on end-of-pipe technologies to meet ever-increasing legislation or they can be viewed as an opportunity to introduce cleaner processes, which are more efficient and cost-effective. The choice should be obvious but we need a culture change, starting with education. For example, a chemist who uses dichloromethane as a solvent throughout their Ph.D. is likely to want to continue using it in industry! Many of the benefits green chemistry has to offer can be achieved with existing technology applied in a different way, but we also need a steady input of new, more efficient and green technologies. These will enable new plants and processes to be built to meet all the requirements of the triple bottom line.

References

1 R. A. Sheldon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 31.
2 S. J. Cook, *Green Chem.*, 1999, **5**, G138.

NEWS

Green and Sustainable Chemistry Network, Japan

The Green and Sustainable Chemistry Network, Japan, was established in March 2000. This followed an agreement among the Japanese chemistry-related academia, industry and national institutions at the Green Chemistry workshop held in Tokyo on November 26–27, 1999. The Network will deal with chemical technologies which do not harm human and environmental health and are based on minimisation of energy and resources usage, through improvements in product and process design, including selection of feedstocks, formulations, applications and resource recycling. The whole life cycle of the chemical product should be taken into account for every step of production.

The members of the Network are:

- Association for the Progress of New Chemistry
- Chemical Evaluation and Research Institute
- Japan Association for International Chemical Information
- Japan Biochemistry Association
- Japan Chemical Industry Association
- Japan Chemical Innovation Institute
- National Institute of Materials and Chemical Research
- The Chemical Society of Japan
- The Society of Chemical Engineers, Japan
- The Society of Polymer Science, Japan

MITI, NEDO and IUPAC will act as observers.

The organisation of the Network will be as follows:

General assembly
Chairman (The President of the JCII)
Vice Chairmen (the Chairmen of the
Chemical Society of Japan, the
Society of Chemical Engineers, and
the Society of Polymer Science)
Steering committee
Secretariat (JCII)

Working groups: major R&D areas

- Evaluation methods
- Research promotion (subjects to be proposed to the Government, and awarding systems)
- Research support (information exchange, completion and dissemination, symposia and newsletter)
- Information systems (design, establishment, running, improvement, maintenance, information system)
- Education group (educational materials, supporting education)
- International cooperation

The Network Office will be located in the JCII office. It plans to hold its first symposium in the fall of 2000.

The JCII is the Japan Chemical Innovation Institute which is a not-for-profit organisation established in 1998. It consists of four divisions:

- Technological Strategy and Planning Division
- Research and Development Division
- High Polymer Test and Evaluation Centre
- Advanced Materials Laboratory

The objectives of the Technological Strategy and Planning Division are to promote innovative research and development in chemical science and technology for the sustainable development of society and to strengthen the international competitiveness of the Japanese chemical industry.

Foresight and green chemistry

Several of the UK Governments Foresight panels have a relevance to green chemistry (see www.foresight.gov.uk).

Chemicals Panel

This panel has identified green chemistry/clean technology as one of its areas of particular interest. The panel, chaired by the President of the UK Chemicals Industries Association, Dr Joe Baker, is currently engaged in trying to establish the environment in which the chemicals industry is likely to operate in the future, what it will need to do to meet the challenges of that future and what will happen if it does not take such action. The four areas it has identified as being of particular interest are:

- The future structure of the (UK) chemical industry
- Green chemistry/clean technology
- Feedstocks
- Water treatment

The panel is committed to discussing its work with the chemical community and others. Although extensive use will be made of the Foresight Knowledge Pool to communicate electronically, direct contributions are welcome.

The following organisations are currently running associate programmes of particular interest to the Chemicals Panel:

- The British Agrochemicals Association is developing a statement of the long-term research requirements of the crop protection industry, focusing on their relevance to sustainability.
- An associate programme in molecular biosciences is exploring the possibilities for: developing cross-disciplinary postgraduate training; centralising tools and methods for biomedical research on large populations; and developing the profile of bioremediation interests within Foresight.
- The Institution of Chemical Engineers is looking at sustainable development; new process requirements; influencing government; education and training; and the employment or equipping of members to cope with change.
- The Royal Society of Chemistry has set up specialist technical and industry sector groups to highlight the most exciting future developments in chemistry and its applications.
- The Specialist Organic Chemicals Sector Association is developing short-term survival and long-term growth recommendations for the organic chemicals' sector.

For further information about the work of the Chemicals Panel and how you can contribute, contact: John Baker at the Office of Science and Technology Bay 589, 1 Victoria Street, London SW1H 0ET, email: john.baker@osct.dti.gov.uk (tel: +(0)20 7215 6727).

Food Chain & Crops for Industry Panel

This panel has established a task force to look at "Unlocking the potential of industrial crops". This task force is looking to:-

- Identify significant market opportunities and threats, looking beyond normal commercial timescales and outside normal sectoral boundaries.
- Identify emerging capabilities of and demand for science, engineering and technology together with the expansion and further development of collaborative networks.
- Highlight areas of policy, regulation, education and training where government action would deliver widespread benefits
- Identify areas for action by the business, scientific, voluntary and public sectors to increase national wealth and quality of life.
- Promote engagement in Foresight by fostering the expansion and further development of collaborative networks.

Members of the task force are currently gathering information from interested parties with a view to producing a report for the main panel by September 2000. Contact with panel members can be made *via* the Foresight web site. In a recent meeting at the RSC, the task force presented some of their initial SWOT findings. Much of the ensuing discussion centred around the availability of oil during the next 50 years and whether R&D effort should be better targeted at producing bulk or speciality chemicals from crops. The RSC's Forward Look For Chemistry documents (http://www.rsc.org/lap/polacts/forwardlook.htm) have addressed many relevant issues *via* its divisions and sub-groups.

Olympics–Sydney ready to host green games

Sydney's Olympic environment watchdog has said that the city would stage the “greenest” Games in Olympic history.

“These will truly be the Green Games,” said Earth Council chairman Maurice Strong in delivering his last report on Sydney before the start of the Games in September.

“Sydney will be setting the environmental standard, the benchmark, for all other Olympics,” said Strong, the man behind the 1992 U.N. Earth Summit in Rio.

The Earth Council report praised the rehabilitation of a toxic waste dump in Sydney's western suburbs into a state-of-the-art, environmentally friendly Olympic site.

It said there had been consistent use of natural lighting and ventilation, with energy efficient features in Olympic facilities, saving approximately 10,000 tonnes of greenhouse gases per year. Innovative designs would see rainwater captured for re-use, with the main Olympic stadium providing 100% of its annual pitch irrigation from rainwater captured off its sloping roof. The report said the waste management plan, which will cater for Olympics venues, athletes, officials and an estimated 1.6 million visitors to Sydney, was ambitious.

Strong said the most disappointing aspect of preparations had been the use of ozone-depleting gases in refrigeration, rating efforts to avoid such gases seven out of 10. However the council said that it was not totally Sydney’s fault, as there was a limit to alternative materials in the marketplace.

“We have searched the world to find better systems and they have not been there and we have had to make some trade-offs,” said David Richmond, chief of the Olympic Co-ordination Authority, which built the Olympic infrastructure and commissioned the Earth Council reports.

BACS consider cleaner greener chemistry

There is growing interest from chemical companies in the UK in the potential benefits green chemistry has to offer. The British Association of Chemical Specialities (BACS) represents around 170 companies in the UK who either manufacture or market speciality chemicals. The theme of this year’s AGM, held at the Portman Hotel, London, was to "To Consider Cleaner Greener Chemistry."

Dr Tony Bastock from Contract Chemicals put forward the case for adopting greener processes based on experiences at Contract Chemicals. He identified some of the key drivers as, better economics, a more sustainable business, improved relationships with stakeholders and lower regulatory costs.

Regulatory and compliance costs amount to around £1m, or 2.5% of turnover. By adopting the principles of green chemistry and having multi-disciplinary process development teams which look at issues such as atom efficiency and solvent reduction the company are looking to minimise these costs. Examples of green technology developments the company has made include Envirocats as a replacement for Friedel–Crafts catalysts such as aluminium chloride, a non-phosphorus containing bromination catalyst and reverse osmosis equipment to ensure clean separation of water from a diol in one of their major processes.

Dr Keith Brunt from Microbial Systems International gave a talk on Safe Killers—The Greening of Biocides. Biocides are currently a high profile topic controlled by ever more stringent legislation. Conventional organic biocides are effective but have many drawbacks, including irritant and allergenic properties, and bioaccumulation.

Many attempts have been made to use natural biocides, of which there are many. However, there are also many problems with these including odour, cost and the requirement for high concentrations. With the exception of the use of peroxidase enzymes in cosmetic formulations they have not gained wide commercial acceptance. The newest forms of green biocides are also some of the oldest being based on silver metal. Formulations based on silver zeolites and silver/alumina composites have a good spectrum of activity, are environmentally benign, and are active at low levels.

Mike Lancaster from the Green Chemistry Network spoke on the subject of “Lean, Mean & Green—can we have it all?” (see page G65). The chemical industry in the UK is spending over £1 billion annually on environmental technology. A significant portion of this is on end-of-pipe technology. Case studies were presented which highlight the overall cost savings which can be made through adopting green processes, thus avoiding the need for sophisticated end-of-pipe technology.

Perspectives

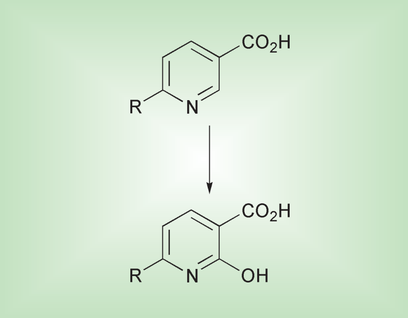
Biotransformations

Preparative biotransformations

An annual review of preparative biotransformations has just appeared, covering 1998 (S. M. Roberts, *J. Chem. Soc., Perkin Trans 1*, 2000, 611). Around 50% of the literature describes hydrolysis and esterification reactions, redox reactions around 25%, and C–C bond forming reactions much less at 4%. The remaining papers are on a range of subjects, with carbohydrate synthesis being one of the most popular areas.

Biohydroxylations

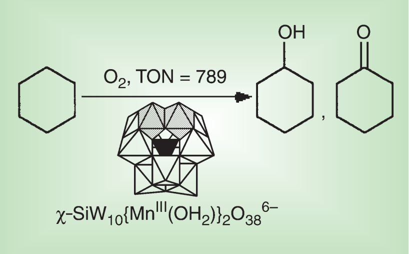
A team led by Andreas Tinschert has published details of work carried out at Lonza AG on the selective hydroxylation of pyridine carboxylic acids using bacteria (*Ralstonia*/*Burkholderia* sp. strain DSM 6920) cultured on 6-methylnicotinic acid, with the biotransformations taking place in phosphate buffer (*Appl. Microbiol. Biotechnol.*, 2000, **53**, 185). Several nicotinic acid derivatives were selectively transformed into the corresponding 2-hydroxy compounds in good yield (70–89%). The products of the biotransformations are important intermediates for a series of pharmaceuticals and other high-value products. Pyrazine carboxylic acids were also hydroxylated, albeit generally in lower yields (51–74%). (See also *Green Chem.*, 1999, **1**, 99)



Selective oxidations

Oxidation of hydrocarbons

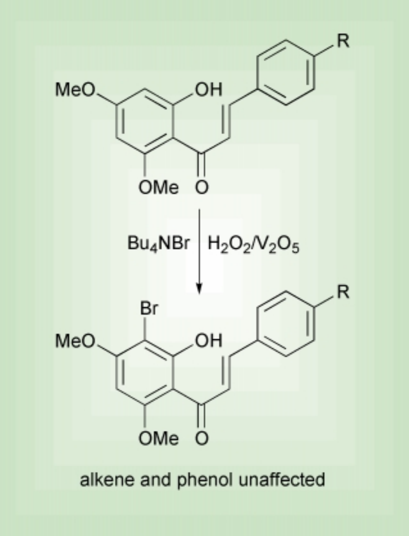
Noritaka Mizuno and co-workers from the University of Tokyo have developed a novel catalyst which has contributed to the search for a genuinely effective system for the selective oxygenation of hydrocarbons (*Chem Commun.*, 2000, 381). They have found that cyclohexane can be oxygenated with molecular oxygen at 80 °C to a mixture of cyclohexanol and cyclohexanone using a dimanganese-substituted silicotungstate, gamma-$SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$. This



particular catalyst is one of a series of similar systems, all of which carry out the reaction, but other members of the series have much lower turnover numbers (TON). The best catalyst of the series has a TON of 789, the next best only 295. When other catalyst types are compared, they have even lower TONs, usually < 180. Thus, this catalyst appears to offer a significant step forward in the search for a high performance oxidation system for alkanes.

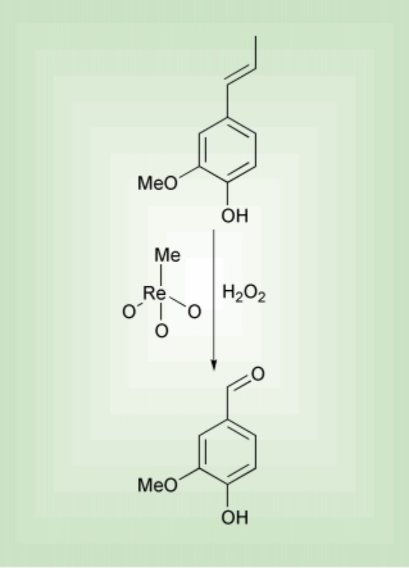
Oxidative bromination

The bromination of aromatics is an important route to many products. While some of these are intermediates which subsequently have the bromine replaced, others have the bromine atom intact in the final product. Even these usually suffer from the problem of only 50% utilisation of bromine, with the second Br being lost as HBr. Oxidative methods, which can oxidise this bromide *in situ*, are thus important targets for the clean, atom efficient synthesis of bromoaromatics. Bhisma Patel and co-workers fcrom the Indian Institute of Technology in Guwahati have just developed such a protocol (*Org. Lett.*, 2000, **2**, 247). They use a combination of hydrogen peroxide as oxidant, and vanadium pentoxide as catalyst to achieve the oxidation of aromatics with quaternary ammonium bromides. The reaction, which proceeds *via* the tribromide, is high yielding and can occur using potassium bromide as a source of bromine. While the optimum conditions reported involve a significant excess of bromide, they authors state that these conditions were used on the basis of giving the highest rates, a few results were given which used a 1:1 stoichiometry with excellent results.



Oxidative synthesis of vanillin from renewable resources

The team led by Wolfgang Herrmann in Munich has published a very interesting application of methyl trioxorhenium catalysis. This transition metal species is known to be an efficient oxidation catalyst in hydrogen peroxide oxidations, and is here applied to the cleavage of isoeugenol and *trans*-ferulic acid, leading to a highly productive synthesis of vanillin (*J. Mol. Cat.*, 2000, **153**, 49).

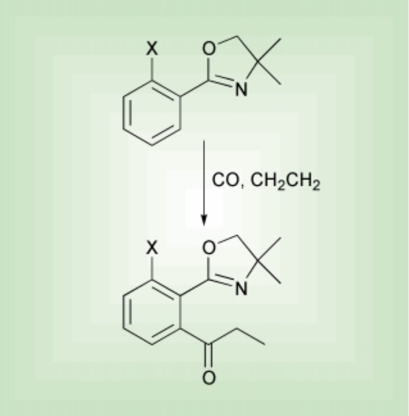


They also show that terminal olefins can be efficiently cleaved to the corresponding aldehydes using the combination of 1 mol% catalyst. This can also be achieved cleanly by *e.g.* ozone, followed by Pd/hydrogen, but this route suffers from the explosive nature of the formaldehyde oxide species formed as co-products. Turnover numbers are 1000–2000. For an overview and discussion of the use and necessity of sustainable resources see *Green Chem.*, 1999, **1**, 107.

Novel synthetic methods

Rh-catalysed carbonylations of aromatics

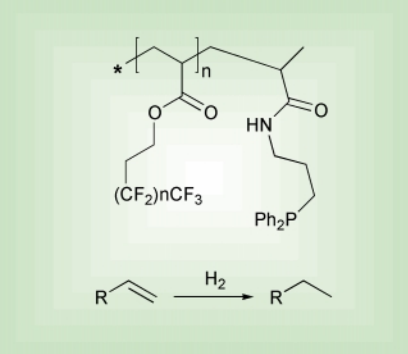
The acylation of aromatics has long been a difficult target for clean technology. The typical Friedel–Crafts conditions are very polluting and heterogeneous alternatives exist only for a very few examples. A group of researchers from Osaka University, led by Shinji Murai, has published a significant extension to earlier work on catalytic carbonylation, which offers an elegant partial solution to this problem (*J. Org. Chem.*, 2000, **65**, 1473). The group has developed a direct route to *ortho*-acyl aromatics, which relies on the coupling of an alkene, the aromatic and carbon monoxide. The catalyst used is $Ru_3(CO)_{12}$. Key to the success of the method is the development of an effective directing group, which is also unreactive under the carbonylation conditions, and which can subsequently be converted to a range of useful substituents. The oxazole ring serves all these purposes admirably, and is a major advance over earlier groups such as imines, which underwent side-reactions. Using this group, a range of acylated aromatics were produced in good to excellent yields. Very good functional group tolerance was observed, with many ring substituents remaining unchanged.



This methodology thus makes a contribution to solving the Friedel–Crafts problem, at least for *ortho* substitution.

Fluorous polymers

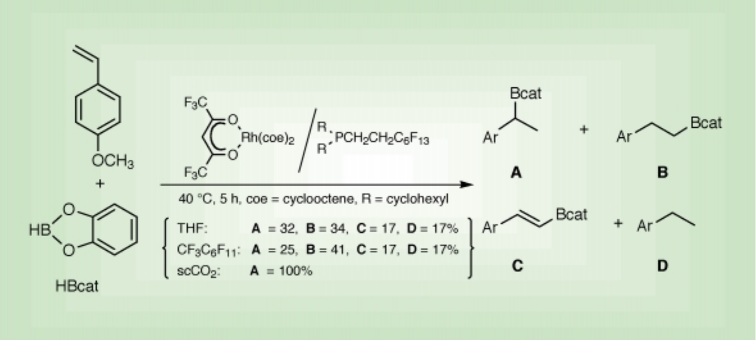
While the majority of fluorous phase soluble catalysts and reagents are prepared by the attachment of fluorous ponytails to a catalyst or reagent, Dave Bergbreiter and colleagues at Texas A&M University have shown that readily available fluoroacrylate polymers can be functionalised to incorporate catalytic centres, and that the resulting polymeric catalyst displays fluorous biphasic behaviour (*Org. Lett.*, 2000, **2**, 393). Thus, they functionalised fluorinated acrylates with phosphines, formed a



rhodium hydrogenation catalyst, and carried out hydrogenations with it. The reaction is carried out in a single mixed fluorous/hydrocarbon phase, which then separates after reaction to regenerate the fluorous phase, containing the catalyst, and the hydrocarbon phase, containing the product. The catalyst solution can be reused easily, but must be handled under anaerobic conditions to avoid oxidation of the phosphine. Catalyst activity is good.

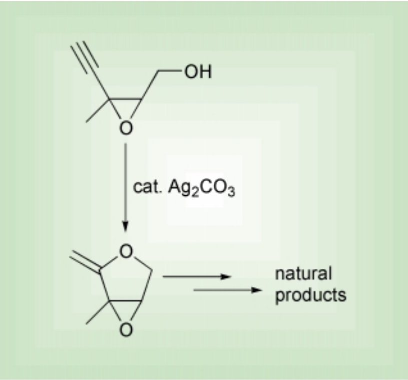
Hydroboration in supercritical fluids

Bill Tumas and co-workers at Los Alamos National Laboratories in New Mexico have reported that the regioselectivity of hydroboration is greatly influenced by solvent, and that the optimum selectivity can be achieved in supercritical carbon dioxide using a rhodium catalyst with fluorous ligands (*Chem. Commun.*, 2000, 347). They showed that the hydroboration of 4-vinyl anisole with catecholborane proceeded smoothly under mild conditions (40 °C and *ca*. 20 atm.) without reaction of the B–H bond with the solvent. Conversions were excellent (88–100%) and the selectivity to compound A was dependent on the phosphine ligand in the catalyst. The best ligand they found was dicyclohexyl perfluoroalkylphosphine, which gave both 100% conversion and 100% selectivity. A more remarkable result was the changes in regioselectivity in different solvents. In THF, the best selectivity seen was 84%, although with diphenyl perfluoroalkylphosphine; in perfluoromethylcyclohexane (a good solvent for fluorous ligand–metal complexes) 80%, again with diphenyl perfluoroalkylphosphine. In these cases conversion was lower. With the optimum ligand, conversions were 100%, 91% and 100% in THF, perfluoromethylcyclohexane and $scCO_2$ respectively, with selectivities being 32%, 25% and 100% respectively.



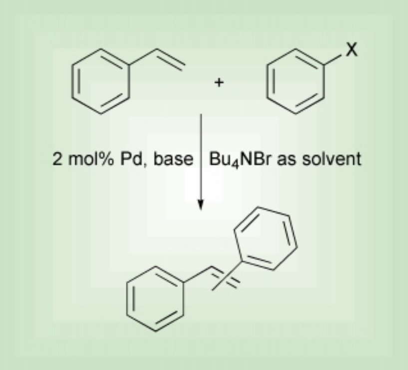
New catalytic route to 2-methylene oxolanes

The preparation of 2-methylene oxolanes forms a key part of the synthesis of a range of natural products, some of which have interesting biological activity. However, most routes have not been particularly attractive from an environmental point of view. A new approach has been published by Patrick Pale and Josselin Chuche of the CNRS in Strasbourg (*Eur. J. Org. Chem*., 2000, 1019). They have developed a method which uses basic silver salts such as silver carbonate to catalyse the cyclisation of hydroxy alkynes. Excellent yields of product were obtained in a range of solvents with 10 mol% of silver carbonate, which appears not to be soluble in the reaction medium, although no mention was made of recovery and reuse. Nonetheless, the method represents a significant improvement over existing procedures which often utilise stoichiometric quantities of salts, including mercury.



Novel ionic liquids route for the Heck reaction

The Heck reaction represents a very versatile method for C–C bond formation. Separation of the components (product, catalyst, solvent and base) after the reaction can often make the process less efficient, especially since dipolar aprotics are frequently the best solvents. Wolfgang Hermann and Volker Böhm have now found an alternative reaction medium which allows these difficulties to be circumvented (*Eur. J. Chem.*, 2000, **6**, 1017) They have found that ionic liquids are well suited to the Heck reaction. They found that the commonly used imidazolium salts were unsuitable, but they found that simple tetrabutyl ammonium bromide was a very useful solvent above its melting point. In this system they showed that aryl iodides, bromides and even chlorides and anhydrides are active, with the phosphapalladacycle shown above giving turnover numbers up to 1,000,000, although several hundred cycles was a more typical value. In many cases the product can be distilled from the system directly, leaving the solvent/catalyst mixture ready for a second charge of reactants and base. This process could be continued up to 12 times, with isolated yields of product of >90%.



Amidocarbonylation

Matthias Beller and Markus Eckert have published a useful and detailed review on amidocarbonylation reactions (*Angew. Chem., Int. Ed*., 2000, **39**, 1010). This family of reactions are atom-efficient routes to a range of amino acid derivatives *via* the three component coupling of aldehydes, amides and CO. The review discusses the major features of the reaction, which can be used to prepare, in a highly atom-efficient manner, amino acid derivatives such as *N*-acyl amino acids, hydantoins, succinimido acids, and oxazolines, under the influence of Co or Pd catalysts.

Solvent-free reactions

Koichi Tanaka of Ehime University and Fumio Toda from the Okayama University of Science have published a comprehensive review of solvent-free reactions (*Chem. Rev*., 2000, **100**, 1025). This documents a wide range of reactions which have been carried out in the solid state, including those in inclusion crystals and one or more solid reagents, where no solvent has been used to influence mixing. A wide range of reaction types can be successfully carried out using these techniques. Examples of both thermal and photochemical transformations are given.

Teaching the environmental sciences in the new millennium

Leo Salter, Chairman of the Environmental Chemistry Group, reports on a conference that discussed the need to ensure that environmental education addresses real issues of concern

The conference, held at Burlington House, London, on 25 March 2000, was organised jointly by the Environmental Chemistry Group, the Green Chemistry Network and the Education Department of the Royal Society of Chemistry.

Opening session

John Westaway (QCA) (“*Education for Sustainable Development: a whole school perspective*”) talked about the way in which requirements and opportunities for Environmental Education (EE) have been replaced by those requiring Education for Sustainable Development (ESD) and he elucidated the consequences of this for both curriculum delivery and the management of educational institutions. Opportunities for promoting ESD are identified in the national curriculum subject curriculum booklets for Geography, Science, D&T, History, Art & Design, ICT, PE and Citizenship and it is clearly expected to become an important part of the curriculum from September 2000. What is not so clear is the manner in which the messages of government and the Panel for Sustainable Development Education will be taken up. Indeed, there seems to be a lack of real understanding about what “sustainable development” actually means! In a study performed a few years go only 16% of school heads saw EE as essential and only 7% of schools had a single comprehensive EE policy document. The reality of inclusion of EE/ESD into school curricula and planning seems to be resistant to government exhortations.

Colin Osborne (Royal Society of Chemistry) followed this opening presentation with a paper entitled, “*The Relevance of Environmental Chemistry to the Science Curriculum*” which began by pointing out that, although England, Wales and Northern Ireland have broadly similar curricula, Scotland has a different system in which science for the 5–14 age group is taught under the heading of “Environmental Studies”. Dr Osborne then directed attention to the detail of the National Curriculum (NC) in which sustainability issues are ubiquitous. The curriculum describes a need to raise students’ awareness that decision-making based on sound science is an integral part of the political agenda and he gave several examples of the way in which data and other facts could be used to offer learning and teaching contexts for delivery of these aspects of the NC. Global warming, ozone layer depletion and energy use were seen as topics which could be used—especially when facts and data specifically designed for integration into classes are becoming available. Dr Osborne presented draft material being prepared by the RSC’s 1999-2000 Teacher Fellow (Dorothy Warren) at The University of York Science Education Group to be published in early 2001.

New research

The two lectures following this opening session (Dr Rob Mackenzie, Lancaster University, *“The Stratospheric Chemistry of Ozone Depletion and Climate Change”* and Dr Tony Stebbing, Plymouth Marine Laboratory, *“Why Ecotoxicology is Important”*) dealt with aspects of new research in environmental science.

Rob Mackenzie pointed out the advances that have been made in understanding the nature of stratospheric chemistry and the circulation of the atmosphere. Of major importance is a greater understanding of how cloud formation (PSCs—Polar Stratospheric Clouds) affect ozone depletion and how particles (from, for instance, volcanic eruptions) influence stratospheric chemistry. Several case studies are available for teachers and lecturers to develop these themes:

- www.es.lancs.ac.uk/casestud/index.htm
- www.atm.ch.cam.ac.uk

Tony Stebbing used studies of the North Sea to illustrate the point that although ecotoxicology was an interdisciplinary subject, its practitioners were groups of subject specialists (chemists, physiologists, computer modellers, physicists, biochemists, hydrodynamicists *etc*.). The concern for the studies of the environment is that teaching science subjects within disciplines creates artificial barriers to those who in later life will be addressing environmental problems that are inherently interdisciplinary. If subjects are taught largely within disciplines, at what stage does one introduce interdisciplinarity? He also emphasised that sustainable development is implicitly connected with economic development—the assimilative capacity of coastal seas globally is estimated to be 7% of the global GNP and hence there will be substantial costs if unsustainable use is continued. Globally, the monetary value of goods associated with the environment is $33 trillion pa (as compared to a global GNP of $18 trillion)—damage to the environment represents a continued undervaluing of the provision of "services" by the globe.

Greening under economic pressure

The last two lectures *("The Greening of Chemistry"* (Professor James Clark, University of York) and *"Green Developments in Industrial Processes"* (Dr Mike Lancaster, Green Chemistry Centre, University of York)) discussed the ways the chemical industry has changed production methods because of economic pressures derived from environmental costs. James Clark began by showing that the UK chemical sector had increased expenditure on environmental control from £547m in 1994 to £1042m in 1997 and that this expenditure was chiefly in response to effects on profitability due to waste disposal costs—waste disposal costs were becoming more expensive than raw materials. In speciality chemicals (including pharmaceuticals) waste costs are greater than 50% of manufacturing costs! The industries which have traditionally been seen as the major polluters (oil refining, bulk chemicals) are now those with the highest manufacturing efficiency and have minimal waste. Public perceptions concerning environmental impact caused by the chemical industry have not kept pace with the changes that industry has (and is) making and, in education, these same perceptions are creating a dramatic shortfall in the supply of chemical engineers in the UK and the US. In the UK there has been a 20% decline in university applications to read chemical engineering over the last 2 years and a 20% decline for chemistry over the last 4 years; chemistry applications in the current year are down by 7%. The Green Chemistry Network (www.rsc.org/greenchem) is designed to promote awareness of changes in the chemical industry and to facilitate the use and transfer of technologies within the industry itself.

Mike Lancaster followed James Clark's lecture with four case studies (phenol, sodium carbonate, detergents and nylon) of changes in chemical manufacturing processes which were economically efficient and environmentally effective. The detail of the presentation highlighted the way in which textbooks and examination syllabuses have failed to reflect the important changes in these classic processes—the increasing use of specialised zeolite technology and the potential for use of enzymes for nylon manufacture from glucose are but two examples of this.

Issues highlighted

The conference highlighted five issues:

- the expectations of universities from their first year students and the substance of A-level syllabuses are not seamless and more communication between the two sectors would be valuable.
- issues associated with sustainable development are not clearly defined by syllabi and consequently not examined significantly. This leads to their marginalisation by teachers and lecturers.
- because of time and cost, sustainable development initiatives are also marginalised by management.
- the decline of recruitment into specialised subject areas (like chemistry) may have consequences for environmental research and for the chemical industries. A significant factor in this decline is the poor perceptions of school leavers about the chemical industry. In order to counteract these (increasingly erroneous) perceptions efforts should be made to design A-level chemistry syllabuses with better use of environmental contexts to deliver the necessary material.
- A-level examination boards and textbooks associated with A-level delivery need to be more aware of changes at the forefront of their disciplines—especially those changes which are relevant to the environment.

Cobalt minimisation in willemite ($Co_xZn_{2-x}SiO_4$) ceramic pigments

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Industrially available blue ceramic pigments, with the exception of vanadium–zircon blue, (Zr,V)SiO_4, contain Co. To minimise the use of toxic and scarce cobalt, while also maintaining an intense blue colour, the performance as blue ceramic pigments of both Co^{2+}–Zn_2SiO_4 (willemite) and Zn^{2+}–Co_2SiO_4 (olivine) solid solutions was studied. The addition of cobalt in the willemite lattice was minimised. A wide range of compositions, $Co_xZn_{2-x}SiO_4$ (x = 2, 1.95, 1.5, 1, 0.9, 0.5, 0.05 and 0), were prepared and characterised by X-ray diffraction, lattice parameter measurements, UV–VIS–NIR spectroscopy, CIE-$L^*a^*b^*$ colour measurements and electronic microscopy (SEM/EDAX). The results show that an intense and more blue ceramic pigment is obtained based on the willemite lattice, with an optimised, low Co content, ranging from 25 mol% Co ($Co_{0.5}Zn_{1.5}SiO_4$) to 2.5 mol% Co ($Co_{0.05}Zn_{1.95}SiO_4$). This last composition (with only 2.5 mol% Co) exhibits the best blue hue once enamelled ($b^* = -39$), though it is also considerably lighter ($L^* = 57$).

Introduction

The industrial manufacture of blue ceramic pigments is important in the ceramic tile industry, not only for the production of blue-coloured ceramic glazes for floors or walls, but also in the bulk coloration of polished, unglazed, porcelainised stoneware (homogeneous or vitrified floor tiles, also known as *gres porcellanato*),[1,2] which is an industrial sector of growing interest. Apart from the less intense (though more stable and reproducible), turquoise blue pigment of vanadium zircon, (Zr,V)SiO_4, classified with the DCMA number[3] 14-42-2, the traditional and unavoidable source of blue in a ceramic pigment is the cobalt ion,[4] known from ancient times. This transition metal ion is an efficient colouring agent in glasses and ceramic glazes because of the mobility of its 3d electrons.

Two major cobalt-containing crystalline structures are commonly used: cobalt orthosilicate or olivine (Co_2SiO_4), DCMA 5-08-2, and the blue or blue–green cobalt spinels, such as cobalt aluminate blue ($CoAl_2O_4$), DCMA 13-26-2, cobalt stannate blue (Co_2SnO_4), DCMA 13-27-2, cobalt zinc aluminate blue [(Co,Zn)Al_2O_4], DCMA 13-28-2, cobalt chromite blue–green [Co(Al,Cr)$_2O_4$], DCMA 13-29-2, or even the greener cobalt chromite ($CoCr_2O_4$), DCMA 13-30-3, and cobalt titanate (Co_2TiO_4), DCMA 13-31-3. Cobalt aluminates are widely preferred to olivine, since a navy blue colour can be obtained with nearly half the cobalt content (33% in $CoAl_2O_4$ against 56% in Co_2SiO_4), resulting in a lower cost. The range of green shades that are available if desired[5] with the aluminates is also an important advantage.

Apart from the olivine and spinel structures, another intense blue colour can be obtained by doping the zinc silicate, (Co,Zn)$_2SiO_4$ with cobalt (DCMA number 7-10-2). The zinc silicate or willemite (Zn_2SiO_4, ASTM card 37-1485), is an orthosilicate of the phenacite group, where the Zn^{2+} ions are found occupying 3/8 of the tetrahedral sites, resulting in a hexagonal symmetry with lattice parameters $a = b = 13.9381$, and $c = 9.3100$ Å.[6] In this willemite blue pigment, as in cobalt aluminates, the cobalt ions occupy the tetrahedral positions substituting for the zinc ions, which is responsible for the more intense blue colour.

Nevertheless, it is becoming of the utmost importance to minimise or avoid as much as possible the use of cobalt in the formulations of ceramic pigments[7] to respond to both environmental and energetic (economic or sustainability) considerations. Regarding environmental aspects, cobalt and its related salts are widely considered to be toxic and/or hazardous substances in the legislation (for instance, cobalt appears in the list of the 94/904/EEC European Decision or in the 91/689/EEC European Directive). Though being an essential microelement in small quantities for all higher animals and for man, excessive exposure to cobalt-containing dusts in the workplace, or to excessive concentration in drinking waters, can cause damage to lungs, heart and skin. According to legal limitations for dust exposure, the technical guiding concentration in Germany (TRK) was set at 0.5 mg Co m^{-3} air, while the Threshold Limit Value (TLV) established in the USA by the ACGIH[8] was 0.05 mg m^{-3} for Co and 0.10 mg m^{-3} for its inorganic salts. Regarding cobalt toxicity in drinking waters, toxic effects have been observed in rats exposed to waters containing only 2 mg L^{-1}; in addition, cobalt is also considered an occupational carcinogen.

On the other hand, focusing on energetic, economic or sustainability considerations, the scarcity of Co in the earth

Green Context

The production of pigments and dyes is a major industry which utilises a wide range of chemistry. Many pigments contain transition metal ions and complexes as colour centres, and therefore their synthesis involves potentially toxic and hazardous waste streams. The study presented here shows results on the synthesis of one such pigment which is intended to produce the pigment, without compromising its activity (colour and permanence) while reducing the quantities of cobalt required in its' synthesis. The authors have shown that significant reductions are possible while maintaining the properties of the pigment.
DJM

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(19–29 ppm of the earth's crust, ranking the 32nd element in abundance) makes this element an inestimable resource. In addition, the restricted or localised geographical emplacements of the cobalt ores in the world (mainly in Zambia and Zaire) and its difficult metallurgy (0.1 MTon year^{-1}) make the use of cobalt raw materials expensive.

In order to minimise the use of cobalt in the preparation of blue ceramic pigments, the zinc aluminate spinel (or gahnite), $ZnAl_2O_4$, and the zinc orthosilicate or willemite (Zn_2SiO_4), prove to be the best host lattices (apart from the zircon lattice): both allow the development of intense blue colours with small amounts (non stoichiometric) of cobalt as a solid substitution for zinc ions. Zinc is considerably more abundant (76 ppm of the earth's crust) than cobalt; in addition, the toxicity of zinc and of most zinc-containing compounds is much lower and, with certain exceptions, of minor importance. The oral toxicity of zinc salts in laboratory animals is remarkably low with LD_{50} values around 1000 to 2500 mg kg^{-1} body weight (and even $>$5000 mg kg^{-1} for ZnO). On the other hand, though inhalation of zinc oxide fumes can cause so-called metal fume fever, the corresponding TLV for ZnO is substantially higher (5 mg m^{-3}) than that for cobalt compounds (0.05–0.10 mg m^{-3}). Thus, a maximisation of cobalt replacement by zinc in the willemite or gahnite solid solutions can reduce the negative environmental or hazardous effects and lower the production costs.

The work presented here focuses on Co^{2+}–Zn_2SiO_4 (willemite) and Zn^{2+}–Co_2SiO_4 (olivine) blue ceramic pigments. In order to optimise cobalt addition, it can be helpful to determine approximately the ranges of solid solution between the olivine Co_2SiO_4 and willemite. Since Co^{2+} ions are very similar in size to Mg^{2+} [$r_{Co}{}^{2+}$ = 0.72 (tetrahedral)–0.89 Å (octahedral, high spin); $r_{Mg}{}^{2+}$ = 0.71 (tetrahedral)–0.86 Å (octahedral)],[9] one can expect a similar behaviour to that found between the olivine forsterite (Mg_2SiO_4) and willemite, which form a 'simple eutectic system'.[10] Forsterite and willemite are not isostructural[11] and, therefore, do not present a complete range of solid solution, despite the similar ionic radii of Mg^{2+} and Zn^{2+} [$r_{Zn}{}^{2+}$ = 0.74 (tetrahedral)–0.88 Å (octahedral)]:[9] the olivine forsterite (Mg_2SiO_4), contains approximately hexagonal close packed oxide layers, which are not present in willemite; both contain SiO_4 tetrahedra but magnesium (or Co) is coordinated octahedrally in olivine and zinc is coordinated tetrahedrally in willemite. Both magnesium (or Co) and zinc are flexible ions in their coordination requirements, and can be in either tetrahedral or octahedral coordination. Thus, in forsterite solid solutions, $(Mg_{2-x}Zn_x)SiO_4$, zinc replaces magnesium in octahedral sites whereas in the willemite solid solutions, $(Zn_{2-x}Co_x)SiO_4$, magnesium replaces zinc in tetrahedral sites.

In this work, the performance as blue ceramic pigments of both Co^{2+}–Zn_2SiO_4 (willemite) and Zn^{2+}–Co_2SiO_4 (olivine) solid solutions are compared. The addition of cobalt in the willemite lattice is minimised while also maintaining an intense blue colour. A maximum replacement of cobalt by zinc is intended with the aim of reducing the environmental and hazardous effects and lowering production costs.

Experimental

The traditional ceramic procedure (mechanical mixture of the oxide precursors) was employed to prepare the samples with the compositions and nomenclature shown in Table 1. As may be seen, a complete range of compositions $Co_xZn_{2-x}SiO_4$ was prepared, ranging from the olivine (**B1** sample, x = 2: Co_2SiO_4) to the willemite (**B8** sample, x = 0: Zn_2SiO_4) crystalline structures. Therefore, the solid solution of Zn^{2+} in the olivine lattice and that of Co^{2+} in the willemite lattice, were analysed.

Quartz of industrial quality (Sibelco, 98% SiO_2), chemically pure commercial zinc oxide, and commercial cobalt oxide (Co_3O_4, with a minimum 70% Co) were employed as precursors. To prepare the samples, the appropriate amounts of precursors to obtain 20 g of solid solution were ball-milled (10 min at 800 rpm) in acetone. Residual acetone was removed by evaporation and the dried powders were homogenised in an agate mortar. The dried powders obtained were then fired in a muffled electrical furnace (Nanneti). The firing treatment consisted of heating the powders to the suitable temperature (1000, 1200 and 1300 °C), with a heating rate of 10 °C min^{-1}, and with a soaking time of 2 h. Since some fired powders appeared partially melted after firing at 1300 °C/2 h, all the raw compositions were also fired at 1300 °C with a soaking time of only 1 h and at 1200 °C with a soaking time of 5 h.

To analyse the development of crystalline phases with composition (x) and with firing temperature, X-ray diffraction (XRD) patterns of the calcined samples were obtained using conventional powder techniques in a Siemens D-500 diffractometer with Ni filtered Cu-Kα radiation (from 10 to 75° 2θ, with a goniometer speed of 0.05° 2θ step^{-1}, and 1 s of counting time per step). In addition, the unit cell parameters and size (unit cell volume) corresponding to the formed Zn^{2+}–olivine and Co^{2+}–willemite solid solutions in representative 1200 °C/5 h-fired samples were also measured using the POWCAL (powder-calculation) and LSQC (least-squares-calculation) programs from the Chemistry Department of Aberdeen University (United Kingdom). The former refines the d values of tested polycrystals with an internal standard mixed with the sample; the latter calculates the crystallographic unit cell parameters by comparing their refined d values with the standard values.[12] With this aim, α-Al_2O_3 (50%) was used as internal standard in the XRD run between 15 and 75° 2θ at a lower goniometer speed (0.02° 2θ s^{-1}).

In order to test their efficiency as blue ceramic pigments, representative olivine and willemite-based compositions fired at 1200 °C/5 h and at 1300 °C/1 h were also 5% enamelled with two different transparent (or crystalline) glazes (single-firing and double-firing glazes) onto commercial ceramic biscuits. The approximate oxide composition of both glazes expressed as Seger formulae is as shown in Scheme 1.

With this aim, the glazes (or frits) and the colours (5% of colour) were ball-milled adding water (40%) and kaolin (5%). The as-obtained slip was dip-coated onto ceramic biscuits, and then fired following a fast firing scheme (52 min and a maximum temperature of 1085 °C for the single-firing glaze, and 60 min with a maximum temperature of 1000 °C for the double-firing glaze).

Information about the oxidation state and coordination environment (tetrahedral or octahedral) of the chromophore ion (cobalt) in representative fired compositions was also obtained by UV–VIS–NIR spectroscopy (diffuse reflectance) performed with a Perkin-Elmer (lambda 2000) spectrophotometer between 300 and 1600 nm. In addition, $L^*a^*b^*$ colour parameters of fired powders and of enamelled samples were measured with a Perkin-Elmer spectrophotometer using a standard lighting C, following the CIE-$L^*a^*b^*$ colourimetric method recommended

Table 1 Nomenclature of prepared compositions $(Co_xZn_{2-x})SiO_4$

Sample	Composition
B1 (x = 2.00)	Co_2SiO_4
B2 (x = 1.95)	$Co_{1.95}Zn_{0.05}SiO_4$
B3 (x = 1.50)	$Co_{1.5}Zn_{0.5}SiO_4$
B4 (x = 1.00)	$CoZnSiO_4$
B5 (x = 0.90)	$Co_{0.9}Zn_{1.1}SiO_4$
B6 (x = 0.50)	$Co_{0.5}Zn_{1.5}SiO_4$
B7 (x = 0.05)	$Co_{0.05}Zn_{1.95}SiO_4$
B8 (x = 0.00)	Zn_2SiO_4

by the CIE (Commission Internationale de l'Eclairage).[13] By this method, L^* is the lightness axis [black (0) ⟶ white (100)], b^* is the blue (−) ⟶ yellow (+) axis, and a^* is the green (−) ⟶ red (+) axis. From the diffuse reflectance (R) spectra obtained with the spectrophotometer, it was also possible to obtain the Kubelka–Munk absorption function, conventionally referred to as Remission Function, $[F(R) = (1 - R)^2/(2R)]$. The employment of $F(R)$ spectra is strongly advantageous to better compare the colour intensity of ceramic pigments and also to relate colour intensity to pigment concentration, as suggested by Eppler and Eppler.[14]

Finally, the microstructure and chemical homogeneity of representative fired compositions were also characterised by Scanning Electron Microscopy (SEM), using a Leo-440i Leyca electron microscope equipped with an Energy Dispersion X-ray (EDAX) attachment by Oxford University.

Results and discussion

X-Ray diffraction (XRD) characterisation

The development of crystalline phases and powder colour with heating and with the amount of cobalt (x) introduced in the composition ($Co_xZn_{2-x}SiO_4$) is summarised in Table 2. The following points can be made:

(i) The great stability of the cobalt spinel (Co_3O_4) used as the cobalt source strongly limits the system reactivity: important amounts of the unreacted cobalt spinel still remains at 1200 °C (or even at 1300 °C); consequently, an appreciable development of the olivine or willemite crystalline phases is only accomplished from 1200 °C, the temperature at which this spinel starts decomposing to CoO (observed from 1200 °C/5 h). The highest reactivity was observed at 1300 °C, though some compositions

(*a*) crystalline double-firing glaze:

K_2O	0.094				
Na_2O	0.576				
MgO	-	Al_2O_3	0.633	SiO_2	6.916
CaO	0.193				
PbO	0.137				

(*b*) crystalline single-firing glaze:

K_2O	0.106				
Na_2O	-				
MgO	-	Al_2O_3	0.323	SiO_2	1.972
CaO	0.565				
ZnO	0.329				

Scheme 1 Seger formulae of the glazes.

Table 2 Evolution of crystalline phases (XRD)[a] and powder colour with firing temperature and with composition

Sample/Calcination	1000 °C (2 h)	1200 °C (2 h)	1200 °C (5 h)	1300 °C (1 h)	1300 °C (2 h)
B1	C (80)	C (62)	C (49)	C (18)	C (30)
Co_2SiO_4	O (55)	O (69)	O (64)	O (60)	O (105)
			C′ (14)	C′ (30)	C′ (30)
	blue	blue–violet	violet	violet	blue–violet
B2		C (54)	C (56)	O (78)	C (24)
$Co_{1.95}Zn_{0.05}SiO_4$		O (64)	O (84)	C′ (40)	O (70)
		C′ (26)		C′ (50)	
		blue–violet	violet	violet	blue–violet
B3		C (65)	C (25)	O (115)	O (110)
$Co_{1.5}Zn_{0.5}SiO_4$		O (110)	O (77)	C′ (30)	C′ (45)
			C′ (40)		melts
		blue–violet	violet	violet	blue–violet
B4	C (145)	C (75)	C (25)		O (30)
$CoZnSiO_4$		O (30)	C′ (30)		C′ (50)
		W (175)	W (220)		W (240)
	blue	blue	blue	melts	melts
					blue
B5		C (100)	C (20)		C′ (20)
$Co_{0.9}Zn_{1.1}SiO_4$		W (240)	W (155)		W (180)
			C′ (20)		melts
		blue	blue	melts	blue
B6		C (100)	C (100)	W (250)	W (380)
$Co_{0.5}Zn_{1.5}SiO_4$		W (370)	W (440)		
		Q (30)			
		Z (110)			
		blue	blue	blue	blue
B7		W (540)	W (880)	W (1100)	W (870)
$Co_{0.05}Zn_{1.95}SiO_4$		Z (620)	Z (490)	Z (150)	Z (200)
		Q (180)	Q (120)		
		turquoise	blue	blue	blue
B8	Q (190)	Q (300)			Q (70)
Zn_2SiO_4	Z (790)	W (580)			W (1170)
		Z (830)			Z (300)
	white	white			white

Crystalline phases: O = Olivine (Co_2SiO_4), C = Co_3O_4, C′ = CoO, W = Willemite (Zn_2SiO_4), Z = ZnO, and Q = Quartz (SiO_2).

[a] The XRD intensity (counts) of the main peak is shown in parentheses.

(from $x = 1.5–0.9$) melted after this thermal treatment.

(ii) The ranges of solid solution between Co_2SiO_4 and Zn_2SiO_4 seem to follow a similar scheme to that found in the phase diagram of the Mg_2SiO_4–Zn_2SiO_4 system.[10] For all the temperatures studied, as the amount of Co in the formulation decreases from $x = 2$ (**B1** sample) to $x = 1.5$ (sample **B3**), the cobalt olivine forms first (Co_2SiO_4). Since zinc-containing crystalline phases are not observed by XRD, zinc must be entering the olivine lattice substituting for the Co ions in octahedral sites. At $x = 1$ (sample **B4**) and from 1200 °C, willemite also forms coexisting with olivine. This composition ($CoZnSiO_4$) is partially melted at 1300 °C. If cobalt content is further decreased to $x = 0.9$ (sample **B5**), olivine is not detected and only the most refractory willemite along with residual Co_3O_4 and CoO are observed from 1200 °C/2 h. This composition also appears partially melted at 1300 °C. If the cobalt content is reduced from $x = 0.9$ (not included) to $x = 0$ (samples **B6**, **B7** and **B8**), olivine does not form and willemite becomes the predominant crystalline phase, which is observed as a single phase (sample **B6**) or accompanied by residual phases such as zinc oxide, quartz, or unreacted cobalt spinel (only up to 1200 °C), depending on firing temperature and composition. The absence in these samples of cobalt-containing crystalline phases (such as cobalt oxide) accompanying willemite (apart from unreacted Co_3O_4 at 1200 °C) confirms the entrance of cobalt in the willemite lattice substituting for zinc in tetrahedral sites. Therefore, from these results one can infer that both Zn^{2+}–olivine and Co^{2+}–willemite solid solutions coexist in a range of compositions which approximately would extend over $x = 1.5–0.9$ (limits not included), these compositions being near the euthectic point, which would be between 1200 and 1300 °C. The region presenting a single phase of olivine s.s. would be compressed (approximately) between $x = 2$ (Co_2SiO_4) and $x = 1.5$ ($Co_{1.5}Zn_{0.5}SiO_4$), which means that zinc ions substitute for cobalt ions at least up to 25 mol%. On the other hand, a single solid solution of willemite is formed when $x = 0–0.9$ ($Co_{0.9}Zn_{1.1}SiO_4$), indicating that Co^{2+} ions replace Zn^{2+} ions in the willemite lattice up to 45 mol%. On the basis of the results obtained by XRD, an approximate phase diagram for the system Co_2SiO_4–Zn_2SiO_4 is shown in Fig. 1, valid only as a qualitative reference.

(iii) Important differences in the colour of the fired powders were observed, depending on the stabilised solid solution: from $x = 0.05$ (sample **B7**) to 1.0 (sample B4), the formed willemite solid solution gave rise to intense blue colours, while from $x = 1.5$ (sample **B3**) to 2 (sample **B1**), the presence of the olivine solid solution conferred upon the fired powders a characteristic violet or indigo blue colour. The blue colour of willemite-containing powders confirms the presence of Co substituting for Zn in the willemite structure. Moreover, this blue colour became lighter the more the willemite structure developed, in accordance with the lower cobalt addition.

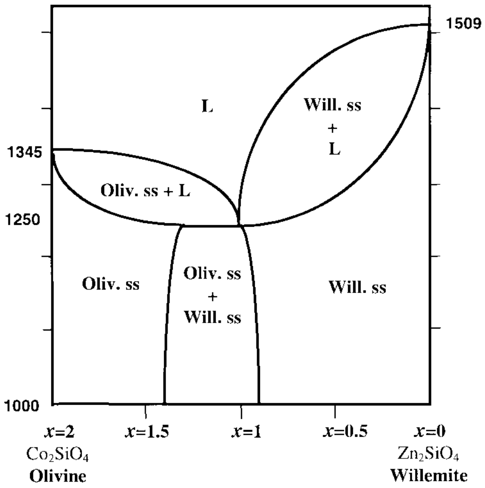

Fig. 1 Approximate phase diagram for the binary Co_2SiO_4/Zn_2SiO_4 system (from XRD results, and valid only as a reference).

On the other hand, the lattice parameters (and unit cell volume) of representative 1200 °C fired powders, determined with the POWCAL and LSQC programmes, are presented in Table 3. According to the similar ionic radii of Co^{2+} and Zn^{2+} ions (0.72/0.89 Å and 0.74/0.88 Å in tetrahedral/octahedral environments, respectively), the exchange between both ions is not expected to greatly affect the lattice size as Zn^{2+} enters in the olivine lattice (samples **B2** and **B3**), or as Co^{2+} enters in the willemite lattice (samples **B7** to **B4**). As may be seen from Table 3, the olivine unit cell volume of samples **B2** and **B3** was very similar, while the lattice parameters and cell volume of the willemite solid solution were observed to rise slightly with cobalt addition (from **B8** to **B4**). In general, the measured unit cell volumes were very close to the values of the corresponding standard cells (ASTM).[12]

UV–VIS–NIR Characterisation

The energy-level diagram for Co(II) of 3d^7 configuration, in both octahedral and tetrahedral ligand field, presents three spin-allowed transitions. The transitions for the Co(II) in an octahedral ligand field are:

$$\nu_1: {}^4T_1\,(F) \rightarrow {}^4T_2\,(F)$$
$$\nu_2: {}^4T_1\,(F) \rightarrow {}^4A_1\,(F)$$
$$\nu_3: {}^4T_1\,(F) \rightarrow {}^4T_1\,(P)$$

For the olivine pigment (Co_2SiO_4), Corma and Lambies[15] assigned the first band (ν_1) at 1350 nm, the second (ν_2) at 570 nm and the third (ν_3) at 490 nm (commonly, a multiple band around 510 nm is seen due to a rhombic distortion of the octahedral coordination caused by the Jahn–Teller effect).

Regarding Co(II) in a tetrahedral ligand field, the spin-allowed transitions are:

$$\nu_1: {}^4A_2\,(F) \rightarrow {}^4T_2\,(F)$$
$$\nu_2: {}^4A_2\,(F) \rightarrow {}^4T_1\,(F)$$
$$\nu_3: {}^4A_2\,(F) \rightarrow {}^4T_1\,(P)$$

According to the literature, in the case of the complex tetrahedral ion $(CoCl_4)^{2-}$, the two first spin-allowed bands fall in the infrared and only the third is present in the red spectral region of the visible region around 667 nm. This band in the

Table 3 Lattice parameters (a,b and c) and unit cell volume[a] of 1200 °C/5 h-fired powders

	a/Å	b/Å	c/Å	V/Å^3
ASTM Co_2SiO_4 15-0865	6.0074	10.310	4.7823	296.2
B2 $Co_{1.95}Zn_{0.05}SiO_4$	6.000(5)	10.30(1)	4.781(4)	295.5(8)
B3 $Co_{1.5}Zn_{0.5}SiO_4$	6.007(2)	10.297(3)	4.769(3)	295.0(4)
ASTM Zn_2SiO_4 (37-1485)	13.1381	13.1381	9.3100	1566.3(2)
B4 $CoZnSiO_4$	13.956(2)	13.956(2)	9.329(2)	1573.6(8)
B5 $Co_{0.9}Zn_{1.1}SiO_4$	13.957(3)	13.957(3)	9.334(3)	1575(1)
B6 $Co_{0.5}Zn_{1.5}SiO_4$	13.944(1)	13.944(1)	9.322(1)	1569.7(4)
B7 $Co_{0.05}Zn_{1.95}SiO_4$	13.932(2)	13.932(2)	9.309(1)	1564.8(6)
B8 Zn_2SiO_4	13.929(5)	13.929(5)	9.305(3)	1563(2)

[a] The lattice is the olivine (Co_2SiO_4) for samples **B2** and **B3**, and the willemite (Zn_2SiO_4) for samples **B4** to **B8**.

visible region also has been seen at lower wavelengths, as reported by Corma and Lambies.[15] Bates assigns the ν_3 transition at 606 nm for the solid solution of Co(II) in ZnO, and Jaffre–Paris at 588 nm for the mixed oxide $(Co_{0.1}Mg_{0.9})O$, in agreement with Reinen's data. Usually, this band in the visible region has been found to consist of a triple signal around 540 (green region), 590 (yellow-orange region) and 640 nm (red region), which gives rise to a blue coloration. This triple band has been attributed to a Jahn–Teller distortion of the tetrahedral structure, according to Bamford,[16] or to an interaction between L and S quantic numbers, according to Bates.[17]

Therefore, the general form of the spectra, the shift of the third spin-allowed transition to higher wavelengths (540–640 nm), along with the presence of a single band or two bands in the infrared region, can be used to distinguish both octahedral and tetrahedral Co(II) coordinations.[18]

The UV–VIS–NIR absorption curves of representative powders fired at 1200 °C/5 h and at 1300 °C/1 h are shown in Fig. 2(*a*) and (*b*), respectively. At both temperatures, a clear distinction between the presence of octahedral or tetrahedral Co^{2+} can be made, in accord with the spin-allowed transitions previously mentioned. In the case of samples **B1**, **B2** and **B3**, which contain olivine as the main crystalline phase, the typical bands of octahedral cobalt are present: a single, very wide band may be seen (see representative **B1** and **B3** curves) in the infrared region around 1350–1400 nm, which could be associated with the ν_1 transition, along with a second wide band with two peaks between 502 and 592 nm, which would include the ν_3 and ν_2 transitions, according to McClure.[19] **B1** and **B3** absorption curves also present two shoulders at 660 and 770 nm, being more developed in 1200 °C/5 h fired powders. Both shoulders could be attributed to the presence of unreacted cobalt spinel (Co_3O_4) and/or residual cobalt oxide (CoO) accompanying the cobalt olivine.

In the case of samples **B4** (only shown the spectrum of 1200 °C/5 h fired powder), **B6** and **B7**, the accommodation of Co(II) in tetrahedral coordination in the willemite structure (Zn_2SiO_4) is confirmed by the shift of the ν_3 band to higher wavelengths in the visible region: a wide band between 555 and 650 nm is observed, which seems to be composed of three different signals (around 540, 590 and 640 nm), in agreement with Bamford's[16] and Bates'[17] assumptions; in addition, **B4**, **B6** and **B7** spectra exhibit a double band in the infrared region (around 1300 and 1440 nm) which could be associated with ν_1 and ν_2 cobalt transitions in a tetrahedral field, in contrast with the single band observed in the powders containing cobalt in octahedral coordination. The improvement of reactivity and of crystallisation yield with firing treatment can also be appreciated from the narrower and sharper absorption bands exhibited by the powders at 1300 °C [compare Fig. 2(*a*) and (*b*)]. At this temperature, **B1** and **B3** samples still present a shoulder at around 760 nm, since these samples still contain residual cobalt oxides (Co_3O_4 and/or CoO) (as shown by XRD), in contrast to samples **B6** and **B7**. On the other hand, the shift in the absorption minimum to higher wavelengths (from 450 to 480 nm), the lower the cobalt content, is responsible for the colour change from violet to blue observed in the fired powders.

CIE-*L*a*b** Colour measurements

Tables 4 and 5 show the CIE-*L*a*b** colour parameters of representative powders fired at 1200 °C/5 h and at 1300 °C/1 h. The maximums of the Remission Function F(R), obtained from the diffuse reflectance curves, are also presented. The yield of blue colour is mainly governed by the parameter *b**: the more negative the *b** value, the bluer the colour hue. As may be seen, samples with the olivine structure (**B1**, **B2** and **B3**) exhibited an achromatic (very low *a** and *b** values) violet colour at both temperatures, while samples containing tetrahedral Co(II) in the willemite lattice (**B4** to **B7**) showed a much more negative *b** value, indicative of a much bluer colour hue. This change from violet to bluer colour hues was also confirmed by the higher characteristic wavelength of willemite-containing powders (480 nm) with respect to olivine-containing samples (450 nm). From an environmental point of view, it is remarkable that those

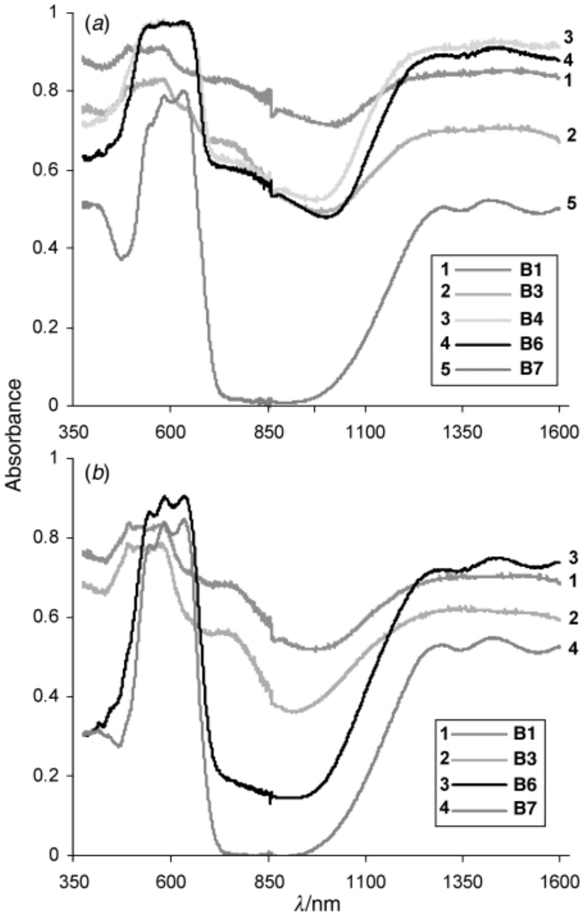

Fig. 2 UV–VIS–NIR absorption spectra (absorbance) of representative powders fired at 1200 °C/5 h (*a*) and at 1300 °C/1 h (*b*).

Table 4 Colour parameters (*L*a*b*) and Kubelka–Munk Remission Function [*F*(*R*)][a] of 1200 °C/5 h fired powders

Sample	*L**	*a**	*b**	*F*(*R*)[a]
B1	42.6	2.1	−1.8	3.1
B2	45.2	3.2	−2.8	2.8
B3	45.9	3.5	−4.2	2.4
B4	40.9	3.3	−14.6	3.7
B5	39.8	3.5	−12.9	3.8
B6	40.7	4.4	−19.8	3.7
B7	55.81	−9.3	−20.3	2.2

[a] At 590 nm in olivine samples (**B1** to **B3**), and at 650 nm in willemite samples (**B4** to **B7**).

Table 5 Colour parameters (*L*a*b*) and Kubelka–Munk Remission Function [*F*(*R*)][a] of representative 1300 °C/1 h fired powders

Sample	*L**	*a**	*b**	*F*(*R*)[a]
B1	45.7	5.1	−3.2	2.5
B3	48.7	8.0	−4.1	2.1
B6	48.5	7.2	−36.5	3.1
B7	54.1	0.1	−36.3	2.5

[a] At 590 nm in olivine samples (**B1** to **B3**), and at 650 nm in willemite samples (**B4** to **B7**).

compositions prepared with the minimum Co addition (samples **B6**, $Co_{0.5}Zn_{1.5}SiO_4$ and **B7**, $Co_{0.05}Zn_{1.95}SiO_4$) presented the bluer colour hue. In addition, both samples exhibited a huge increase in the blue parameter at 1300 °C ($-b^* = 36$), with respect to the value presented at 1200 °C ($-b^* = 20$). However, these compositions with a much bluer hue, presented also a higher L^* value, indicating a less intense or lighter colour. The value of the $F(R)$ at a wavelength around the maximum absorbance is appropriate for comparison of the colour intensity of the pigments.[14] In the powders fired at 1200 °C/5 h, samples **B4**, **B5** and **B6** showed a similar $F(R)$ value (around 3.7), irrespective of the cobalt content, but a slight decrease was observed in sample **B7** [$F(R) = 2.2$], which is the composition with the lower cobalt content (2.5 mol%). This decrease in the value of $F(R)$ observed in sample **B7**, also at 1300 °C (see Fig. 3(*a*)], is indicative of a less intense colour, in agreement with the higher L^* value (around 55).

On the other hand, a colourimetric evaluation of representative enamelled samples was also carried out to compare the colour performance of the prepared pigments in different glazes. Tables 6 and 7 summarise the colour parameters (L^*, a^*, b^*) and the values of the Remission Function $F(R)$ at the maximum absorbance of representative pigments (fired at 1200 °C/5 h and at 1300 °C/1 h) enamelled (5% of colour) with the single-firing and with the double-firing glaze. As observed with the fired powders, the samples enamelled with the olivine pigments (**B1** to **B3**) produced a violet colour, while the samples enamelled with the willemite pigments (**B4**, **B5** and especially **B6** and **B7**) gave rise to much bluer hues. This fact is in accordance with the observed shift of the maximum reflectance to higher wavelengths (from 400 to 450 nm), as may be seen in Fig. 3(*b*) for samples enamelled with the single-firing glaze. In addition, an important increase in the blue component ($-b^*$) from 1200 to 1300 °C was observed in the case of the single-firing glaze, while no relevant differences could be appreciated with the double-firing glaze. The bluer colour hue was obtained with composition **B7** (fired at 1300 °C) enamelled with the single-firing glaze ($-b^* = 39$), which in turn was also lighter ($L^* = 57$). This sudden increase in lightness (higher L^*) observed in sample **B7** was also confirmed by the decrease of $F(R)$ (see Tables 6 and 7). As an important result, sample **B6** proved to have a colour intensity similar to or even higher than compositions with a higher cobalt content.

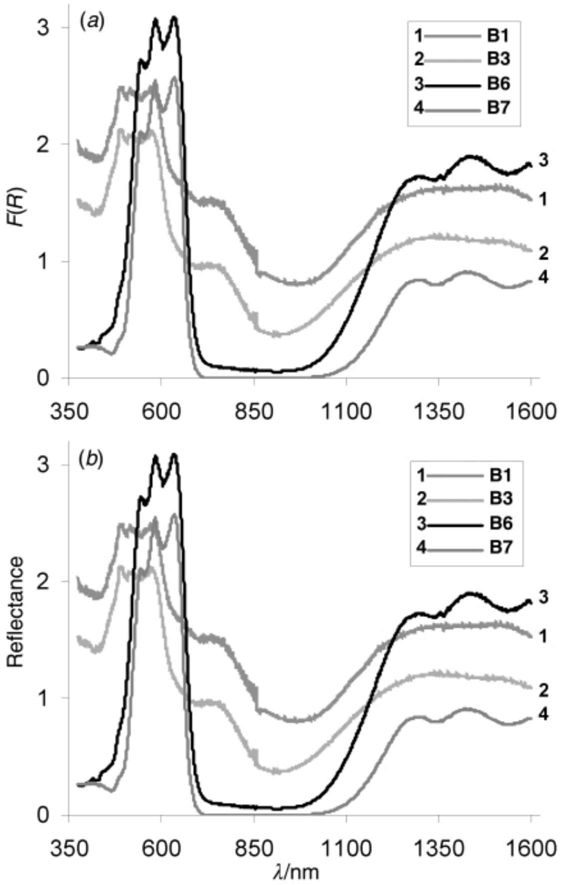

Fig. 3 Kubelka–Munk Remission Function spectra, $F(R)$, of representative powders fired at 1300 °C/1 h (*a*), and diffuse reflectance (R) spectra of the same 1300 °C fired powders enamelled with the single-firing glaze (*b*).

In conclusion, it was found that willemite-based pigments are better than olivine-based pigments in giving a blue colour rather than violet or purple. Moreover, it is possible to obtain an intense and much bluer colour with a cobalt addition as low as 25 mol% (sample **B6**, $Co_{0.5}Zn_{1.5}SiO_4$). If the cobalt content is further reduced to 2.5 mol% (sample **B7**, $Co_{0.05}Zn_{1.95}SiO_4$), which would be positive according to environmental and economic criteria, the colour hue becomes much bluer, but the colour intensity diminishes producing lighter colours. Therefore, a nice palette of blue ceramic pigments with different colour intensities can be obtained based on the willemite lattice, with an optimised, very low Co content, ranging from 25 to 2.5 mol% Co.

Microstructure characterisation (SEM/EDAX)

A final microstructure characterisation of representative fired pigments was carried out by electron microscopy (SEM/EDAX). Fig. 4 shows two SEM micrographs corresponding to **B3** and **B6** fired powders (1300 °C/1 h) with a magnification of ×4500 and ×2250, respectively. Both fired pigments were found to consist of large, irregularly-shaped monoliths (*ca.* 50–70 μm), which according to XRD correspond to olivine (**B3** sample) and willemite (**B6** sample). Smaller aggregates, along with much smaller particles, were also present in the fired powders. The size of the smaller particles ranged between 2 and 10 μm in the **B3** sample and between 1 and 2 μm in the **B6**

Table 6 Colour parameters ($L^*a^*b^*$) and Kubelka–Munk Remission Function $[F(R)]^a$ of representative enamelled samples (with 1200 °C/5 h fired powders)

Double-firing glaze	L^*	a^*	b^*	$F(R)^a$
B1	31.7	4.0	−12.6	9.4
B6	32.6	7.7	−21.8	7.6
B7	52.2	−0.3	−26.6	2.0
Single-firing glaze	L^*	a^*	b^*	$F(R)$
B1	27.5	6.2	−14.8	6.1
B6	32.1	12.1	−27.4	6.3
B7	54.7	2.8	−28.0	2.4

[a] At 650 nm.

Table 7 Colour parameters ($L^*a^*b^*$) and Kubelka–Munk Remission Function $[F(R)]^a$ of representative enamelled samples (with 1300 °C/1 h fired powders)

Double-firing glaze	L^*	a^*	b^*	$F(R)^a$
B1	29.1	5.2	−3.2	7.7
B3	27.5	5.2	−14.3	8.6
B6	25.7	7.6	−17.6	10.2
B7	48.2	3.7	−30.1	2.9
Single-firing glaze	L^*	a^*	b^*	$F(R)$
B1	33.5	10.9	−27.2	6.5
B3	34.7	10.9	−28.2	6.2
B6	35.6	12.8	−31.9	6.1
B7	57.3	6.3	−39.1	1.9

[a] At 650 nm.

sample. Therefore, the morphology and size distribution was irregular in both pigments.

A semiquantitative chemical analysis of these fired pigments (**B3** and **B6**) was also performed by EDAX to determine their chemical homogeneity. The theoretical and observed compositions are shown in Table 8 (B3 sample) and Table 9 (**B6** sample). The results obtained in the EDAX analysis of the **B3** fired pigment evidenced quite an homogeneous chemical composition in all the spots studied, but in all cases a considerable Co excess was detected (or Zn and Si defect) with respect to the theoretical composition formulated. A micrograph with the EDAX mapping distribution corresponding to the spot analysed in EDAX no. 7 (magnification ×2200) is shown in Fig. 5. As may be seen, while Zn is evenly distributed (not segregated) through the powder, Co appears clearly segregated in some regions, which can mainly be associated with the smaller particles observed by SEM. This segregated Co is responsible for the Co excess detected in the analysis, and could correspond to unreacted CoO accompanying the olivine solid solution aggregates, as also detected by XRD at 1300 °C in this composition.

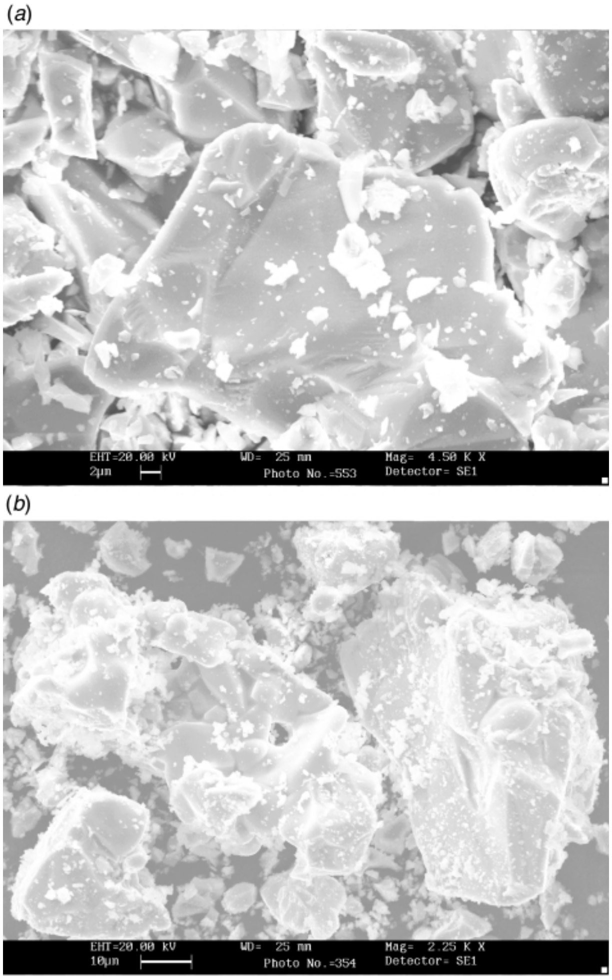

Fig. 4 SEM micrographs (secondary emission detector) of representative pigments fired at 1300 °C/1 h: (*a*) **B3** sample ($Co_{1.5}Zn_{0.5}SiO_4$) with a magnification of 4500, (*b*) **B6** sample ($Co_{0.5}Zn_{1.5}SiO_4$) with a magnification of 2250.

Table 8 EDAX analysis of **B3** pigment ($Co_{1.5}Zn_{0.5}SiO_4$) fired at 1300 °C/1 h

EDAX analysis	n° ions Zn	n° ions Co	n° ions Si	Wt% ZnO	Wt% CoO	Wt% SiO_2
Theoretical composition	0.50	1.50	1.00	19.09	52.73	28.18
1 ×800	0.39	2.16	0.73	13.31	68.28	18.41
2 ×1000	0.34	1.95	0.85	12.45	64.93	22.62
3 ×800	0.35	1.88	0.88	12.71	63.43	23.85
4 ×2000	0.41	2.10	0.75	14.16	66.78	19.06
5 ×1500	0.35	2.23	0.69	11.90	70.95	17.15
6 ×1000	0.36	2.12	0.76	12.65	67.91	19.44
7 ×2200	0.37	1.97	0.83	13.22	64.81	21.96
8 ×4500	0.38	2.04	0.79	13.35	66.18	20.47

Table 9 EDAX analysis of **B6** pigment ($Co_{0.5}Zn_{1.5}SiO_4$) fired at 1300 °C/1 h

EDAX analysis	n° ions Zn	n° ions Co	n° ions Si	Wt% ZnO	Wt% CoO	Wt% SiO_2
Theoretical composition	1.50	0.50	1.00	55.58	17.06	27.36
1 ×2000	1.67	0.74	0.80	56.77	23.23	20.00
2 ×3500	1.55	0.68	0.88	54.91	22.00	23.08
3 ×8000	1.46	0.56	0.99	54.05	19.02	26.93
4 ×10000	1.58	0.72	0.85	55.12	23.02	21.86

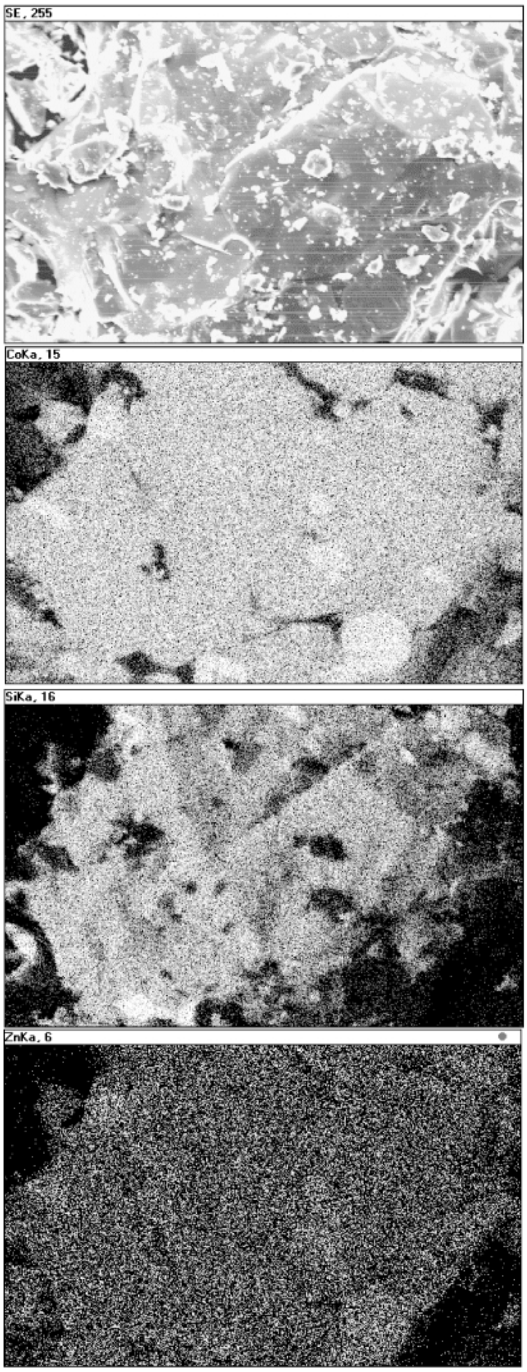

Fig. 5 EDAX mapping of a representative region of **B3** pigment ($Co_{1.5}Zn_{0.5}SiO_4$) fired at 1300 °C/1 h.

On the other hand, the EDAX analysis of sample **B6** (see Table 7) also showed an acceptable chemical homogeneity, which in this case was very close to the theoretical composition formulated. As may be seen in the EDAX mapping of this sample shown in Fig. 6 (EDAX no. 4, ×10000), and in contrast with **B3** sample, Co and Zn are evenly distributed in the bulk powder. Therefore, in this sample Co seems to be fully integrated in the willemite solid solution, as also confirmed by XRD (willemite was detected as a single phase). This observation is in agreement with the limit of Co solid solution in the willemite lattice, which appeared to be around 45 mol% (up to $x = 0.9$) according to XRD characterisation.

Conclusions

The performance of Co^{2+}–olivine and Co^{2+}–willemite solid solutions as blue ceramic pigments has been compared. The results obtained have shown that the amount of Co introduced in the willemite lattice can be minimised to a great extent whilst maintaining an intense and pure blue colour. In particular: (i) According to XRD characterisation, the ranges of solid solution between Co_2SiO_4 and Zn_2SiO_4 proved to follow a similar scheme to that found in the phase diagram of the binary Mg_2SiO_4/Zn_2SiO_4 system, which forms a simple eutectic system.[10] From 1200 °C (after Co_3O_4 decomposition), Zn^{2+} ions substitute for Co^{2+} ions up to at least 25 mol% forming a violet solid solution in the olivine lattice. Similarly, Co^{2+} ions form a blue solid solution in the willemite lattice substituting for Zn^{2+} ions up to 45 mol% (at 1300 °C). (ii) Olivine and willemite lattice parameters do not change substantially with the Co^{2+}–Zn^{2+} exchange, due to their similar ionic radii. (iii) UV–VIS–NIR characterisation confirms the octahedral location of Co^{2+} ions in olivine-containing samples which results in an achromatic violet colour; in contrast, Co^{2+} ions are accommodated in the tetrahedral sites in the willemite solid solutions, producing much bluer colour hues. (iv) The measurements of $L^*a^*b^*$ colour parameters and of the Kubelka–Munk Remission Function, $F(R)$, have shown that it is possible to obtain an intense and much bluer colour with a cobalt addition as low as 25 mol% ($Co_{0.5}Zn_{1.5}SiO_4$). If the cobalt content is further reduced to 2.5 mol% ($Co_{0.05}Zn_{1.95}SiO_4$), which would be positive according to environmental and economic criteria, the colour hue becomes much bluer, but the colour intensity diminishes producing lighter colours. Therefore, a nice palette of blue ceramic pigments with different colour intensities can be obtained based on the willemite lattice, with an optimised, very low Co content, ranging from 25 Co mol% to 2.5 Co mol%. (v) EDAX analysis confirms that Co is fully and evenly integrated in the willemite lattice, while some Co segregation (unreacted CoO) is observed accompanying the olivine solid solutions, due to the great stability of the cobalt precursor (Co_3O_4).

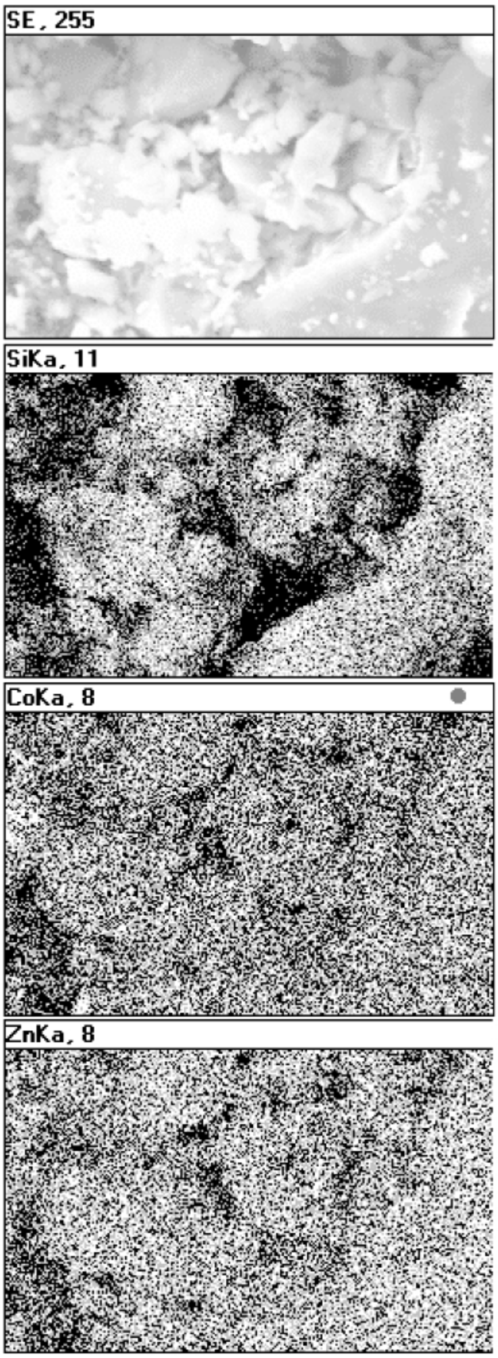

Fig. 6 EDAX mapping of a representative region of **B6** pigment ($Co_{0.5}Zn_{1.5}SiO_4$) fired at 1300 °C/1 h.

References

1 K. Hudson, H. Winbow and J. Cowley, *Ceram. Eng. Sci. Proc.*, 1996, **17**, 102.
2 G. Monari and T. Manfredini, *Ceram. Eng. Sci. Proc.*, 1996, **17**, 167.
3 DCMA, Classification and Chemical Description of Mixed Metal-Oxide Inorganic Coloured Pigments, Mixed Metal Oxide and Ceramic Colors Subcommittee. Ecology Committee. Dry Colors Manufacturers Association, Arlington, USA, 1979.
4 R. K. Mason, *Am. Ceram. Soc. Bull.*, 1961, **40**, 5.
5 R. A. Eppler and D. R. Eppler, *Ceram. Eng. Sci. Proc.*, 1994, **15**, 281.
6 G. N. Maslennikova, N. P. Fomina and A. I. Glebycheva, *Steklo i Keramika*, 1976, **7**, 28.
7 R. Eppler, *Am. Ceram. Soc. Bull.*, 1981, **60**, 562.
8 American Conference of Govermental Industry Hygienists (ACGIH), *Threshold Limit Values for Chemical Substances in the Work Environment*, Cincinnati (OH), USA, 1988.
9 R. D. Shannon, *Acta Crystallogr.*, 1976, **32**, 751.
10 E. R. Segnit and A. E. Holland, *J. Am. Ceram. Soc.*, 1965, **48**, 412.
11 A. R. West, in *Solid State Chemistry and its Applications*, John Wiley & Sons Ltd., New York, 1984, pp. 359–360.
12 ASTM card 37-1485 for Zn_2SiO_4 and number 15-0865 for Co_2SiO_4.
13 CIE, *Recommendations on Uniform Colour Spaces, Colour Difference Equations, Psychometrics Colour Terms.* Suplement no. 2 of CIE Publ. No. 15 (E1-1.31) 1971, Bureau Central de la CIE, Paris, 1978.
14 D. R. Eppler and R. A. Eppler, *Ceram. Eng. Sci. Proc.*, 1996, **17**, 77.
15 F. Corma and V. Lambies, *Revue de Chimie minérale*, 1980, **17**, 110.
16 C. R. Bamford, *Phys. Chem. Glasses*, 1962, **3**, 189.
17 T. Bates, in *Modern Aspects of the Vitreous State*, ed. J. D. Mackenzie, Butterworths, London, 1961, vol. 2, pp. 195–254.
18 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., Interscience, New York, 1972, p. 881.
19 D. S. McClure, *Solid State Phys.*, 1959, **9**, 399.

Clean synthesis in water: uncatalysed preparation of ylidenemalononitriles

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A simple, efficient and environment-friendly procedure is developed for the condensation of malononitrile with aromatic, heteroaromatic and aliphatic aldehydes in water. The ylidenemalononitriles **3** are synthesised in high yields (84–98%) and selectivities (87–98%) in distilled water at 65 °C for 1 h, avoiding the addition of any catalyst.

Introduction

The reagent malononitrile is a methylene active compound largely used in the Knoevenagel condensation, an important C–C bond forming reaction which has been extensively studied.[1] The ylidenemalononitriles thus obtained have found increasing applications in industry, agriculture, medicine and biological science.[2] They are important intermediates for the synthesis of various organic compounds, mainly by cyclization reactions.[2,3] Indeed, different kinds of nitrogen and oxygen-containing heterocycles were obtained (*e.g.* pyridines,[4b,f,i] pyrans,[4c,d,f,i] pyrimidines,[4i] pyranopyrimidines,[4d,g] pyranopyrazoles[4d,f] and phthalazines[4e]).

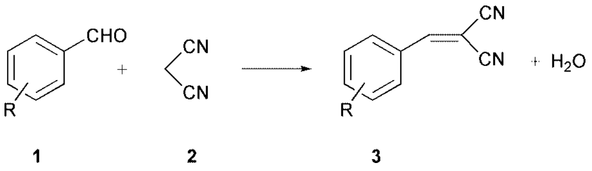
Moreover, benzylidenemalononitriles were reported to be effective anti-fouling agents, fungicides and insecticides. The chemical properties of benzylidenemalononitriles and their effects on, and interactions with, living organisms were extensively reviewed by Jones,[5] due to their use as cytotoxic agents against tumours or as riot control agents. Hydroxylated benzylidenemalononitriles were described as protein tyrosine kinase inhibitors with antiproliferative activity.[6]

The condensation of aromatic aldehydes and malononitrile is generally catalysed by bases, such as piperidine,[7] sodium ethoxide[8] or sodium hydroxide,[9] in organic solvents. Lewis acids were also reported to catalyze the reaction.[10]

In recent years a great effort has been made to prepare solid catalysts with basic properties in order to accomplish cleaner syntheses. Indeed, the increasing demands of environmental legislation require the minimisation or, preferably, the elimination of waste production in chemical manufacture with particular interest to inorganic and organic salts which are often obtained in large amounts as by-products.[11] Different heterogeneous catalysts were employed to synthesise benzylidenemalononitriles, in particular zeolites[12] and cation-exchanged zeolites[13] or mesoporous materials,[14] metal oxides,[15] xonotlyte,[16] hydrotalcites,[13a,17] ammine-functionalized clays,[18] MCM-41[19] and silica gel.[20] Our recent results obtained in the synthesis of coumarin-3-carboxylic acids[21] promoted by a cheap clay catalyst in water, montmorillonite KSF, prompted us to investigate the Knöevenagel condensation of malononitrile and aromatic aldehydes in aqueous medium (Scheme 1). The reaction of 4-chlorobenzaldehyde **1a** (R = 4-Cl) and malononitrile **2** was carried out in water at 100 °C for 2 h in the presence of montmorillonite KSF as catalyst. The benzylidenemalonitrile **3a** was obtained in high yield (97%) and selectivity (98%).

Results and discussion

To better understand the role of the clay catalyst, a comparison reaction was performed using the aldehyde **1a** and malononitrile in distilled water without any catalyst. It was surprising to observe that the reaction occurred with similar high yield (96%) and selectivity (99%). To investigate this surprising reactivity we first examined the solvent effect on the reaction. Solvents with different properties, like polarity and proticity, were employed in the model reaction between 4-chlorobenzaldehyde **1a** and malononitrile **2** at the same temperature, 65 °C, for 2 h. The data reported in Table 1 showed that the reaction requires a solvent and is favoured in polar ones. Indeed using toluene or THF the product was obtained in negligible yield, though the yield increased to 25 and 15% respectively on heating at reflux. It is known that the Knöevenagel reaction is solvent dependent and that usually dipolar aprotic solvents, like dimethylformamide, are especially useful in this condensation, because the second step, 1,2-elimination, is inhibited by protic solvent.[22] On the contrary, we observed that the reaction easily occurs in protic medium and also in water, although the Knöevenagel



Scheme 1

Green Context

The use of water as solvent in organic reactions is often surprisingly effective, even for reactions which traditionally are carried out under anhydrous conditions. Here the condensation of C–H acids with aldehydes is shown to be facile using water as solvent with no added catalyst, despite the fact the reaction involves a dehydration step. The products are important in a variety of applications, and are prepared in high yields and selectivity from environmentally benign water. ***DJM***

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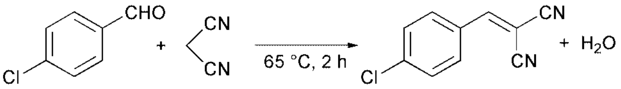
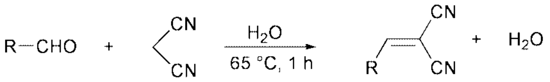
Table 1 Solvent effect on the yield and selectivity of **3a** from **1** and **2**



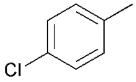
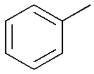
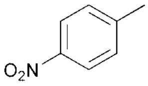
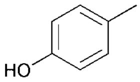
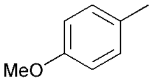
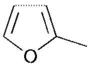
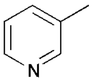
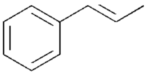
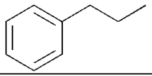
1a **2** **3a**

Entry	Solvent	Yield(%)	Selectivity(%)
1	Water	97	98
2	None	15	84
3	Toluene	4	97
4	THF	6	96
5	DMF	98	99
6	DMSO	96	98
7	Propan-2-ol	83	97
8	Ethanol	96	98
9	Methanol	94	98

Table 2 Uncatalysed syntheses of ylidenemalononitriles



1 **2** **3**

Entry	R	Product 3	Yield (%)	Selectivity (%)
1		**a**	96	99
2		**b**	94	99
3		**c**	98	99
4		**d**	98	99
5		**e**	90	92
6		**f**	98	99
7		**g**	98	99
8		**h**	84	87
9		**i**	94	98

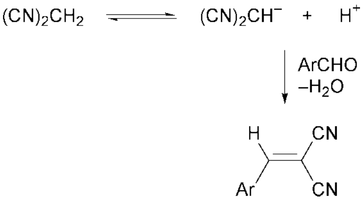
condensation is a net dehydration. Similar unexpected solvent effects have been previously found by other authors[23] and by ourselves,[21,24] but always in the presence of a catalyst.

It is remarkable that the reaction affords arylidenemalononitriles **3** in excellent yields and selectivities without adding any catalyst. The protic solvents are favourable over the usual DMSO or DMF, which are toxic, teratogenic and suspected carcinogen solvents.[25] Further, even if the reaction occurs with very high yield in methanol or ethanol at room temperature, we selected water as the medium of choice because it displays some advantages due to its low cost, no inflammability and easy product isolation by Bückner filtration.

The use of water as solvent in organic chemistry has received increasing attention in the last decade.[26] The enhanced reactivity and selectivity observed in some reactions were rationalised by various authors as a consequence of hydrophobic effects[26a] and enforced hydrophobic interactions.[27] The good results that we obtained carrying out the reaction in alcoholic solutions, where both the reagents are soluble, suggest that hydrophobic effects, if present, do not play an important role. Since the reaction easily occurs in non-basic aqueous medium (the pK_a value of malononitrile is 11.2[2a]) glass-catalysed processes were excluded by carrying out the reaction in a polyethylene vessel, which gave unchanged high yield. The reactivity of malononitrile under basic conditions is still under investigation.[28–30] Further, the stabilization of the negative charge by the cyano substituents is a matter of debate in the literature.[31]

To rationalize the reactivity of malononitrile in the present uncatalized Knöevenagel condensation we performed NMR studies in D$_2$O. The ^{1}H NMR spectrum showed a triplet at δ 4.07 (J = 3.0 Hz) and ^{13}C NMR experiments, with proton decoupling, showed a singlet at δ 115.16 (C≡N) and a triplet at δ 12.28 (CH, J 21.7 Hz).[32] This evidenced the exchange for deuterium of one methylene hydrogen, due to dissociation. We could propose a mechanism involving the ionization of malononitrile (Scheme 2) rather than the formation of keteneimine tautomer.[33]

As reported in the literature,[34] the reprotonation reaction is not a diffusion-controlled process. The dicyanomethyl carbanion can thus react with the electrophilic carbonyl group of the aldehyde. To explore the general validity of this process, different aldehydes were employed including aromatic, heteroaromatic as well as aliphatic ones (Table 2).[35]



Scheme 2

As usual, aromatic aldehydes bearing electron-donor groups are slightly less reactive (4-OCH$_3$ < H < Cl < NO$_2$), except 4-hydroxybenzaldehyde that afforded 4-hydroxybenzylidenemalononitrile **3d**, a biologically active compound,[6a,b] in quantitative yield. The α,β-unsaturated aldehyde **1h** reacted selectively to afford the highly conjugated compound **3h**, used as a model of substituted polyenes with donor–acceptor charge transfer properties.[36] Finally, it is noteworthy that the aliphatic aldehyde **1i** gives the corresponding alkylidenemalononitrile **3i** in excellent yield (94%) and selectivity (98 %) (Table 2, entry 9). It is important to mention that all of the products **3** are easily isolated by simple Büchner filtration,[37] avoiding the use of solvents usually required in the extraction and purification steps. The good results obtained following our simple procedure are surprising in view of the numerous catalysts, both homogeneous and heterogeneous, employed in organic solvents to synthesise this class of compounds.

Conclusions

We have shown that alkyl- and arylidenemalononitriles are easily prepared in very high yields and selectivities from malononitrile and aldehydes in distilled water at 65 °C for 1 h. Water is, without doubt, an excellent solvent in terms of cost, availability and environmental impact. In addition, this uncatalysed method represents a convenient, salt-free and efficient procedure to synthesise this class of compounds.

Experimental

Typical procedure

In a round-bottomed flask 4-chlorobenzaldehyde (1.40 g, 10 mmol) was added to a solution of malononitrile (0.66 g, 10 mmol) in 10 ml of distilled water. The reaction was heated at 65 °C for 1 h, then, after cooling to 10 °C, the product **3a** was isolated by Büchner filtration. The other 2-substituted 1,1-dicyanoethenes were also obtained following the same procedure, except product **3i** which was isolated by extraction with diethyl ether. All the products gave mps and spectral data consistent with the reported ones.

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References

1 (*a*) G. Jones, *Organic Reactions*, Wiley, New York, 1967, vol. 15, p. 204; (*b*) L. F. Tietze and U. Beifuss, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and C. H. Heathcock, Pergamon Press, Oxford, 1991, vol. 2, ch. 1.11, p. 341.

2 (*a*) A. J. Fatiadi, *Synthesis*, 1978, 165 and 241 and references cited therein; (*b*) F. Freeman, *Chem. Rev.*, 1980, **80**, 329.

3 E. Campaigne and S. W. Schneller, *Synthesis*, 1976, 705.

4 (*a*) J. L. Soto, C. Seoane, P. Zamorano and F. J. Cuadrado, *Synthesis*, 1981, 529; (*b*) S. Kambe and K. Saito, *Synthesis*, 1981, 531; (*c*) N. Martìn, C. Pascual, C. Seoane and J. L. Soto, *Heterocycles*, 1987, **26**, 2811; (*d*) M. H. Elnagdi, R. M. Abdel-Motaleb and M. Mustafa, *J. Heterocycl. Chem.*, 1987, **24**, 1677; (*e*) F. F. Abdel-Latif, *Bull. Soc. Chim. Fr.*, 1990, **127**, 129; (*f*) F. F. Abdel-Latif and R. M. Shaker, *Indian J. Chem., Sect. B*, 1990, **29**, 322; (*g*) J. M. Quintela, C. Peinador and M. J. Moreira, *Tetrahedron*, 1995, **51**, 5901; (*h*) R. M. Shaker, *Pharmazie*, 1996, **51**, 148; (*i*) F. F. Abdel-Latif, R. M. Shaker and N. S. Abdel-Aziz, *Heterocycl. Commun.*, 1997, **3**, 245.

5 G. R. N. Jones, *Nature*, 1972, **235**, 257.

6 (*a*) A. Gazit, P. Yaish, C. Gilon and A. Levitzki, *J. Med. Chem.*, 1989, **32**, 2344; (*b*) S. Hussoin, G. B. Fitzgerald and M. M. Wick, *J. Pharm. Sci.*, 1991, **80**, 416; (*c*) A. Gazit, N. Osherov, I. Posner, P. Yaish, E. Poradosu, C. Gilon and A. Levitzki, *J. Med. Chem.*, 1991, **34**, 1896.

7 (*a*) S. Cenini, F. Porta, M. Pizzotti and G. La Monica, *J. Chem. Soc., Dalton Trans.*, 1984, 355; (*b*) A. Robert, S. Jaguelin and J. L. Guinamant, *Tetrahedron*, 1986, **42**, 2275; (*c*) P. Milart and J. Sepiol, *Z. Naturforsch., Teil B*, 1986, **41**, 371; (*d*) N. Martin, C. Seoane, J. Carlos and J. L. Soto, *Tetrahedron*, 1988, **44**, 5861; (*e*) Y. El-Ahmad, J.-D. Brion and P. Reynaud, *Heterocycles*, 1993, **36**, 1979; (*f*) S. A.-E. Ayoubi, F. Texier-Boullet and J. Hamelin, *Synthesis*, 1994, 258; (*g*) H. Bock, W. Seitz, N. Nagel, R. Baur and J. W. Bats, *Z. Naturforsch., Teil B*, 1997, **52**, 1125.

8 I. G. Binev, Y. I. Binev, B. A. Stamboliyska and I. N. Juchnovski, *J. Mol. Struct.*, 1997, **435**, 235.

9 (*a*) G. Brufola, F. Fringuelli, O. Piermatti and F. Pizzo, *Heterocycles*, 1996, **43**, 1257; (*b*) 1997, **45**, 1715.

10 (*a*) P. S. Rao and R. V. Venkataratnam, *Tetrahedron Lett.*, 1991, **32**, 5821; (*b*) D. Prajapati, J. Sandhu and S. Jagir, *Chem. Lett.*, 1992, 1945; (*c*) D. Prajapati and J. S. Sandhu, , *J. Chem. Soc., Perkin Trans. 1*, 1993, 739; (*d*) R. H. Khan, H. Rahat, R. K. Mathur and A. C. Ghosh, *Synth. Commun.*, 1996, **26**, 683.

11 R. A. Sheldon, *Chem. Ind.*, 1997, 12.

12 (*a*) Q. L. Wang, Y. D. Ma and B. J. Zuo, *Synth. Commun.*, 1997, **27**, 4107; (*b*) M. M. Heravi, M. Tajbakhsh, B. Mohajerani and M. Ghassemzadeh, *Ind. J. Chem., Sect. B. Org. Chem.*, 1999, **38**, 857.

13 (*a*) A. Corma and R. M. Martìn-Aranda, *Appl. Catal. A: General*, 1993, **105**, 271; (*b*) T. I. Reddy and R. S. Varma, *Tetrahedron Lett.*, 1997, **38**, 1721.

14 S. Ernst, T. Bongers, C. Casel and S. Munsch, *Stud. Surf. Sci. Catal.*, 1999, **125**, 367.

15 (*a*) F. Texier-Boullet and A. Foucaud, *Tetrahedron Lett.*, 1982, **23**, 4927; (*b*) J. A. Cabello, J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, *J. Org. Chem.*, 1984, **49**, 5195; (*c*) H. Moison, F. Texier-Boullet and A. Foucaud, *Tetrahedron*, 1987, **43**, 537; (*d*) A. Foucaud, H. Moison and F. Texier-Boullet, *Mol. Cryst. Liq. Cryst.*, 1988, 517.

16 S. Chalais, P. Laszlo and A. Mathy, *Tetrahedron Lett.*, 1985, **26**, 4453.

17 M. L. Kantam, B. M. Choudary, C. V. Reddy, K. K. Rao and F. Figueras, *Chem. Commun.*, 1998, 1033.

18 Y. V. S. Rao and B. M. Choudary, *Synth. Commun.*, 1991, **21**, 1163.

19 Y. V. S. Rao, D. E. De Vos and P. A. Jacobs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2661.

20 (*a*) E. Angeletti, C. Canepa, G. Martinetti and P. Venturello, *J. Chem. Soc., Perkin Trans. 1*, 1989, 105; (*b*) A. Katz and M. E. Davis, *Nature*, 2000, **403**, 286.

21 F. Bigi, L. Chesini, R. Maggi and G. Sartori, *J. Org. Chem.*, 1999, **64**, 1033.

22 L. F. Tietze and U. Beifuss, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and C. H. Heathcock, Pergamon Press, Oxford, 1991, vol. 2, ch. 1.11, p. 341.

23 (*a*) P. Laszlo, *Acc. Chem. Res.*, 1986, **19**, 121; (*b*) K. R. Kloestra and H. van Bekkum, *J. Chem. Soc., Chem. Commun.*, 1995, 1005; (*c*) P. W. Lednor and R. de Ruiter, *J. Chem. Soc., Chem. Commun.*, 1991, 1625.

24 F. Bigi, S. Carloni, B. Frullanti, R. Maggi and G. Sartori, *Tetrahedron Lett.*, 1999, **40**, 3465.

25 N. I. Sax, *Dangerous Properties of Industrial Materials*, 7 edn., N.Y., 1989.

26 For review on organic synthesis in water see: (*a*) R. Breslow, *Acc. Chem. Res.*, 1991, **24**, 159; (*b*) C. J. Li, *Chem. Rev.*, 1993, **93**, 2023; (*c*) A. Lubineau, J. Augè and J. Queneau, *Synthesis*, 1994, 741; (*d*) R. Breslow, K. Groves and M. U. Mayer, *Org. Lett.*, 1999, **1**, 117.

27 W. Blokzijl, M. J. Blandamer and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1991, **113**, 4241.

28 C. F. Bernasconi, J. L. Zitomer, J. P. Fox and K. A. Howard, *J. Org. Chem.*, 1984, **49**, 482.

29 I. Lee, C. K. Kim, B-S. Lee, C. K. Kim, H. W. Lee and I. S. Han, *J. Phys. Org. Chem.*, 1997, **10**, 908.

30 S. El-Taher, *Int. J. Quantum Chem.*, 1997, **62**, 419.

31 J. P. Richard, G. Williams and J. Gao, *J. Am. Chem. Soc.*, 1999, **121**, 715 and references cited therein.

32 An additional signal, a quintet at δ 12.18 (CD_2, J = 21.7 Hz), is due to the exchange of both hydrogens.

33 K. Sung, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1169.

34 M. Hojatti, A. J. Kresge and W.–H. Wang, *J. Am. Chem. Soc.*, 1987, **109**, 4023.

35 In a preliminary experiment we observed that the reaction time can be decreased to 1 h.

36 L. N. Kurkovskaya, N. K. Genkina and V. L. Shugol, *J. Struct. Chem.*, 1995, **35**, 638.

37 The purification from traces of the starting aldehyde, if present, was performed by crystallisation.

Liquid phase acylation of amines with acetic acid over HY zeolite†

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Alkyl, aryl and heterocyclic amines are efficiently converted to the corresponding amides with acetic acid over HY zeolite; the catalyst can be re-used with no loss of activity.

Introduction

The acylation of an amino group is a fundamental process in organic chemistry and has great importance in organic synthesis.[1] The reaction is generally carried out using acid anhydrides or acid chlorides in the presence of tertiary amines.[2] Recently clays such as K-10 and KSF were reported[3] for the acylation of amines with acetic anhydride. More recently LiCl has been reported[4] to promote the acylation of amines with acetic anhydride. Tetrabutylammonium salts,[5] cyanide anions[6] and $Cp_2Sm(thf)_2$[7] are also used in the acylation of amines with esters.

Heterogeneous organic reactions over zeolites,[8] montmorillonite[9] and hydrotalcites[10] have received much attention due to the following advantages: (i) easy separation from the reaction mixture, (ii) reusable catalysts, (iii) easy modification of their surface and pore structure, and (iv) eco-friendly nature. The use of acetic acid rather than acetic anhydride or acetyl chloride is both economically and environmentally advantageous. Herein we report an efficient method for the acylation of amines to the corresponding amides using acetic acid catalyzed by HY zeolite.

Results and discussion

Table 1 shows the acylation of various amines with acetic acid in the presence of HY zeolite. The reaction proceeds smoothly at the reflux temperature of acetic acid for 5–24 h (Scheme 1). It is interesting, though perhaps not surprising to note that electron donating groups facilitate the reaction whereas electron withdrawing groups slow down the reaction. Aryl amines undergo reaction at a relatively faster rate when compared to alkyl amines. Among the heterocyclic amines, the reaction is slower for 2-aminopyridine when compared to furfuryl amine. It is noteworthy to observe that the amino groups could be preferentially acylated in the presence of a hydroxy group (Table 1, entry 15). As can be seen from Table 1, the application of this method to a variety of different substrates shows the generality and versatility of the process. In the control experiment without catalyst only small quantities of benzylamine was converted to the amide in the same reaction time.

Here we present a possible mechanism of this acylation. At the Bronsted acid sites of HY zeolite the carbonyl group is protonated and the resulting acylium ion further reacts with amine to give the corresponding amide (Scheme 2).

The zeolite was easily separated from the reaction mixture by simple filtration. Further, HY zeolite was reused in the acylation of benzylamine. The results are shown in Table 2. The high catalytic activity and selectivity were maintained even after third reuse. The catalyst was highly crystalline before and after the reaction which was confirmed by XRD. There was no leaching of aluminum or silicon from HY zeolite observed by elemental analysis.

Conclusions

We have demonstrated the use of HY zeolite as a catalyst for the acylation of amines with excellent yields using acetic acid as the acetyl source. The present method is applicable to a variety of alkyl, aryl and heterocycle amines.

Experimental

HY zeolite was obtained from Zeolyst Corporation, USA. The SiO_2/Al_2O_3 ratio was 5.2 and surface area 690 $m^2\ g^{-1}$. In a typical procedure a 50 ml two necked round bottomed flask was charged with 300 mg of HY zeolite, benzylamine (214 mg, 2 mmol) and acetic acid (4 ml). The reaction was carried out at the reflux temperature (116 °C) of acetic acid with stirring. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction the catalyst was filtered off and the solid obtained washed with ethyl acetate. The combined filtrates were washed with saturated sodium hydrogencarbonate solution. The organic extract was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to yield 295 mg (99%) of *N*-benzylacetamide.

Green Context

The acylation of amines is one of the most important organic transformations. Normally acid halides or anhydrides are used as reagents. Several solid catalysts including clays have been reported as being effective in such reactions although clays can be difficult to reuse without some loss in activity. Here a clean synthesis approach to this reaction is employed with the reagent being acetic acid (leading to water waste only) and the catalyst an HY zeolite which can be easily recovered from a batch reaction (though could also be the basis of a continuous process) and reused with no loss in activity. ***JHC***

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† IICT Communication No. 4457.

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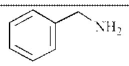
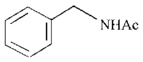
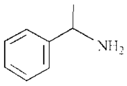
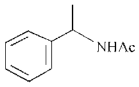
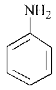
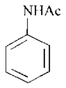
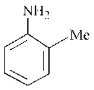
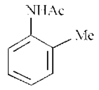
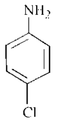
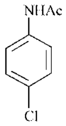
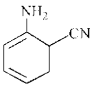
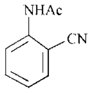
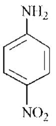
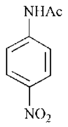
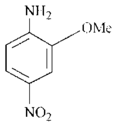
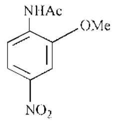
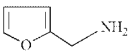
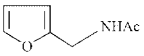
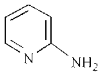
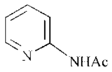
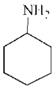
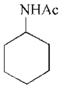
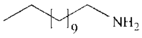
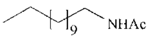
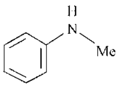
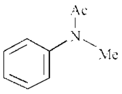
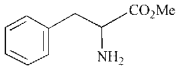
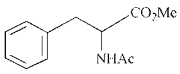
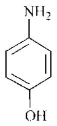
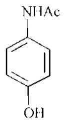
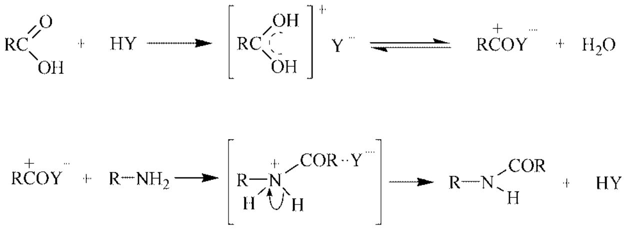
Table 1 Acylation of amines with acetic acid over HY zeolite

Entry	Substrate	Product[a]	t/h	Yield(%)
1			5	99
2			5	98
3			6	99
4			6	99
5			6	99
6			8	< 10
7			20	78
8			24	56
9			6	98
10			24	85
11			8	98
12			8	40
13			20	81
14			8	98
15			8	95

[a] Characterized by NMR, MS and GC analysis.

$$RNH_2 \xrightarrow[116\ ^\circ C,\ 5\text{–}24\ h]{AcOH,\ HY\ zeolite} RNHAc + H_2O$$

Scheme 1



Scheme 2

Table 2 Recycling of the HY zeolite catalyst in the acylation of benzylamine

Recycle no.	Conversion of benzylamine(%)	Yield of amide (%)
1	98	95
2	99	97
3	99	98

Acknowledgments

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References

1 T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Wiley, New York, 2nd edn., 1991.
2 H. Hofle, W. Steglich and H. Vorbruggen, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 569.
3 A. X. Li, T. S. Li and T. H. Ding, *Chem. Commun.*, 1997, 1389.
4 G. Sabitha, B. V. Subba Reddy, R. Srividya and J. S. Yadav, *Synth. Commun.*, 1999, **29**, 2711.
5 Y. Watanabe and T. Mukaiyama, *Chem. Lett.*, 1981, 285.
6 T. Hogberg, P. Strom, M. Ebner and S. Ramsby, *J. Org. Chem.*, 1987, **52**, 2033; S. J. Chen, S. T. Chen, S. Y. Chen and K. T. Wang, *Tetrahedron Lett.*, 1994, **35**, 3583.
7 Y. Ishii, M. Takeno, Y. Kawasaki, A. Muromachi, Y. Nishiyama and S. Sakaguchi, *J. Org. Chem.*, 1996, **61**, 3088.
8 W. Holderich, M. Hesse and F. Naumann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 226; K. A. Koyono and T. Tatsumi, *Chem. Commun.*, 1996, 145.
9 J. I. Tateiwa, E. Hayama, T. Nishimura and S. Uemura, *J. Chem. Soc., Perkin Trans 1*, 1997, 1923; G. Guiu, A. Gill, M. Montes and P. Grange, *J. Catal.*, 1997, **168**, 450.
10 C. Cativiela, F. Figueras, J. M. Fraile, J. I. Garcia and J. A. Mayoral, *Tetrahedron Lett.*, 1995, **36**, 4125.

Selective *O*-alkylation of cresols with methanol: catalysis by Cs loaded silica, a solid base

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The *O*-alkylation of hydroxy aromatic compounds such as cresols is conveniently carried out over easy to prepare alkali loaded silica catalysts in the vapour phase with high selectivities (*ca.* 99%). The activities of the catalysts increase with alkali loading and the basicity of the metal (Cs > K > Na > Li). In the case of *p*-cresol over Cs/SiO_2, the yield of the *o*-alkylated product is as high as 94%.

Introduction

Methyl anisoles are important chemicals used in the production of dyes and agrochemicals besides finding use as antioxidants for oils and greases and as stabilizers for plastics. Conventionally, methyl anisoles are produced by the methylation of cresols with dimethyl sulfate and alkali or with a methyl halide and sodium hydroxide in tetrahydrofuran. The above methylating agents are corrosive and toxic. Moreover, these conventional processes are atom inefficient and generate waste. For example, if cresol was alkylated stoichiometrically with dimethyl sulfate and the H_2SO_4 neutralized with sodium carbonate, the atom efficiency[1] (AE) would only be 0.58. On the other hand, the direct methylation with methanol will have an AE of 0.87, the only by-product being water. Methanol is far cheaper and easier to handle than methyl sulfate.

The conventional methylation reactions are carried out in the liquid phase in batch reactors with attendant economic penalties due to their noncontinuous nature and difficulties in product work-up. On the other hand, continuous processes using solid catalysts and fixed bed reactors offer many advantages such as ease of separation of catalyst and product, catalyst reusability, ease of product work-up and continuity of operation. The fixed bed vapour phase methylation of a number of aromatic hydroxy compounds using methanol or dimethylcarbonate has been reported over basic catalysts. For example, Ono *et al.*[2,3] have alkylated catechol with dimethylcarbonate (DMC) to veratrole over K/Al_2O_3 and to guiacol over Al_2O_3. The alkylation of phenol to anisole with DMC[4] and methanol[5] has been reported over basic X-zeolite. Other catalysts used in the *O*-alkylation of phenol are ZSM-5,[6] $AlPO_4$/SAPO molecular sieves[7] and metal sulfates/Al_2O_3.[8] To the best of our knowledge, the vapour phase methylation of cresols has not been reported. Here we report the vapour phase methylation of cresols with high selectivities and conversions over Cs loaded silica.

Experimental

Fumed silica (Cab-O-Sil; Fluka, surface area = 166 $m^2\ g^{-1}$) was used as a support for the alkali metal oxides. The different alkali loaded catalysts were prepared by an impregnation procedure using minimum amounts of aqueous metal hydroxide (Li, Na and K) or acetate (Cs) solutions (incipient wetness method). The catalysts were dried at 373 K (6 h) and calcined at 773 K (6 h).

The catalytic experiments were carried out in a vertical downflow glass reactor (15 mm i.d.). The catalyst (2 g) was used in the form of granules (10–22 mesh) prepared by pelleting the powders and crushing into the desired size. The zone (*ca.* 15 cm long) above the catalyst bed packed with ceramic beads served as the feed preheater. The reactor was placed inside a temperature controlled furnace (Geomecanique, France) with a thermocouple placed at the center of the catalyst bed for measuring the reaction temperature. The catalyst was activated in flowing air (20 ml min^{-1}) at 773 K for 3 h prior to flushing in N_2 and adjustment of temperature for the start of the experiment. The feed (cresol–methanol, mole ratio 1:5) was passed using a syringe pump (Braun, Germany) along with a small amount of N_2 gas. The product was cooled in a water-cooled (ice cold) condenser, collected in a receiver and analyzed in a gas chromatograph (HP5880A; capillary column HP1, 50 m × 0.2 mm; FID detector). Products were identified by GC-MS and GC-IR.

Results and discussion

The catalytic activities of silica samples loaded with different alkali metals (20 wt% as metal) in the *O*-alkylation of the three cresols at 673 K are presented in Table 1. Fumed silica alone had negligible activity under the conditions of the reaction. Though the selectivities of the *O*-alkylated products are nearly

Green Context

This article tackles two important issues relevant to green chemistry, the avoidance of salt waste in an important process and the move from batch to continuous processing. Salts represent a high proportion of the waste generated by chemical manufacturing. Even a simple methylation of a phenolic compound using traditional methods leads to salt waste. This can be avoided by use of methanol rather than a methyl halide so that the only by-product is water. Most chemical processes used by use of the fine and speciality chemicals manufacturing industries are carried out in batch reactors with the associated downtime and waste generated in changing from batch to batch. In many cases it may be feasible to move to continuous processing and here, for the first time, a continuous process for cresol methylation is described. At the heart of the new process is a solid base which can have good on-line lifetimes. ***JHC***

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the same (about 99% over all the catalysts for all the cresols), the conversions increase with the basicity of the alkali metal (Cs > K > Na > Li) and in the order: *p*-cresol > *m*-cresol > *o*-cresol. As Cs/SiO_2 was found to be the most active catalyst, more experiments were carried out at different Cs loading, WHSV (weight hourly space velocity) and temperatures over Cs/SiO_2 catalysts. These data are presented in Table 2 and Fig. 1. A general trend of increasing activity with increasing alkali metal loading and temperature is noticed. With increasing space velocity, though there is a slight decrease in activity, the drop is only about 12% when the space velocity is increased four fold (from 1.33 to 5.32 h^{-1}). Similarly, time on stream (TOS) studies also reveal only a small decrease in activity [*ca.* 13% in 5 h for Cs(20)SiO_2] with increasing duration of run (studied up to 5 h). The above catalyst exhibited very little activity loss (< 5%) after 3 regenerations in air (773 K, 6 h) and reuse. The mechanism of the reaction probably involves the formation of a transient phenolate species on the basic O^{2-} on the surface and its reaction with a $(CH_3)^{\delta+}(OH)^{\delta-}$ species adsorbed on the adjacent alkali ion as shown below. The relative activities of the three isomers over the different catalysts probably depend on parameters such as the relative ease of formation of the phenolate ion at the surface, its stabilization and steric effects.

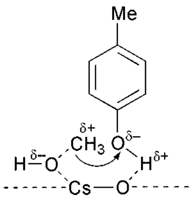

Table 1 Influence of the nature of the alkali metal on conversion and selectivity

	Surface	*o*-Cresol		*m*-Cresol		*p*-Cresol	
Catalyst[a]	area[b]/ $m^2 g^{-1}$	Conv. (mol%)	Sel. (mol%)	Conv. (mol%)	Sel. (mol%)	Conv. (mol%)	Sel. (mol%)
Li(20)Si	104	6.6	> 99	7.4	> 99	9.1	> 99
Na(20)Si	99	7.4	> 99	8.1	> 99	9.8	> 99
K(20)Si	91	32.5	> 99	36.6	> 99	38.6	> 99
Cs(20)Si	70	79.0	> 99	81.9	> 99	88.5	> 99

[a] The number in brackets denotes the wt% of alkali metal loaded on SiO_2. Conditions: 673 K; time on stream = 1 h; WHSV (h^{-1}) = 2.66; N_2 flow = 1.08 l h^{-1}. [b] Measured by N_2 adsorption (BET method).

Table 2 Influence of Cs loading on activity and selectivity

	Surface	*o*-Cresol		*m*-Cresol		*p*-Cresol	
Catalyst[a]	area[b]/ $m^2 g^{-1}$	Conv. (mol%)	Sel. (mol%)	Conv. (mol%)	Sel. (mol%)	Conv. (mol%)	Sel. (mol%)
Cs(1)Si	149	22.9	> 99	31.8	> 99	13.9	> 99
Cs(5)Si	121	52.3	> 99	68.8	> 99	58.2	> 99
Cs(10)Si	102	64.5	> 99	72.5	> 99	77.2	> 99
Cs(20)Si	70	79.0	> 99	81.9	> 99	88.5	> 99
Cs(30)Si	56	84.5	> 99	88.0	> 99	94.0	> 99

[a] The number in brackets denotes the wt% of Cs loaded on SiO_2. Conditions: 673 K; time on stream = 1 h; WHSV (h^{-1}) = 2.66; N_2 flow = 1.08 l h^{-1}. [b] Measured by N_2 adsorption (BET method).

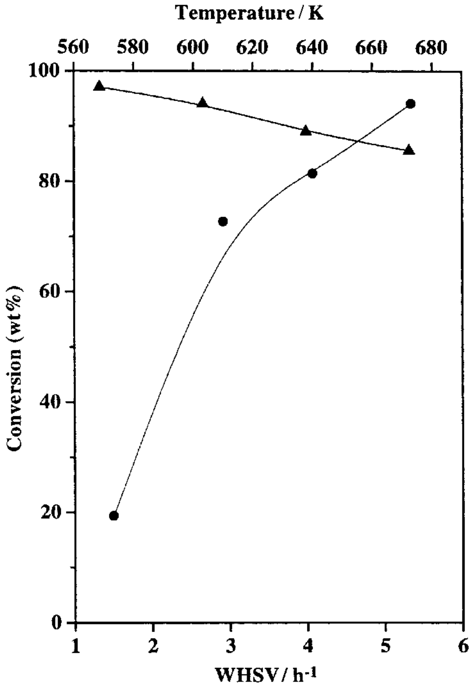

Fig. 1 Influence of temperature and space velocity on conversion of *p*-cresol over Cs(30)SiO_2. ▲ WHSV *vs.* conversion (conditions: 673 K; *p*-cresol: MeOH = 0.2 (mol/mol); time on stream = 1 h; N_2 flow = 1.08 l h^{-1}). ● Temperature *vs.* conversion (conditions: WHSV (h^{-1}) = 2.66; *p*-cresol: MeOH = 0.2 (mol/mol); time on stream = 1 h; N_2 flow = 1.08 l h^{-1}).

Conclusions

The studies reveal that Cs loaded fumed silica is an excellent catalyst for the *O*-alkylation of cresols in the vapour phase. High conversions at high *O*-alkylation selectivities are revealed.

References

1 R. A. Sheldon, *Chem. Ind. (London)*, 6th Jan. 1997, p. 13.
2 Yue Fu, T. Baba and Y. Ono, *Appl. Catal. A: General*, 1999, **176**, 201.
3 Yue Fu, T. Baba and Y. Ono, *Appl. Catal. A: General*, 1998, **166**, 419.
4 Zi-Hua Fu and Y. Ono, *Catal. Lett.*, 1993, **21**, 43.
5 S. C. Lee, S. W. Lee, K. S. Kim, T. J. Lee, D. H. Kim and J. C. Kim, *Catal. Today*, 1998, **44**, 253.
6 M. Renaud, P. D. Chantal and S. Kaliaguine, *Can. J. Chem. Eng.*, 1986, **64**, 787.
7 V. Durgakumari, S. Narayanan and L. Guczi, *Catal. Lett.*, 1990, **5**, 377.
8 M. C. Samolada, E. Grigoriadou, Z. Kiparissides and I. A. Vasalos, *J. Catal.*, 1995, **152**, 52.

Illustrations towards quantifying the sustainability of technology

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This paper attempts to quantify the sustainability of technological processes. It is based on thermodynamics with energy carriers and materials (products, waste, *etc.*) expressed in the same calculable quantity–exergy (Joule). The results have three considerations. One factor reflects to that extent renewable resources are used. In addition, the technological efficiency has to be accounted for as it affects sustainability. Finally, the results take into account the generation of waste products and the exergy required for converting the waste into products which are harmless or assimilable in the ecosphere. The proposed measure of sustainability has been illustrated for two types of products. In the first illustration, ethanol production was studied. Two routes were investigated, one starting from fossil oil and the other from agricultural products. Additionally, a route based on the synthesis from carbon dioxide and hydrogen was examined, in which hydrogen was generated by splitting water with electricity from photovoltaic solar energy conversion. The second product studied was electricity, generated from the combustion of natural gas or from photovoltaic solar energy conversion. The merit of the obtained results are that they treat technological sustainability not only in qualitative but also in quantitative terms. The insights obtained can help to account for sustainability in the development of new concepts of chemical technology.

Introduction

The term ‘sustainability’ has several definitions. The current definition by Brundlandt in 1987 is widely accepted: ‘Sustainable development is a social development which fulfils the needs of present generations without endangering the possibilities of fulfilment of the needs of future generations’.[1] From this definition, it is clear that sustainable development can only be accomplished if it is approached in a multidisciplinary way. The definition raises questions in philosophic, economic, political, social and natural sciences.

In this view, natural sciences are highly important. They generate the technology to manufacture goods for society, starting from natural resources. Although these ‘applied sciences’ or technology are essential for the delivery of goods, they can simultaneously endanger current and future generations. The threat can be direct (acute danger or toxicity) or, on a longer time scale, the technosphere can endanger future generations in two ways. The technosphere interacts with the ecosphere *via* two mechanisms. It extracts material and energy resources from the ecosphere. So, the first threat of the technology on sustainability lies in the rate of consumption of resources. If the consumption rate of these resources in technological applications is higher than the rate of resource production in the ecosphere, then the needs of mankind in the future may be endangered. Secondly, the technosphere emits waste products into the ecosphere. This means that these emitted products may damage the ecological mechanisms and hence the resource production capacity of the ecosphere.

Sustainable development can only be guaranteed if a number of boundary conditions, drawn from different science fields, are fulfilled. From the previous paragraph, it is clear that from the applied natural sciences two direct boundary conditions can be mentioned: resources required for producing goods must not run out and emissions from the technosphere must not endanger the ecological system since it can affect natural resource production. These two important boundary conditions are also reflected in the life cycle analysis approach.[2,3] From these two conditions, it is evident that a sustainable technology must be as efficient as possible. High efficiencies reduce the required amount of input resources and generated output emissions. The efficiency can be seen as a third indirect condition of sustainability for the technosphere.[4] In this view van den Berg *et al.*[5] identified three aspects of sustainability: use of renewable resources, efficiency of processes and emissions.

The first sustainability condition requires an insight into the different resources available in the ecosystem. First, mineral resources are available, *e.g.* metal ores, mineral oils, which need millions of years to be generated and hence are non-renewable. These stocks can be seen as natural deposits. Secondly, there are

Green Context

Sustainability is a much used but also much mis-used term. This paper examines the meaning of the word in the context of technology and attempts to introduce a degree of quantification to it. A technological process such as the manufacture of a chemical product can be non-sustaining if it takes raw materials from the ecosphere at a rate faster than the raw material is being generated or if it produces products (typically waste) that can damage the ecological mechanisms and hence resource production. Here, three aspects of sustainability, the use of renewable resources, the technological efficiency and the waste produced, are quantified for two types of products. It seems very likely that this type of calculation will be increasingly applied as we seek the least eco-threatening option for future manufacturing. ***JHC***

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so-called renewable resources, which are delivered by the ecosphere on a time scale of years and can be considered as funds.

The second condition for a sustainable technosphere is the prevention of emissions interfering with processes in the ecosphere. Emissions of damaging products, like chlorofluorocarbons and dioxins, must be avoided. Indeed the assimilation capacity of the ecosphere for these types of compounds is very limited. However, even this prerequisite can be unsatisfactory to meet the second condition: too high emission rates of 'harmless' compounds might disturb the ecosphere (*e.g.* CO_2). The second condition for sustainability implies also that the production of 'harmless' (waste) products may not exceed the assimilative uptake rate of these compounds in the ecosphere. The two previous points can be unified into one overall condition: the solar driven closed cycle of materials exchange between ecosphere and technosphere. This is represented in Fig. 1. High quality products delivered by the ecosphere as wood and wheat, are consumed by the technosphere and subsequently returned to the ecosphere as low quality products, carbon dioxide and water. Thanks to solar power, the ecosphere is able to assimilate these waste products and to deliver high quality products.

Technology is basically a set of processes in which input materials and energy carriers are transformed. The second law of thermodynamics states that all these processes generate entropy, reflecting a quality loss of the input energy. The exergy concept, related to availability, is the thermodynamic tool which expresses the quality of energy: it is the amount of the work that can be obtained from a non equilibrium state with respect to an equilibrium environmental state, the so-called dead state, *via* a reversible process initially adiabatically to T_0, isothermally to P_0 and finally into equilibrium with the dead state. There is extensive information available in the literature about the exergy concept.[6–10] The theoretical background has been developed for decades as presented in the overview of Gaggioli;[11] however the implementation in practice was rather limited. Nowadays, increasing attention is paid to the development of technological operations in the thermomechanical and chemical technology field, see Bejan[12] and Hinderink *et al.*[13,14] Wall explored the potential of the exergy concept in several fields, *e.g.* in analysing national economies.[15–17] He proposed to introduce an exergy tax to improve present resource use and to decrease environmental destruction.[15] The potential to use exergy as an ecological indicator has been recently investigated by Gong.[18]

The irreversibility of each technological process and the inherent degradation of the quality of energy is related to a decrease of exergy. This degradation process in the technosphere is illustrated in Fig. 1. Starting from high exergetic materials delivered by the ecosphere, the technosphere degrades the exergy content. The exergy approach provides a quantitative base with the same unit (Joule) for all types of energy carriers and materials. The exergy concept has the capability to serve as a basis to quantify the sustainability of the technological aspect of the society. All different types of material streams, including resources, products and non-products (wastes), and technological operation efficiencies can be judged on the same scale.

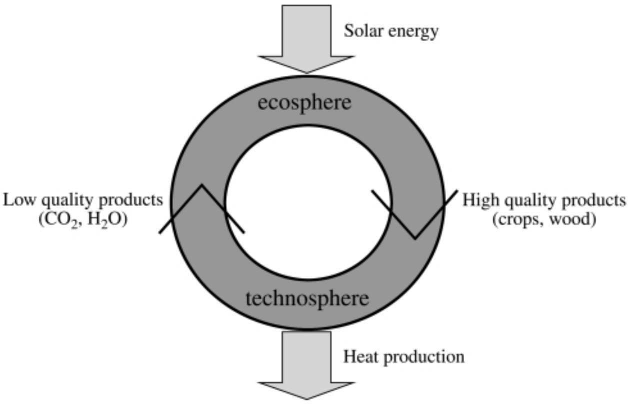

Fig. 1 Solar driven closed cycle condition for a sustainable ecosphere/technosphere interaction.

The aim of this work is to find a measure to quantify sustainability. Nowadays technologies are not completely sustainable, therefore it is useful to develop a quantitative tool indicating in how far technology is sustainable. In a first step, different thermodynamically based factors contributing to sustainability will be treated. Starting from these contributions, a sustainability coefficient is to be defined. Further on, the developed quantitative approach of sustainability will be illustrated for two types of product. In a first illustration, three technological options to produce ethanol will be compared for their sustainability. Secondly, two routes to produce electricity will be treated.

Proposed quantification of sustainability

As a first element in investigating the sustainability of technological processes, the nature of the resources has to be considered. First, a distinction has to be made between resources that are renewable and those that are non-renewable resources. Renewable resources are defined as resources that are generated at a rate at least as high as the consumption rate; and non-renewables are those with a higher consumption rate than production rate. This is illustrated in eqn (1), *i.e.* for a renewable resource the renewability condition ρ is equal to or higher than 1:

$$\rho = \frac{R_{\text{prod}}}{R_{\text{cons}}} \tag{1}$$

Now, based on the renewability condition, consumed resources can be divided into renewables and non-renewables. Next, a renewability parameter α can be defined as the fraction of renewable exergy consumption with respect to the total exergy consumption:

$$\alpha = \frac{R_{\text{cons, renewable}}}{R_{\text{cons}}} \tag{2}$$

If one wants to calculate the coefficient α, then all resources used in the production processes to manufacture the product have to be considered. All energy carriers brought into the production process have to be traced back to the resources from the ecosphere required to produce them. Main extractables are fossil organic resources ($\rho = 0$), inorganic ores ($\rho = 0$) and solar energy ($\rho = 1$). The first two categories are non-renewable. By consequence, the coefficient α reflects the fraction of direct solar exergy in the exergy consumption of a process.

Apart from solar energy, some other resources based on solar energy such as wind or hydropower are renewable. These two resources are driven by solar energy in an indirect way: wind is generated by solar induced atmospheric pressure gradients whereas hydropower is available due to rainfall produced *via* solar driven water evaporation. Next to the main 'high quality' (or high exergetic) inputs as solar energy, mineral resources and fossil fuels, processes may need some 'low quality' products, *e.g.* carbon dioxide or water. In exergetic calculations, their role is almost negligible: atmospheric carbon dioxide, important for photosynthesis, has a zero exergy value, whereas the exergy of liquid water at 25 °C is only 0.05 MJ kg^{-1} in the environment as defined by Szargut *et al.*[9] Basically these resources are renewable provided that they are recycled into the ecosphere in the same form.

Sustainable technology has to meet a second condition: no harmful products are to be emitted by the technosphere. All resources consumed must include exergy required for the production of the desired product, but also for the abatement of harmful emissions generated both during the production and destruction stage of the product. This is represented in Fig. 2. The total exergy required for a production process is:

$$R_{\text{cons}} = R_1 + R_2 + R_3 \tag{3}$$

with R_1 the exergy required for the abatement of emissions during production, R_2 the exergy required for the production process and R_3 the exergy required for transforming the product, after its use and if possible recycling, into harmless products (all in GJ yr^{-1}). The emission of harmful waste streams is basically a double loss for a process. Indeed, the waste stream can contain exergy which may be used in the process. Secondly, it can require an abatement exergy.

Now we can define an environmental parameter η_1 of the production process:

$$\eta_1 = \frac{R_2}{R_1 + R_2 + R_3} \tag{4}$$

where $0 \leqslant \eta_1 \leqslant 1$. If we have an environmental parameter $\eta_1 = 1$ for the production process, the abatement exergy requirements R_1 and R_3 become zero. The second condition does not mean that the emitted compounds have no exergy content after treatment: this is not always necessary. The emissions have to be treated using exergy inputs R_1 and R_3 so that they can be assimilated by the ecosphere or at least that they do not affect the resource production capacities of the ecosphere.

Next to the environmental parameter, the efficiency of the production process is also important to express sustainability: the more efficient a process can generate a product out of a fixed number of exergy resources, the higher the sustainability. A production efficiency parameter η_2 is defined as

$$\eta_2 = \frac{P}{E + P + I_P} \tag{5}$$

with $0 \leqslant \eta_2 \leqslant 1$ and $E + P + I_P = R_2$ (see Fig. 2). E represents the non-useful exergetic emission rate of the production process (in GJ yr^{-1}), whereas P is the exergetic production rate of useful products (GJ yr^{-1}). The irreversibility of the process is expressed by I_P (GJ yr^{-1}). By combination of the eqns. (4) and (5) and considering eqn. (3), it can be found that the resource consumption is proportional to the exergy content of the useful products generation rate P (GJ yr^{-1}) and inversely proportional to the environmental and production efficiency parameters η_1 and η_2:

$$R_{\text{cons}} = \frac{P}{\eta_1 \eta_2} \tag{6}$$

or

$$R_{\text{cons}} = \frac{P}{\eta} \tag{7}$$

in which $\eta = \eta_1\eta_2$ is the overall exergetic efficiency of the technosphere.

From the two previous paragraphs expliciting the two boundary conditions for sustainability in quantitative terms, it is deduced that the maximal level of sustainability of the technosphere is attained if it does not extract resources faster than produced by the ecosphere ($\alpha = 1$) and if all extracted resources are fully transformed into products, without damaging the ecosphere ($\eta = 1$). From this point of view, a sustainability coefficient (S) can be defined:

$$S = S_\alpha + S_\eta = \frac{(\alpha + \eta)}{2} \tag{8}$$

The meaning of the coefficient S is illustrated graphically in Fig. 3. A technology can score values of $0 < \alpha/2 < 1/2$ and $0 < \eta/2 < 1/2$ on the renewability and efficiency axis, respectively. Projecting these scores on the sustainability axis, contributions to sustainability due to renewability and efficiency results in $0 < S_\alpha < 1/2$ and $0 < S_\eta < 1/2$, so that the sustainability coefficient $S = S_\alpha + S_\eta$ is normalised between 0 and 1. The higher the coefficients α and η, the closer the technosphere is to overall sustainability. If both coefficients are equal to 1, then $S = 1$. The case with the largest distance to sustainability ($\alpha = \eta = 0$) gives rise to $S = 0$.

Illustrations

The measures of sustainability as proposed in the previous section, are now applied to two products: ethanol and electricity. Ethanol is a widely used chemical produced by industry as well from mineral resources *via* cracking of ethylene

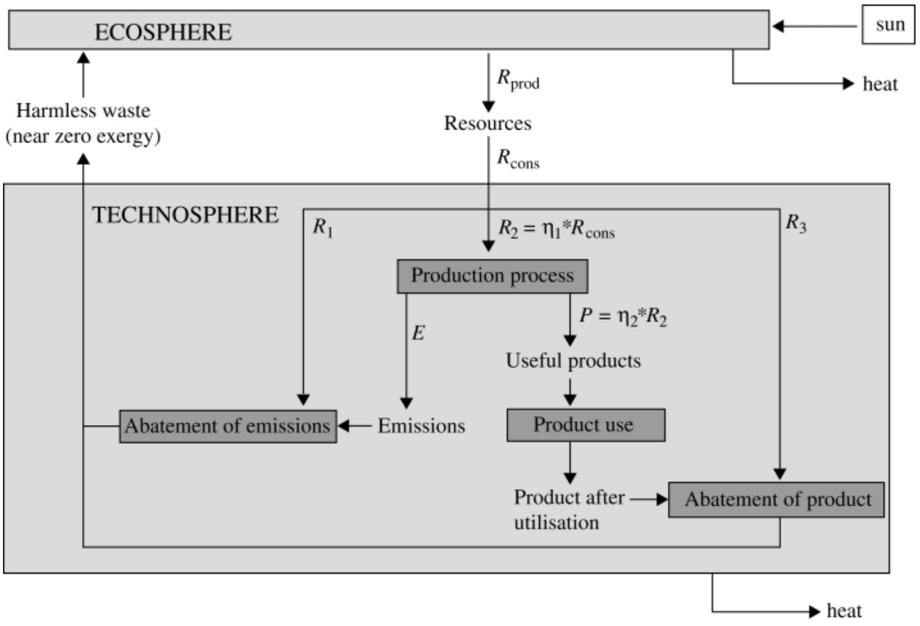

Fig. 2 Exchange of resources and waste in a sustainable ecosphere/technosphere system.

and hydration to ethanol, as by a combination of agriculture and fermentation. It can serve as an energy carrier for *e.g.* vehicles (Brazil, United States), and as a solvent or chemical reacting agent in industry. Moreover, ethanol produced from agricultural products is consumed by man in several types of beverages. Mulder *et al.*[19] have evaluated the exergetic efficiency of several technological pathways for the production of ethanol. First, they examined the ethanol production from fossil resources and the pathway *via* agriculture and fermentation. Next, they examined the production *via* hydrogen by use of photovoltaic cells and water electrolysis. In this route ethanol is synthesised in a second step, starting from hydrogen and carbon dioxide, the latter captured from flue gases from power plants. The basic idea was to enhance the content of renewable resources (solar energy) in the final product and to close the material cycle as much as possible. As in agriculture, which can be seen as a technology based on the same biological mechanisms as occurring in the ecosphere, the basic resources are water and carbon dioxide, converted by means of solar energy into high quality products (photosynthesis). These products are degraded in nature into the initial low quality products, CO_2 and H_2O, as also after use as fuel in furnaces to produce steam and/or electricity, closing the material cycles.

Next, electricity can be generated by combustion of fossil fuels such as gas, coal and oil. For example, Tsatsaronis and Moran[20] evaluated an electric power cogeneration system, fueled by natural gas, delivering electricity and steam. Next to this cogeneration power system, the production of electricity by multicrystalline silicon photovoltaic solar cells can be considered based upon already available production facilities.[19]

Evaluation of the sustainability parameters of ethanol production routes

The required inputs for the production of ethanol from fossil resources are presented in Table 1. The input requirements for the ethylene intermediate are those for an averaged weighted situation over 19 European production facilities, where the process consists of two main steps, *i.e.* oil refining and nafta cracking.[21] Next to this input, ethanol production without damaging the environment requires that all ‘harmful’ waste products from the production process and from the waste product are treated. The input of non-renewable fuels, which are transformed into CO_2 and H_2O, gives rise to environmental problems by increasing the atmospheric CO_2 concentration. So the ideal sustainable way to emit this product, would be to transform it into the original fuel and store it into its original underground location. However, from a technological point of view this is not an option: there is no technology available at the moment. One of the leading options to reduce the impact of CO_2 is to store it underground in depleted oil and gas wells.[22] In this way, impact on climate change is avoided. Therefore, CO_2 has to be recovered from flue gases and subsequently pumped underground. Based on the data on CO_2 recovery *via* ethanolamine absorption and stripping, and subsequent compression to 80 atm[23] for storage underground, it can be calculated that 5.86 MJ exergy is required per kg CO_2 produced from non-renewables. So from the information on the required fossil resources to produce ethylene[21] and considering the amount of carbon remaining in the intermediate ethylene, the amount of emitted CO_2 during the ethylene production stage can be calculated (0.97 kg CO_2/kg EtOH). If ethylene is converted to ethanol at 60 atm and 300 °C with zeolite catalysts,[24] then it can be calculated that 158.6 kJ of compression work/mole EtOH has to be delivered. If the compressor has an exergetic efficiency of 80% and if the electricity delivery, using *e.g.* natural gas, for the compressor has a 35.3% efficiency,[20] then 0.305 kg natural gas/kg EtOH is needed, resulting in a CO_2 production of 0.65 kg/kg EtOH. So, given that 0.97 and 0.65 kg CO_2 are produced per kg ethanol at the ethylene production and hydration stage respectively, an abatement exergy of $R_1 = 9.5$ MJ/kg EtOH is required. Next, ethanol is converted to CO_2 and water, *e.g.* when it is used as a fuel or by combustion after its use as a solvent. With a production of 1.91 kg CO_2/kg EtOH, an abatement exergy R_3 of 11.2 MJ/kg EtOH must be delivered.

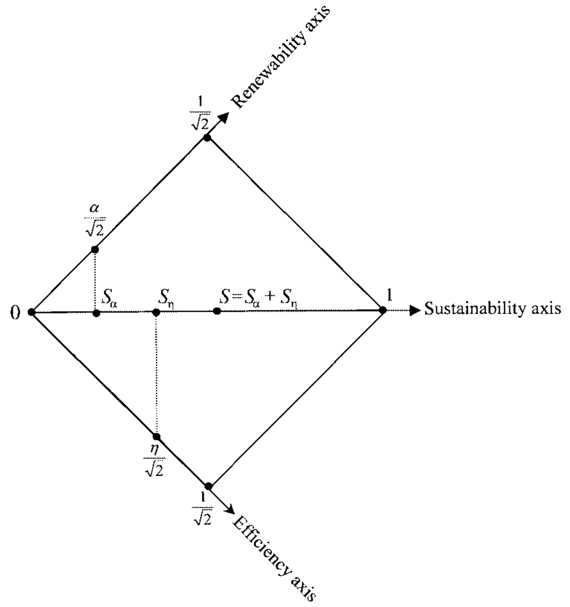

Fig. 3 Graphical representation of the sustainability S on the sustainability axis, with contributions by renewability S_α and efficiency S_η; and the scores $\alpha/ 2$ and $\eta/ 2$ on the renewability and efficiency axis, respectively.

Concerning the agriculture/fermentation pathway, at a first glance one could expect a coefficient $\alpha = 1$, since the main source input is solar energy. However, industrial agriculture and fermentation require mineral resources and fossil fuels for the production of nutrients and pesticides, and power for the use of machinery in agriculture and fermentation (Table 2). Furthermore, this production method delivers also wheat straw (from agriculture), gluten and cake (both from fermentation), being all useful products. Therefore the resources in the agricultural step must be attributed in a proportional way to ethanol and the other useful products (Table 2). So it is found that the production of ethanol requires an input of $R_2 = 13243$ GJ/ha yr.

Next to this input, to produce ethanol without damaging the environment, all ‘harmful’ waste products from the production process and from the waste product must be treated. The abatement exergy R_3 of the product is zero, since it is converted back into CO_2 and H_2O, closing the material cycle. Also the CO_2 emitted by converting starch into ethanol and CO_2 does not have to be treated since it closes the carbon cycle. However, at

Table 1 Exergetic inputs, intermediates and outputs for the production of ethanol from fossil resources

	Products	GJ/ha yr Total
Inputs		
	Oil for ethylene production	23.12
	Gas for ethylene production	23.85
	Other mineral resources for ethylene production	0.94
	Gas for work production for hydration	12.20
	Water input for hydration	0.02
Intermediate		
	Ethylene	29.6
Outputs		
	Ethanol	29.5

Input data for the production of ethylene are mean European data [19] the agricultural production step and during the fermentation, non-renewable resources are used. For the production of wheat, diesel fuel for mechanical power is required, next to fossil resources for the production of nutrients and pesticides,[19] resulting in an emission of 1064 kg CO_2/ha. Next, use of natural gas for electricity and steam production[19] for fermentation results in an emission of 1179 kg CO_2/ha. This means that an abatement exergy to be attributed to ethanol of $R_1 = 6.94$ GJ/ha yr is required.

As a third option, Mulder *et al.*[19] evaluated the ethanol production *via* solar cells based on currently available production techniques. The exergetic inputs and outputs are shown in Table 3. Similar to the agricultural/fermentation route, all exergetic inputs must be attributed in a proportional way to the outputs (see Table 3). Next, all CO_2 emissions caused by input of non-renewables have to be treated. So, with a production of 106.2×10^3 kg CO_2/ha yr from non-renewables, a total abatement exergy of 733 GJ/ha yr is needed, resulting in an emission abatement exergy of $R_1 = 106$ GJ/ha yr for ethanol. Similar as for the agricultural/fermentation pathway, the abatement exergy R_3 is zero.

Table 2 Exergetic inputs, intermediates and outputs for the production of ethanol *via* agriculture/fermentation[19]

	Products	GJ/ha yr Total	GJ/ha yr Attributed to EtOH
Inputs			
	Sun	33480	13220
	Seeding material	2.4	0.9
	Fuel for agriculture	5.6	2.2
	Fuel for nutrients/ pesticides	13	5.1
	Fuel for fermentation	24	15.5
Intermediate			
	Wheat grain	147	147
Outputs			
	Wheat straw	91	
	Gluten	44	
	Cake	6	
	Ethanol	92	92

Table 3 Exergetic inputs, intermediates and outputs for the production of ethanol based on hydrogen production *via* solar cells and hydrolysis, and CO_2 from flue gases[19]

	Products	GJ/ha yr Total	GJ/ha yr Attributed to EtOH
Inputs			
	Solar power	33480	4681
	Solar cell production	658	92
	Water for electrolysis	11	1.5
	Flue gas delivering CO_2	80	11.2
	Fuel for CO_2 recovery	944	132
	Fuel for EtOH synthesis from CO_2/H_2	921	129
Intermediates			
	Electricity	4285	599
	Hydrogen	2883	403
	CO_2	81	11
Outputs			
	Ethanol	409	409
	Methanol	145	
	CH_4 + CO	2035	
	Steam	336	

Based on the theoretical development and data presented in the previous paragraphs, the renewability coefficient α, the environmental efficiency coefficient η_1, the production efficiency coefficient η_2 and the overall efficiency η are presented in Table 4, for the production of ethanol from fossil fuels, *via* the agriculture/fermentation route and the hydrogen/CO_2 synthesis process, based on solar driven hydrogen production.

The ethanol production starting from mineral oil cannot be fully sustainable, because of its large input of non-renewables. The coefficient α for this production pathway is almost zero ($\alpha = 0.0002$, reflecting water input). The process efficiency η_2 is high ($\eta_2 = 0.49$), but due to its low environmental efficiency (high CO_2 production) ($\eta_1 = 0.74$), the overall efficiency decreases to $\eta = 0.365$. These figures result in the smallest sustainability S of all ethanol synthesis pathways ($S = 0.18$).

From Table 4, it is noticed that agriculture and fermentation show a higher ratio of renewables ($\alpha = 0.998$). Also the coefficient η_1 ($= 0.9995$) is higher for the photosynthesis based pathway, due to the fact that less non-renewables have to be treated. On the other hand, the production efficiency of the biologically based route is the lowest one of all routes ($\eta_2 = 0.00695$): less ethanol can be produced out of the same amount solar exergy than for the solar cell/hydrogen route. This low efficiency for the bio-route is due to the agriculture step. Indeed, the conversion of solar exergy into wheat grain and straw is low. The production efficiency factor η_2 is higher for the solar cell/hydrolysis route than for the agricultural/fermentation route ($\eta_2 = 0.081$). The combination of η_2 with both parameters α and η_1 results in a better sustainability S for the agriculture/fermentation route. So in conclusion, it can be stated that the agriculture route is more sustainable than the solar driven CO_2/H_2 synthesis route, due to its higher renewable resources coefficient α and its higher environmental efficiency η_1, although it has a lower production efficiency factor η_2.

Evaluation of the sustainability of electricity production routes

Electricity production of 30 MW_e by a cogeneration plant as described by Tsatsaronis and Moran[20] shows exergetic inputs of natural gas and water of 84.99 and 0.06 MW respectively, resulting in two useful outputs: net power of 30.00 MW and steam with an exergetic flow of 12.81 MW. Next, flue gas is produced (2.77 MW). In order to reduce the impact of the emissions into the eco-system, CO_2 in the emitted flue gases must be removed. The emission rate of CO_2 is 0.577 kg s^{-1} and with an exergetic requirement of 5.862 MJ/kg CO_2, a total abatement exergy rate of 3.38 MW is needed. This abatement exergy rate is not complete since it doesn't take into account the abatement of other emissions, waste products and of CO_2 emission during fossil fuel production. However, it gives an idea of the required amount of abatement exergy.

Table 4 Ethanol production: renewability coefficient α, environmental efficiency coefficient η_1, production efficiency coefficient η_2, overall efficiency η, and sustainability S

Production pathway	α	η_1	η_2	η	S
Synthesis from fossil resources	0.0002	0.744	0.491	0.365	0.18
Agriculture/Fermentation	0.998	0.9995	0.00694	0.00694	0.50
Synthesis from Hydrogen/CO_2, with solar driven H_2 production	0.909	0.978	0.081	0.0792	0.49

The production of electricity by means of multicrystalline silicon photovoltaic solar cells[19] delivers 4285 GJ/yr ha net power. An exergetic input to construct the solar cells of 885 GJ/ha yr non-renewable resources is needed, producing 40360 kg CO_2/ha yr and requiring an abatement exergy of 236.6 GJ/ha yr. Based on these figures, parameters reflecting sustainability are presented in Table 5.

The electricity generation *via* solar cells scores better on the use of renewable resources ($\alpha = 0.9676$ *vs.* 0.0007), since the only input of renewables in the natural gas fueled system is water for the production of steam. Just because of the extensive use of non-renewables, the gas fueled system requires a higher input of exergy for the abatement of emissions resulting in a lower η_1-coefficient ($\eta_1 = 0.9932$ *vs.* 0.9617). On the other hand, the conversion of inputs into useful outputs is much higher for the gas based power system, showing an overall exergetic efficiency of $\eta_2 = 0.5033$. In this sense, the solar cell system is inferior ($\eta_2 = 0.1247$). Taking into account all these contributions in order to assess the overall sustainability, it is demonstrated by the sustainability coefficient S that the solar cell driven electricity generation is more sustainable than the gas powered generation ($S = 0.55$ *vs.* 0.24). However, also solar photovoltaic conversion cannot achieve 100% sustainability. First, it needs an input of non-renewables to produce the conversion facilities. Secondly, from a theoretical point of view, solar conversion by photovoltaics can attain a maximally possible efficiency of 40.8%, because only a limited range of the irradiated frequencies can be converted into electricity.[25] Taking into account this efficiency and neglecting exergetic inputs for the production of converters and for the abatement of outputs harmful for the ecosphere, a maximal sustainability S of 0.70 is found for multicrystalline silicon based photovoltaic cells.

Discussion

The proposed judgement of the sustainability of technologies shows that 100% sustainability cannot be attained, because it would require only solar exergy resources (or other nearly 100% renewables as wind energy and hydropower) and reversible processes. On the other hand, the approach demonstrates that technologies used nowadays are always not completely unsustainable ($S > 0$), since they all deliver a product with an exergetic content higher than zero.

The developed coefficient S covers the whole life cycle of a product, starting from the resources delivered by the ecosphere, down to the abatement step of the product at the end of its life cycle. The approach of van den Berg *et al.*[5] also contained a renewability and efficiency aspect. However, their approach considered the life cycle, also starting from the resources, but ending at the end of the production process, resulting in a useful product for society. The effect of emissions and the subsequent fate of the product, *i.e.* its use and its disposal after use, were not considered. The current approach has taken into account the waste production of the technosphere, not only during the manufacturing of the 'useful product', but also during the use and in the disposal phase after the use of the 'useful product'.

In the definition of the sustainability coefficient S, three coefficients α, η_1 and η_2 have been reduced to two coefficients α and η, *i.e.* to a renewability and a total efficiency coefficient. An alternative approach could be to define the sustainability based on 3 parameters in a 3-dimensional space (*cf.* Fig. 3). However, the splitting of η into η_1 and η_2 might be artificial in some cases. For example if a factory treats its wastewater, then the exergetic cost of this treatment can be considered either as an essential element of the production facility or as a treatment to be separated from the essential manufacturing process. In these two approaches, the exergetic cost of the wastewater treatment affects η_2 and η_1. But the overall efficiency η, and hence the sustainability S, remains the same.

The sustainability coefficient S shows several challenges to enhance the level of sustainability of technologies. The first challenge is that technology should be more solar energy driven: it is the only 100% renewable resource ($\alpha = 1$). It results in a direct contribution to higher sustainability by avoiding depletion of non-renewable resources. Moreover, it can enhance in an indirect way the environmental efficiency η_1. Organic products, containing C, H and eventually O, generated by solar driven conversion, do not require abatement exergy—the degradation products CO_2 and water close the material cycle.

Next, each process innovation enhancing the exergetic efficiency (η_2) and decreasing the amount of 'lost work' or irreversibility of the production process (I_P), contributes to sustainability. In this view, the production chain of subsequent process steps starting from the raw material must be limited as much as possible. If for example a process is 100% solar energy driven ($\alpha = 1$) and each production step results in an efficiency $\eta_{step} = 0.4$, then the sustainability S decreases from 0.7 for a single stage process ($\eta = \eta_{step} = 0.4$), down to 0.51 for a four stage process ($\eta = \eta_{step}^4 = 0.026$). Development of technologies with highly efficient operations and with a minimal number of operations is a second challenge. In the design of an overall production process, not only high production efficiencies by decreasing irreversibility must be achieved, attention has to be also paid to the generation of non-products or waste. This means that η_2 can also be increased by reduction of the emissions E. In this sense disciplines such as *e.g.* clean production strategies, green chemistry and implementation of green taxes contribute to a more sustainable technosphere.[15,26–29]

Finally, waste treatment technologies will remain an important technological issue. The approach includes the environmental efficiency (η_1). The abatement technology must be able to reduce the emissions so that the impact of the pollutants does not affect the ecosystem, *e.g.* by enhancing (re)use of product and waste streams for as long as possible within the technosphere. The abatement does not necessarily mean that the waste products are converted into the original resources in a same rate as they are emitted. Carbon dioxide for example, produced by combustion of coal is not transformed back into coal at the same rate as it is extracted from the ecosphere. Full sustainability would mean that the carbon in the produced carbon dioxide would be brought back to its original form, coal. From a technological point of view, this is not a viable option and a possible solution for the time being is the underground storage of carbon dioxide in 'used' gas or oil fields. The emission limits must be based on emission standards, reflecting no negative (harmful) effects onto the ecosystem. Therefore, the emissions of the technosphere are called 'harmless' or 'assimilable', rather than 'zero exergy' emissions. Despite the reduction of waste production by implementation of clean production strategies, near zero exergy or harmless emissions will remain hard to

Table 5 Electricity production: renewable coefficient α, environmental efficiency coefficient η_1, production efficiency coefficient η_2, overall efficiency η, and sustainability S

Production pathway	α	η_1	η_2	η	S
Gas fueled cogeneration power plant	0.0007	0.9617	0.5033	0.4841	0.24
Multicrystalline Si solar cells	0.9676	0.9932	0.1247	0.1238	0.55

achieve. The challenge for the abatement technology discipline is to develop technologies transforming waste streams into harmless products with a minimal requirement of exergy. In addition, these technologies can be made more sustainable by implementing photocatalytic and hence solar driven processes.[30]

The exergy based sustainability coefficient *S*, scaled between 0 and 1, provides a quantitative tool to assess technologies on their sustainability, including the three main steps of technology: resource extraction from the ecosphere, generation of products for the society and delivery of emission outputs to the ecosphere. This tool can be useful in decision making. However, the selection of the technological option will also depend on the preferred type of society.[31] Indeed, the technological option depends on selection criteria in the social, economical and political sector, determining how far the needs of the current generation can be fulfilled, without endangering the needs of the future generations.

Conclusions

For the first time, the assessment of the sustainability of technological processes has been performed in a quantitative way, based on the basic laws of thermodynamics. This should make qualitative discussions on the technological conditions of the sustainability concept more substantial. Indeed, it is possible to associate numbers to proposed technological options. Of course ethanol and electricity are only examples. However, these illustrations indicate the wider applicability of our approach.

References

1 *Our Common Future, The World Commission on Environment and Development*, Oxford University Press, New York, 1987, p. 383.
2 H. Wenzel, M. Hauschild and L. Altig, *Environmental Assessment of Products: Methodology, Tools and Case Studies in Product Development*, Chapman and Hall, London, 1997, vol. 1, p. 543.
3 M. Z. Hauschild and H. Wenzel, *Environmental Assessment of Products: Scientific Background*, Kluwer Academic Publ., Dordrecht, 1997, vol. 2, p. 584.
4 A. P. Hinderink, H. J. van der Kooi and J. de Swaan Arons, *Green Chem.*, 1999, **1**, G176–180.
5 M. M. D. Van den Berg, H. J. van der Kooi and J. de Swaan Arons, *A Thermodynamic Basis for Sustainability*, in *Proceedings of ECOS '99*, 1999, June 8–10, ed. M. Ishida, G. Tsatsaronis, M. J. Moran and H. Kataoka, Tokyo Institute of Technology, Tokyo, Japan, pp. 270–275.
6 Y. A. Çengel and M. A. Boles, *Thermodynamics, an Engineering Approach*, McGraw-Hill Inc., New York, 1994, 2nd edn., pp. 387–448.
7 T. J. Kotas, *The Exergy Method Of Thermal Plant Analysis*, Butterwoods, London, 1985, p. 296.
8 M. J. Moran, *Availability Analysis, a Guide To Efficient Energy Use*, The American Society of Mechanical Engineers, New York, 1989, corrected edn., p. 260.
9 J. Szargut, D. R. Morris and F. R. Steward, *Exergy Analysis of Thermal, Chemical and Metallurgical Processes*, Hemisphere Publ. Corp., New York/Springer Verlag, Berlin, 1988, p. 332.
10 G. Wall, *Exergetics*, (Preliminary version), Mölndal, 1998, p. 149. (http://www.exergy.se/exergetics.pdf).
11 R. A. Gaggioli, *Reflections on the History and Future of Exergy*, in *Proc. of ECOS '99*, 1999, June 8–10, ed. M. Ishida, G. Tsatsaronis, M. J. Moran and H. Kataoka, Tokyo Institute of Technology, Tokyo, Japan pp. 5–13.
12 A. Bejan, *Appl. Phys. Rev.*, 1996, **79**, 1191.
13 A. P. Hinderink, F. P. J. M. Kerkhof, A. B. K. Lie, J. De Swaan, Arons and H. J. Van Der Kooi, *Chem. Eng. Sci.*, 1996, **51**, 4693.
14 A. P. Hinderink F. P. J. M. Kerkhof, A. B. K. Lie, J. De Swaan Arons and H. J. Van Der Kooi, *Chem. Eng. Sci.*, 1996, **51**, 4701.
15 G. Wall, *Exergy, Ecology and Democracy—Concepts of a Vital Society or a Proposal for an Exergy Tax*, Int. Conference on Exergy systems and ecology, 1993, July 5–9, Krakow, Poland, Publ. Proc. ed. J. Szargut, Z. Kolendak, G. Tsatsuronis and A. Zielik, pp. 111–121 (http://exergy.se/goran/eed/index.html).
16 G. Wall, *Exergy—A Useful Concept within Resource Accounting*, Report No. 77–42, Chalmers University of Technology, Göteborg, 1977, p. 58. (http://exergy.se/ftp/paper1.pdf).
17 G. Wall, *Exergy—A Useful Concept*, Chalmers University of Technology, Göteborg, 1986, p. 46. (http://exergy.se/goran/thesis/index.html).
18 M. Gong, *Exergy as an Environmental Indicator*, Chalmers University of Technology, Göteborg, 1999, p. 65.
19 J. Mulder, H. J. van der Kooi, J. de Swaan Arons and J. Dewulf, *Chemicals from renewable resources, Proceedings of ECOS 2000*, July 5–7, 2000, University of Twente, Enschede.
20 G. Tsatsaronis and M. J. Moran, *Energy Convers. Mgmt.*, 1997, **38**, 1535.
21 I. Boustead, *Eco-profiles of the European Plastics Industry*, report 2: *Olefin Feedstock Sources*. A report for the European Centre for Plastics in the Environment (PWMI), Brussels, May 1993, p. 23.
22 H. J. Herzog and E. M. Drake, *Annu. Rev. Energy Environ.*, 1996, **21**, 145.
23 C. Hendriks, Carbon Dioxide Removal from Coal-fired Power Plants, PhD thesis, University of Utrecht, 1994, p. 259.
24 E. S. Mortikov, http://cacr.ioc.ac.ru/Labs/Labs47/pr23.htm, 1997.
25 A. De Vos, *Endoreversible Thermodynamics of Solar Energy Conversion*, Oxford University Press, Oxford, 1992, p. 186.
26 T. Jackson, *Clean Production Strategies, Developing Preventive Environmental Management in the Industrial Economy*, Lewis, Boca Raton, 1993, p. 415.
27 P. T. Anastas and J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford, 1998, p. 135.
28 T. T. Shen, *Industrial Pollution Prevention (Environmental Engineering)*, Springer Verlag, Heidelberg, 1995, p. 371.
29 M. M. El-Halwagi, *Pollution Prevention through Process Integration: Systematic Design Tools*, Academic Press, New York, 1997, p. 328.
30 K. Koike and K. Takeuchi, *Photoenergy Utilization for Solving Energy and Environmental Issues*, J. Japan Inst. Energy, 1998, vol. 77, pp. 396–402.
31 G. Wall, *Exergy, Society and Morals, J. Human Values*, 1997, vol. 3, pp. 193–206, (http://www.exergy.se/ftp/esm.pdf).

Microwave-assisted efficient synthesis of *N*-arylamines in dry media†

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A novel and efficient synthesis of *N*-arylamines by the reaction of activated aryl halides with secondary amines in the presence of basic Al_2O_3 under microwave irradiation in solvent free conditions, is reported.

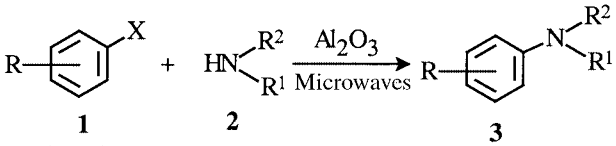
Introduction

Arylamines are versatile intermediates with wide use in polymers, medicine and photography. Further substituted *N*-arylamines are used clinically as antihistamine, antihypertensive and antiinflammatory drugs.[1] They are also an important class of compounds in neuropharmaceuticals.[2] The direct nucleophilic substitution of aryl halides typically requires a large excess of reagents, highly polar solvents such as DMF[3] and DMSO[4] at high temperatures even with highly activated aryl halides[5] under high pressure.[6] In recent years. Pd and Ni catalysed amination of aryl halides with amines have been reported by both Hartwig and Buchwald.[7] Furthermore conventional methods have limitations such as longer reaction times, lower yields, expensive reagents and solvents which require tedious aqueous workup. Consequently there is a need to develop a simple and rapid method for the synthesis of these compounds. Although several *N*-alkylation reactions are reported[8] using microwaves, the *N*-arylation of amines on the surface of basic alumina under microwave irradiation has not been reported.

Results and discussion

In continuation of our interest to develop eco-friendly chemical processes through surface mediated organic transformations[9] on high surface area solids like Al_2O_3, clay and SiO_2, we report herein a rapid and efficient method for the synthesis of *N*-arylamines by the arylation of amines on the surface of basic Al_2O_3 under microwave irradiation[10] in solvent-free conditions. Several activated aryl halides were condensed with alkylamines when subjected to microwave irradiation in the presence of basic Al_2O_3 (Brockmann Activity Grade 1, 70–290 mesh). All the reactions were carried out under solvent free conditions in an open Pyrex test tube. The results summarised in Table 1 clearly show the scope of the reaction with regard to various aryl halides and alkylamines. Secondary alkyl amines such as morpholine, piperidine, pyrrolidine or piperazines show higher reactivity than their acylic counterparts. The reactions proceed rapidly with *o*- and *p*-nitro-substituted halobenzenes when compared to cyano-substituted aryl halides. When these reactions were attempted with other solid supports like SiO_2 or neutral alumina the condensations were only partial (20–30%) which clearly indicated that basic alumina is the best catalyst for this transformation. Basic alumina was activated by microwaves which is known to cleave the heteroatom-H bonds in primary and secondary amines.[11] Further, the liberated HBr or HCl during the reaction was scavenged on the surface of alumina freeing the nitrogen to undergo nucleophilic attack and the yield increased to 73–90%. Further, moderate yields of the products (60–75%) were isolated by heating the reactants at 120 °C in the presence of Al_2O_3. The reactions proceeded only to a minor extent (10–15%) when the reactants were subjected to microwaves in the absence of Al_2O_3. In general, polar media or polar reactants absorb more microwave energy and generate heat energy as required to promote the reaction. Both alumina and amines are polar so they absorb microwaves effectively and so the reaction is complete in a short time. The reaction temperature was controlled in a microwave oven by pulsed irradiation (1 min with 20 s intervals). The temperature was measured at the end of each irradiation. The lowest observed temperature was 85 °C after one minute irradiation at 450 W and the highest observed temperature was 110 °C after 5 min irradiation at the same power.

In conclusion we have described a novel and efficient method for the synthesis of *N*-arylamines through the amination of aryl halides catalysed by basic alumina under microwave irradiation. The method is inexpensive, eco-friendly and high yielding,



Scheme 1

Green Context

This paper describes the fast and efficient preparation of arylamines by the combination of a basic solid support/reaction medium and the use of microwaves for activation. Very high yields are achieved in a very short time. Such processes are energy efficient, rapid and do not require solvent for the reaction. While the present method would need to be modified somewhat to make it feasible on a multi-kg scale, the advantages of the method may well allow an intensive, continuous process to be developed. ***DJM***

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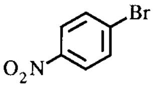
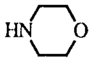
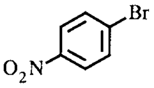
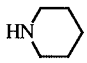
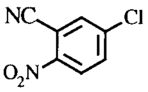
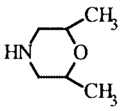
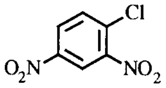
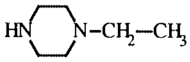
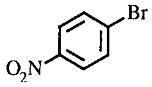
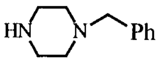
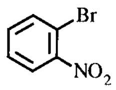
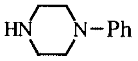
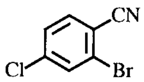
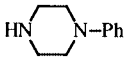
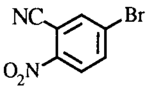
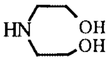
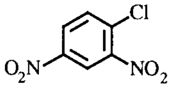
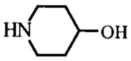
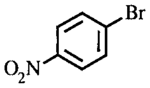
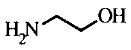
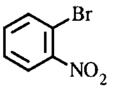
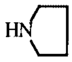
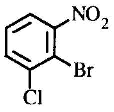
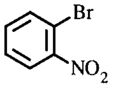
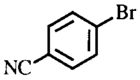
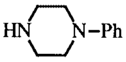
which is a useful addition to the existing procedures for the synthesis of *N*-arylamines.

Table 1 *N*-Arylation of amines in the presence of basic Al_2O_3 under microwave irradiation

		Reaction time (yield(%)[c])	
Halide	Amine	Microwave irradiation[a]	Conventional heating[b]
		4 min (88)	8 h (65)
		3 min (82)	6 h (68)
		4 min (84)	4 h (70)
		3 min (90)	3 h (75)
		4 min (87)	7 h (68)
		4 min (85)	8 h (64)
		5 min (73)	10 h (60)
		5 min (83)	6 h (63)
		3 min (90)	4 h (71)
		4 min (84)	7 h (67)
		4 min (88)	5 h (74)
		5 min (82)	5 h (70)
		3 min (89)	8 h (69)
		5 min (75)	10 h (60)

[a] Pulsed irradiation (1 min with 20 s intervals) at 450 W. [b] Conventional heating in the presence of basic alumina at 120 °C. [c] Unoptimized yields after purification by column chromatograpy.

Experimental

p-Bromonitrobenzene (10 mmol) and *N*-benzylpiperazine (12 mmol) were mixed with basic Al_2O_3 (5 g, Brockmann Activity Grade 1, 70–290 mesh) in a Pyrex test tube and subjected to microwave irradiation at 450 W (BPL BMO 700T) for a specified time. The reaction progress was monitored by TLC. After complete conversion (TLC), the reaction mass was directly charged on a silica gel column (Aldrich 100–200 mesh) and eluted with ethyl acetate–hexane (3:7) to afford the pure product **3e** as a pale yellow crystalline solid. δ_H ($CDCl_3$) 2.6 (s, 4H), 3.4 (s, 4H), 3.6 (s, 2H), 6.8 (d, 2H, J = 8.8 Hz) 7.25–7.40 (m, 5H) and 8.1 (d, 2H, J = 8.8 Hz).

Acknowledgements

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References

1 H. G. Jaisinghani and B. M. Khadilkar, *Tetrahedron Lett.*, 1997, **38**, 6875; R. P. Mull, C. Tannenbaum, M. R. Dapero, M. Bernier, W. Yost and G. De Stevens, *J. Med. Chem.*, 1965, **8**, 332.
2 R. W. Fuller, N. R. Maso and B. B. Molloy, *Biochem. Pharmacol.*, 1980, **29**, 833.
3 Y. H. Cho and J. C. Park, *Tetrahedron Lett.*, 1997, **38**, 8331.
4 G. R. Brown, A. J. Foubister and P.D. Ratcliffe, *Tetrahedron Lett.*, 1999, **40**, 1219; A. J. Belfield and G. R. Brown, *Tetrahedron*, 1999, **55**, 13285.
5 J. E. Shaw, D. C. Kunerth and S. B. Swanson, *J. Org. Chem.*, 1976, **41**, 732.
6 T. Ibata, Y. Isogami and J. Toyada, *Chem. Lett.*, 1987, 1187.
7 J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1998, **37**, 2046; A. J. Belfield, G. R. Brown and A. J. Foubister, *Tetrahedron*, 1999, **55**, 11399.
8 D. Bogdal, J. Pielichowski and A. Boron, *Synlett.*, 1996, 873; P. de la Cruz, A. de la Hoz, L. M. Font, F. Langa and M. C. Perez-Rodriguez, *Tetrahedron Lett.*, 1998, **39**, 6053; D. Bogdal, J. Pielichowski and K. Jaskot, *Synth. Commun.*, 1997, **27**, 1553.
9 H. M. Sampath Kumar, B. V. Subba Reddy, P. K. Mohanty and J. S. Yadav, *Tetrahedron Lett.*, 1997, **38**, 3619; H. M. Sampath Kumar, B. V. Subba Reddy, E. Jagan Reddy and J. S. Yadav, *Tetrahedron Lett.*, 1999, **40**, 2401; H. M. Sampath Kumar, B. V. Subba Reddy and J. S. Yadav, *Chem. Lett.*, 1998, 637; H. M. Sampath Kumar, B. V. Subba Reddy, E. Jagan Reddy and J. S. Yadav, *Green Chem.*, 1999, **1**, 141.
10 A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathe, *Synthesis*, 1998, 1213; R. S. Varma, *Green Chem.*, 1999, **1**, 43; S. Deshayes, M. Liagre, A. Loupy, J. L. Luche and A. Petit, *Tetrahedron*, 1999, **55**, 10851; S. Caddick, *Tetrahedron*, 1995, **51**, 10403; R. A. Abramovitch, *Org. Prep. Proc. Int.*, 1991, **23**, 685.
11 J. M. Parera and J. Figoli, *Catalysis*, 1969, **14**, 303; G. W. Kabalka and R. M. Pagni, *Tetrahedron*, 1997, **53**, 7999.

Organic reaction in water. Part 4.† New synthesis of vicinal diamines using zinc powder-promoted carbon–carbon bond formation

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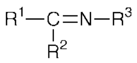
Reductive coupling of aromatic imines is performed by the use of zinc powder and additives such as NH_4Cl and L-tyrosine in water without any organic solvents under mild conditions to give the corresponding vicinal diamines in good yields; cross-coupling of *N*-benzylideneaniline and benzaldehyde similarly proceeds in aqueous media to afford the corresponding 2-aminoalcohol.

Introduction

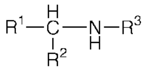
Coupling of imines to vicinal diamines and cross-coupling of imines and carbonyl compounds to 2-aminoalcohols are important reactions in organic synthesis because vicinal diamine and 2-aminoalcohol units are widely used in medicinal products,[1] as chiral ligands in asymmetric reactions[2] and as chiral derivatizing agents in chiral analysis.[3] Therefore, various metallic reagents including Na–THF,[4] $TiCl_4$–Mg(Hg),[5] $TiCl_3$–Li,[6] Yb,[7] SmI_2,[8] Cp_2 VCl_2–$PhMe_3SiCl$–Zn[9] and highly reactive Mn[10] have been developed for the coupling of imines, but, in contrast to the coupling of imines, few metallic reagents have been reported for the cross-coupling of imines and aldehydes or ketones.[11] Since these moisture-sensitive metallic reagents are usually employed in a dried organic solvent under an inert gas, the procedures are troublesome. Consequently, reductive coupling or cross-coupling in aqueous media will contribute to a most convenient and useful method because an aqueous medium as a solvent for organic reactions has many advantages from the viewpoint of cost, safety, ease of handling and the environment, in comparison to the use of an organic solvent. Recently, in view of environmental concerns, organic reactions in only water with no organic solvents are receiving attention.[12] However, to the best of our knowledge, as regards coupling or cross-coupling reactions in aqueous media, only one coupling reaction of aldimines in H_2O–EtOH (50 : 50) using indium has been reported.[13] However, EtOH is required in this reaction. Here we report the first findings that in water, without any organic solvents, the synthesis of vicinal diamines is effectively accomplished in good yields by an operationally easy intermolecular reductive coupling reaction of aromatic imines promoted by zinc powder under mild conditions, and that, furthermore, zinc powder is effective for the cross-coupling of *N*-benzylideneaniline and benzaldehyde in aqueous media.

Results and discussion

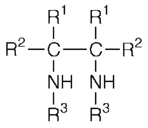
First, we studied the influence of additives on the coupling of *N*-benzylideneaniline **1a** using zinc powder (Scheme 1 and Table 1). We found that some zinc and ammonium salts (Table 1) were effective as an additive for the coupling of **1a** with zinc


$R^1-\underset{R^2}{C}=N-R^3$

1


$R^1-\underset{R^2}{\overset{H}{C}}-\underset{H}{N}-R^3$

2

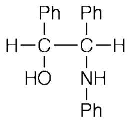

$R^2-\underset{\underset{R^3}{NH}}{\overset{R^1}{C}}-\underset{\underset{R^3}{NH}}{\overset{R^1}{C}}-R^2$

3

	R^1	R^2	R^3
a	Ph	H	Ph
b	$4CH_3$-C_6H_4	H	Ph
c	4F-C_6H_4	H	Ph
d	Ph	H	$4CH_3$-C_6H_4
e	Ph	H	4F-C_6H_4
f	Ph	H	CH_2Ph
g	Ph	H	$(CH_3)_2CH$
h	Ph	H	c-C_6H_{11}
i	Ph	Ph	Ph

Ph-CHO

4


$H-\underset{HO}{\overset{Ph}{C}}-\underset{\underset{Ph}{NH}}{\overset{Ph}{C}}-H$

5

Green Context

2-Aminoalcohols and vicinal diamines are used as chiral ligands in medicinal chemistry and in asymmetric reactions. They can be prepared from cross-coupling reactions of imines and carbonyl compounds and reductive coupling reactions of imines. Commonly used reagents for these reactions are water-sensitive metals and metallic compounds such as sodium and $TiCl_4$–Mg(Hg). Methods described to date have therefore relied on the use of organic solvents. The use of water to replace organic solvents in organic reactions is an important goal in green chemistry. In this article, for the first time, an effective aqueous solvent method is described for both reductive coupling and cross-coupling reactions. *JHC*

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† For Part 3, see: T. Tsukinoki, T. Kanda, G. B. Liu, H. Tsuzuki and M. Tashiro, *Tetrahedron Lett.*, in press. For Part 2, see G.-B. Liu, L. Tsukinoki, T. Kanda, Y. Mitoma and M. Tashiro, *Tetrahedron Lett.*, 1998, **39**, 5991.

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$$\mathbf{1a} \xrightarrow[\text{Water, 60 °C; 8 h, shaking}]{\text{Zn, additives}} \mathbf{2a} + \mathbf{3a}$$

Scheme 1

Table 1 Influence of additives on the coupling reaction[a]

Run	Additive	Yield[b](%) 2a	3a	*dl*:*meso*[c]
1[d]	None	0	0	—
2	$ZnCl_2$	10	79	56:44
3	$ZnSO_4$	16	74	52:48
4	NH_4Cl	7	82	52:48
5	$(NH_4)_2SO_4$	10	77	53:47
6	CH_3COONH_4	7	84	53:47
7	0.1 M CH_3COOH	9	82	52:48
8	DL-α-Alanine	10	78	53:47
9[e]	L-Tyrosine	1	83	48:52

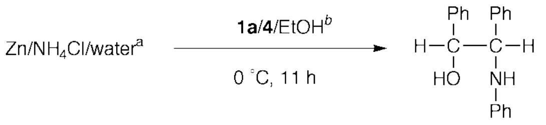
[a] **1a**: 5 mmol, Zn: 76.5 mmol, additive: 36.7 mmol. [b] Isolated yields. [c] Ratios determined by ^1H NMR.[6] [d] **1a** was quantitatively recovered. [e] Reaction time 36 h. Time was shortened by using a stirrer (36 to 5 h).

powder in water to afford the *N*,*N*,1,2-tetraphenylethylenediamine **3a** in good yield without hydrolysis of **1a** to benzaldehyde and aniline (runs 2–6). A small amount of amine **2a** was formed as a by-product. Similarly, the coupling of **1a** also proceeded using 0.1 mol dm^{-3} CH_3COOH. Interestingly, **1a** was smoothly dimerized at a neutral pH by α-amino acid as well as other additives (runs 8 and 9). No reaction was observed in the absence of an additive (run 1). Since this reaction is heterogeneous, when the reaction mixture was stirred mechanically under ultrasonic irradiation instead of using a shaker, coupling of **1a** was accelerated.[14] Ultrasonic irradiation is not always essential.[15]

Under these optimized conditions, we employed NH_4Cl and L-tyrosine among the additives shown in Table 1 and investigated the coupling of various aromatic imines **1** with zinc powder in water (Table 2).[16] To accelerate the reaction, the coupling of **1** was undertaken at 60 °C under ultrasonication in the case of NH_4Cl and at 90 °C in the case of using L-tyrosine, respectively. It was also found that zinc powder/additives such as NH_4Cl and L-tyrosine could be used for the coupling of aromatic imines in water without any organic solvents and the corresponding vicinal diamines **3** were obtained in 62–85% isolated yields. The use of L-tyrosine as an additive was more efficient than using NH_4Cl, as reflected in the yields of **3**. The resulting diamines were a diastereomeric mixture. On the other hand, in benzophenone anil **1i**, interestingly, reduction proceeded in preference to the coupling reaction, and only the secondary amine **2i** was obtained in 74 and 90% yields, respectively (entries 9 and 15).

As a result of applying this method to the cross-coupling of *N*-benzylideneaniline **1a** and benzaldehyde **4**, 2-aminoalcohol **5** was obtained in 63% yield (Scheme 2).[17] To accomplish cross-coupling, **1a** and **4** (in excess) in EtOH must be very slowly added to a mixture of zinc powder and NH_4Cl in water at 0 °C. The reason for employing excess **4** compared to **1a** is to inhibit the coupling of **1a** and to promote cross-coupling between **1a** and **4** because coupling of **1a** occurs faster than the cross-coupling of **1a** and **4**, and coupling of **4** is very slow in comparison with other coupling and cross-coupling reactions.

In conclusion, dimerization of aromatic imines was carried out by using cheap zinc powder/additives like NH_4Cl and L-tyrosine in water without any organic solvents under mild conditions to afford the corresponding vicinal diamines in good yields. Furthermore, with this method, we demonstrated that heterocoupling between **1a** and **4** proceeds in aqueous media to give the 2-aminoalcohol **5** in good yield. This method has some advantages over other methods since the reaction is easily operable in water under mild conditions as it uses no dried organic solvent and/or an inert gas and the zinc powder is not only readily available commercially but is also, of course, cheaper and more easily handled than other reagents. This procedure would be a convenient and practical method for the synthesis of diamines and 2-aminoalcohols. Further investigation on the application of this method is now in progress in our laboratory.



5 (yield : 63%)

[a] Zn/NH_4Cl=34.9/4.4 mmol, water=20 ml.

[b] **1a**/**4**=0.5/2.5 mmol, EtOH=10 ml.

Scheme 2

Table 2 Coupling of imines **1a**–**i** to diamines **3a**–**i**[a] in water

Entry	Imine 1	Additives	*T*/°C	Ultrasonic irradiation	*t*/h	Yield[b](%) 2a	3a	*dl*:*meso*[c]
1	**a**	NH_4Cl	60	irradiation	1	7	80	53:47
2	**b**	NH_4Cl	60	irradiation	0.5	4	82	54:46
3	**c**	NH_4Cl	60	irradiation	0.5	9	75	55:45
4	**d**	NH_4Cl	60	irradiation	0.5	7	75	53:47
5	**e**	NH_4Cl	60	irradiation	0.5	11	71	54:46
6	**f**	NH_4Cl	60	irradiation	0.5	27	62	54:46
7	**g**	NH_4Cl	60	irradiation	0.5	7	66	51:49
8	**h**	NH_4Cl	60	irradiation	0.5	16	71	43:57
9	**i**	NH_4Cl	60	irradiation	1.5	74	0	—
10	**a**	L-Tyrosine	90	none	2	3	82	57:43
11	**b**	L-Tyrosine	90	none	2	7	83	50:50
12	**c**	L-Tyrosine	90	none	5	3	84	53:47
13	**d**	L-Tyrosine	90	none	2	3	85	51:49
14	**e**	L-Tyrosine	90	none	4	5	82	57:43
15	**i**	L-Tyrosine	reflux	none	5	90	0	—

[a] **1**–Zn–NH_4Cl = 5:76.5:36.7 mmol, **1**–Zn–L-tyrosine = 5:40:20 mmol. [b] Isolated yields. [c] Ratios determined by ^1H NMR.

References

1 G. Li, H.-T. Chang and K. B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 451; J. Reedijk, *Chem. Commun.*, 1996, 801; A. Pashini and F. Zunino, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 615.

2 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97; J. Seyden-Penne, *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*, John Wiley & Sons, Inc., New York, 1995, p. 61.

3 R. Fulwood and D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1994, 57; A. Alexakis, J. C. Frutos, S. Mutti and P. Mangeney, *J. Org. Chem.*, 1994, **59**, 3326.

4 J. G. Smith and I. J. Ho, *J. Org. Chem.*, 1972, **37**, 653.

5 P. Mangeney, T. Tejero, A. Alexalcis, F. Grosjean and J. Normaut, *Synthesis*, 1988, 255.

6 S. Talukdar and A. Banerji, *J. Org. Chem.*, 1998, **63**, 3468.

7 K. Takai, Y. Tsubaki, S. Tanaka, F. Beppu and Y. Fujiwara, *Chem. Lett.*, 1990, 203.

8 T. Imamoto and S. Nishimura, *Chem. Lett.*, 1990, 1141; E. J. Enholm, D. C. Forbes and D. P. Holub, *Synth. Commun.*, 1990, **20**, 981; N. Taniguchi and M. Uemura, *Synlett*, 1997, 51.

9 B. Hatano, A. Ogawa and T. Hirao, *J. Org. Chem.*, 1998, **63**, 9421.

10 R. D. Rieke and S.-H. Kim, *J. Org. Chem.*, 1998, **63**, 5235.

11 F. Machrouhi and J.-L. Namy, *Tetrahedron Lett.*, 1999, **40**, 1315; D. P. Steinhuebel and S. J. Lippard, *J. Am. Chem. Soc.*, 1999, **121**, 11762 and references cited therein.

12 C.-J. Li and T.-H. Chan, *Organic Reactions in Aqueous Media*, John Wiley & Sons, New York, 1997; *Organic Synthesis in Water*, ed. P. Grieco, Chapman & Hall, London, 1997.

13 N. Kalyanam and G. Venkateswara Rao, *Tetrahedron Lett.*, 1993, **34**, 1647.

14 For example, in the case of NH_4Cl, reaction time was greatly shortened (8 to 1 h).

15 In the absence of ultrasonication, reaction time was somewhat prolonged (1 to 2 h).

16 *General procedures*: to a stirred mixture of *N*-benzylideneaniline **1a** (906 mg, 5.00 mmol), NH_4Cl (1.96 g, 36.7 mmol) and water (20 ml) at 60 °C under ultrasonic irradiation was gradually added zinc powder (5.00 g) over 10 min. After the reaction mixture was stirred for 1 h at 60 °C under ultrasonic irradiation, the insoluble materials were filtered off and the filtrate was extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and evaporated *in vacuo* to give a residue, which was distilled on a Kugelrohr apparatus (oven temperature: 150–151 °C) under reduced pressure (1.3 Torr), to afford *N*-benzylaniline **2a** (65 mg, 7%) and *N*,*N*′,1,2-tetraphenylethylenediamine **3a** (728 mg, 80%). In the case of using L-tyrosine as an additive, the reaction was carried out by stirring at 90 °C without ultrasonication.

17 *General procedure*: to a stirred mixture of zinc powder (2.28 g), NH_4Cl (240 mg, 4.4 mmol) and water (20 ml) at 0 °C was very slowly added a solution of **1a** (91 mg, 0.5 mmol) and **4a** (26.5 mg, 2.5 mmol) in EtOH (10 ml) for 10 h. After the reaction mixture was stirred for 1 h at 0 °C, the insoluble materials were filtered off and the filtrate extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and evaporated *in vacuo* to give a residue, which was distilled on a Kugelrohr apparatus (oven temperature: 150–151 °C) under reduced pressure (1.5 Torr). The distillate was purified by column chromatography on silica gel (eluent: hexane–diethyl ether, 20:1 to 0:100) to afford 1,2-diphenyl-2-phenylaminoethanol (87 mg, 63%).

Microwave-assisted, solventless Suzuki coupling reactions on palladium-doped alumina

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The generation of carbon–carbon bonds forms the backbone of organic synthesis. In recent years, the use of boron-containing precursors in palladium-assisted bond forming reactions (the Suzuki reaction) has gained prominence because of the vast array of functionally substituted boron containing reagents available to the organic chemist. The development of a solventless, microwave-assisted Suzuki reaction utilizing a readily recyclable solid catalyst offers numerous benefits. These include the straightforward recovery of both product and catalyst, conservation of energy through the use of microwave irradiation, simple commercial scale up, and low waste protocols due to the absence of solvents.

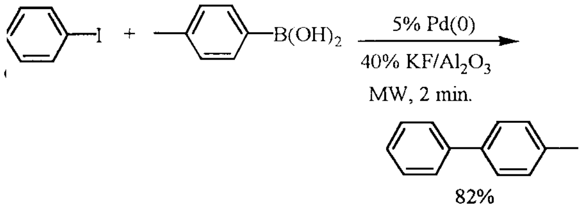
Introduction

The generation of carbon–carbon bonds *via* the palladium catalyzed coupling of organoboranes with organic halides (the Suzuki reaction) has become an integral part of modern organic synthesis.[1,2] The popularity of the Suzuki reaction is a consequence of the ready availability of a wide variety of functionally substituted boron derivatives and the mildness of the coupling reaction itself. Consequently, it is now possible to build rather complex structures from synthons containing reactive functional groups such as carboxylic acids, amides, carbonyl groups, *etc.* Suzuki reactions generally employ organic solvents such as tetrahydrofuran and ethers as well as complex palladium catalysts which are soluble in these solvents. These palladium reagents tend to be expensive and sometimes difficult to manipulate and recover. The solvents pose recyclability (and waste handling) problems of their own.

We recently reported a modification of the Suzuki reaction which solved some of these problems.[3] Using a commercially available Al_2O_3/KF mixture to which we added palladium powder (the least expensive form of palladium available), we were able to carry out Suzuki coupling reactions for a wide variety of aromatic moieties and obviate the use of solvents. In addition, since the palladium catalyst remained on the alumina surface, simple filtration afforded an efficient route to isolating the desired products and recovering the catalyst. This constitutes an important example of a trend in modern synthetic organic chemistry involving the use of solid-phase reactions.[4,5]

Microwave irradiation of organic reactions has gained in popularity in recent years since it was found to accelerate a wide variety of transformations.[6,7] Early experiments utilized solvents with high dielectric constants which permitted rapid heating of reaction solutions. In recent years, a number of reports have appeared in which the organic reagents are coated onto surfaces which themselves absorb little or no microwave energy; in these instances, the reactive species absorb the microwave energy but the bulk temperature of the reaction mixtures tends to rise only modestly. This results in relatively large energy savings as well as making it possible to carry out reactions in relatively simple glassware (open beakers, flasks, *etc.*).

Here we report an energy efficient modification of our solid-state Suzuki chemistry which enhances eco-friendly attributes of the reaction. The new methodology couples microwave irradiation with a solid-state, solvent free approach and leads to enhanced yields of the desired products [eqn. (1)].



(1)

Results and discussion

In our earlier studies, it was determined that Suzuki reactions readily occurred in the presence of relatively inexpensive palladium powder and alumina. The presence of a base was required to achieve high yields of the desired products and a variety of inorganic bases were effective. Potassium fluoride proved to be the most efficient base which was fortuitous since mixtures of potassium fluoride and alumina were commercially available at reasonable cost. In the initial studies, the reactants were mixed (in the absence of a solvent) with palladium-doped,

Green Context

The Suzuki reaction is proving to be an increasingly popular method for forming carbon–carbon bonds. However, like many organic reactions using inorganic reagents and catalysts, the normal procedure suffers from wasted solvent and expensive palladium catalyst that leads to toxic waste. Here, an effective method for these reactions which uses no solvent and a readily recyclable solid catalyst is described. Additionally the method is energy-efficient through the use of microwave irradiation. ***JHC***

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potassium fluoride treated alumina and the mixture heated for four or more hours at temperatures approaching 100 °C.

In the current study, we examined the effectiveness of microwave irradiation for enhancing the rate of these reactions. The feasibility of using microwave irradiation to induce organic reactions on solid surfaces in the absence of solvents has been demonstrated previously.[8] As a probe, we investigated the reaction of *o*-tolylboronic acid with iodobenzene for various periods of time (Table 1). 2-Methylbiphenyl formed readily under a variety of reaction conditions. For convenience, we found it most efficient to simply heat the mixtures for 2 minutes at 100% power. Under these conditions, a small amount of organic material was observed condensing on the cooler portions of the reaction vessel.

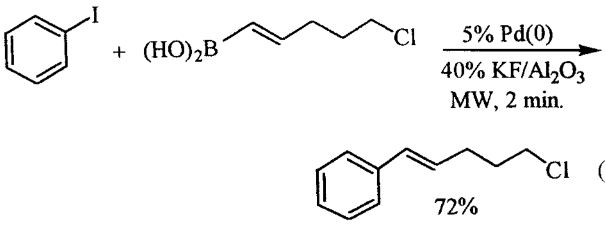
We then examined the reactions of a variety of aryl halides with arylboronic acids containing both electron-donating and electron-withdrawing substituents, (Table 2). As can be seen from the data contained in Table 2, the reaction appears to be insensitive to the substituents on the boronic acid. However, the reaction is most efficient when aryl iodides are used as the co-reactant. In fact the reactivity trend, aryl iodide > aryl bromide > aryl chloride > aryl fluoride, parallels the trend observed in Suzuki reactions carried out in solution.

Table 1 The reaction of *o*-tolylboronic acid with iodobenzene to form 2-methylbiphenyl

Experiment[a]	Microwave power(%)[b]	Reaction time/min[c]	Yield(%)[d]
1	30	5	24
2	30	10	64
3	50	3	34
4	50	6	83
5	100	2	80
6	100	3	78

[a] Reactions were carried out by mixing 1 mmol of *o*-tolylboronic acid with 1 mmol of iodobenzene and 1 g of 5% palladium on KF/alumina. [b] Power setting on commercial microwave unit. [c] Except for experiment 5, reactions were halted at the half way point to allow mixtures to cool. [d] Isolated yield.

Reactions of vinyl boronic acids with aryl halides were also successful [eqn. (2)], but no reactions occurred when alkylboronic acids were utilized or when alkyl halides were used.

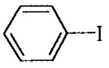
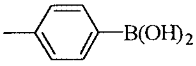
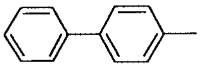
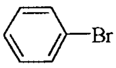
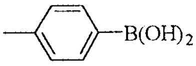
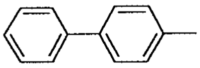
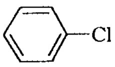
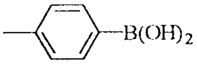
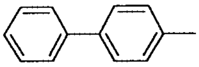
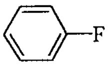
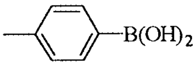
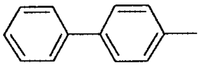
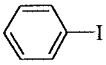
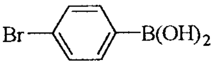
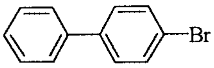
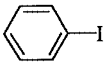
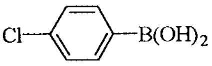
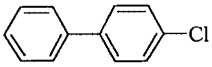
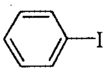
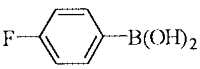
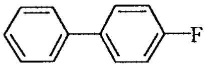
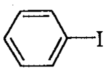
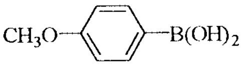
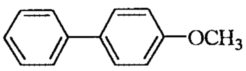
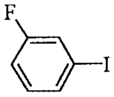
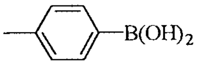
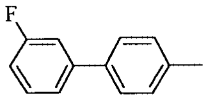


(2)

Experimental

A commercially available Sharp Model R-4A38, 1000 W microwave oven was utilized in the study. The oven was operated between 30 and 100% power for various portions of the study. All reactants were mixed in a round-bottomed flask fitted with a rubber septum which had been punctured by an 18 gauge needle (to eliminate pressure build up). Requisite boronic acids were obtained commercially (Frontier Chem. Co.) or were prepared *via* literature procedures.[9] KF/Al_2O_3 was prepared by dissolving KF in a minimum amount of methanol and adding it to Grade 1 alumina. The ratio of KF to alumina was 40% (by

Table 2 Microwave enhanced reaction of aryl halides (ArX) with boronic acids [$RB(OH)_2$]

Exp.	ArX	$RB(OH)_2$	Product[b]	Yield(%)[c]
1	 I	 $B(OH)_2$		82
2	 Br	 $B(OH)_2$		52
3	 Cl	 $B(OH)_2$		4
4	 F	 $B(OH)_2$		0
5	 I	 Br, $B(OH)_2$	 Br	80
6	 I	 Cl, $B(OH)_2$	 Cl	87
7	 I	 F, $B(OH)_2$	 F	86
8	 I	 CH_3O, $B(OH)_2$	 OCH_3	84
9	 F, I	 $B(OH)_2$	 F	84

[a] Reactions carried out by mixing 1 mmol of aryl halide with 1 mmol of boronic acid and 1 g of 40% KF/Al_2O_3 mixed with 5% palladium powder. [b] All products exhibited physical and spectral characteristics in accord with literature values. [c] Isolated yields.

weight). The methanol was removed under reduced pressure until the KF/Al_2O_3 mixture was powdery (no effort was made to insure 100% removal of the methanol).

The synthesis of 4-methylbiphenyl is representative: to a mixture of KF/Al_2O_3 (0.950 g, 40% by weight) and palladium black (0.050 g, 0.470 mmol, 99.9+% as a submicron powder) contained in a clean, dry, round-bottomed flask was added *p*-methylphenylboronic acid (0.150 g, 1.10 mmol). The solid mixture was stirred at room temperature in the open air until homogeneous. Iodobenzene (0.209 g, 1.02 mmol) was then added with stirring. The mixture was stirred at room temperature for an additional 15–20 min to ensure efficient mixing.

The flask was then fitted with a septum (punctured by an 18 gauge needle), placed in a microwave oven and irradiated at 100% power for 2 min. After cooling, a small quantity of hexane was added and the slurry stirred at room temperature for an additional 20–30 min to ensure product removal from the surface. The mixture was vacuum filtered through a sintered glass funnel and the product isolated *via* flash chromatography to yield 4-methylbiphenyl (82%); mp 44.0–45.5 °C; δ_H ($CDCl_3$) 7.40 (m, 9 H) and 2.37 (s, 3 H).

Conclusions

The use of microwave irradiation in syntheses involving KF/alumina as a solid-phase support for solventless Suzuki reactions offers a convenient, environmentally friendly alternative to traditional reactions. Reaction times are reduced from hours to minutes and, in addition, the solid-phase syntheses provide one of the few successful Suzuki methodologies that can be carried out utilizing ligandless palladium reagents. Although our studies are not complete, the solid-state methodology offers the opportunity to recycle the reagent (*via* simple filtration) which has significant commercial appeal.

Acknowledgements

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References

1 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
2 A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.
3 G. W. Kabalka, R. M. Pagni and C. M. Hair, *Org. Lett.*, 1999, **1**, 1423.
4 B. A. Lorsbach and M. J. Kurth, *Chem. Rev.*, 1999, **99**, 1459.
5 G. W. Kabalka and R. M. Pagni, *Tetrahedron*, 1997, **53**, 7999.
6 R. S. Varma, *Green Chem.*, 1999, **1**, 43.
7 A. K. Bose, B. K. Banik, N. Lavlinskaia, M. Jayaraman and M. S. Manhas, *CHEMTECH*, 1997, **27**, 18.
8 R. S. Varma, *Clean Products Process.*, 1991, **1**, 132.
9 H. C. Brown, N. G. Bhat and V. Somayaji, *Organometallics*, 1992, **11**, 652.