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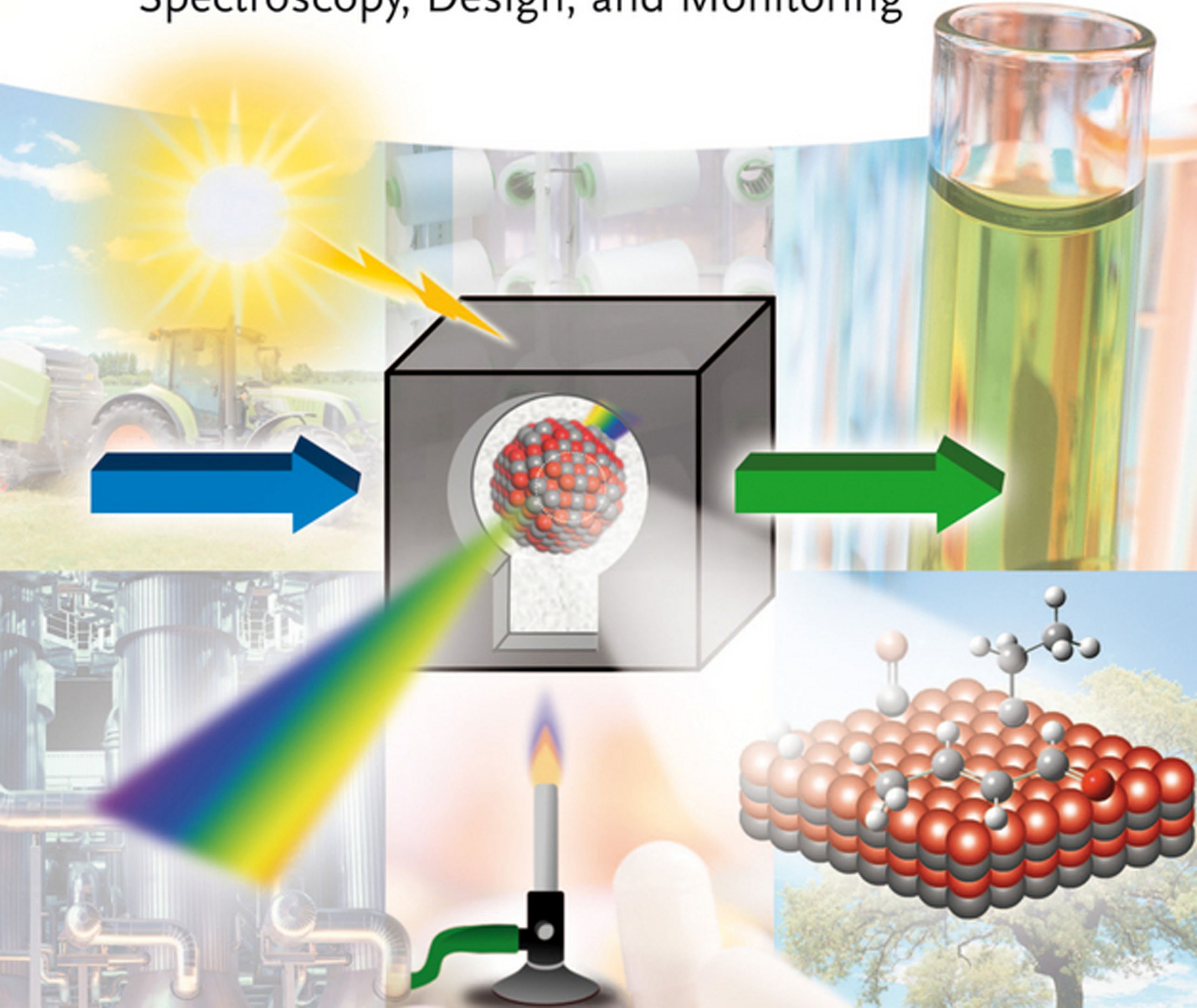
Heterogeneous Catalysts for Clean Technology

Spectroscopy, Design, and Monitoring



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We dedicate this book to the memory of Rodney Stewart Lee.

Contents

Preface

Catalytic technologies play a critical role in the economic development of both the chemicals industry and modern society, underpinning 90% of chemical manufacturing processes and contributing to over 20% of all industrial products. Sustainable chemistry is defined as the design and implementation of chemical products and processes that reduce or eliminate the use or generation of hazardous substances, while employing renewable resources in an atom and energy efficient fashion. In accordance with the 12 Principles of Green Chemistry, first advanced by Anastas and Warner, catalysis is a key tool with which to develop sustainable chemistries. New catalytic routes to the manufacture of fine, speciality and pharmaceutical chemicals offer sustainable solutions with minimal environmental impact. In a post-petroleum era, catalysis researchers will need to rise to the challenge of synthesising chemical intermediates and advanced functional materials and fuels from non-petroleum based feedstocks. Success will require an interdisciplinary approach, uniting physical, inorganic, organic and materials chemistry with biotechnology, reaction and process engineering.

To a large extent, the catalytic transformation of individual atoms and molecules into potent drug therapies, advanced fuels, and efficient fertilisers has (to date) depended upon an equal combination of brilliant science and serendipity. This reflects the complex, interdependent interactions between reactants, products, their surrounding environment, and of course the catalyst itself, which in principle should remain unchanged over thousands of reaction cycles. However, recent advances in chemical synthesis, nanotechnology and spectroscopy now offer an unprecedented opportunity to sculpt the atomic structure of solid catalysts and to peer inside their microscopic workings. Our knowledge of the mechanism by which heterogeneous catalysts operate has traditionally been obtained by comparing freshly prepared materials with their spent counterparts isolated post-reaction. While this approach has undoubtedly aided catalyst development, the importance of adsorbate-induced restructuring in modulating surface reactivity, a concept Gabor Somorjai termed the ‘flexible surface’, is now widely accepted. Step-changing discoveries require intelligent catalyst design, informed by quantitative insight into catalyst behaviour under reaction conditions via *complementary operando studies of the surface, bulk and atomistic properties of catalysts in action*. This book focuses on the development of heterogeneous catalysts for application in clean chemical synthesis, and explores how modern spectroscopic techniques can be employed to aid the design of catalysts (particularly) for use in liquid phase reactions. Examples of catalytic applications to industrially important chemistries including selective oxidation and hydrogenation, solid acid and base catalysed processes, and photocatalytic depollution, while other chapters illustrate the importance of process intensification and use of renewable resources in enhancing the sustainability of chemical processes.

The development of new catalytic processes requires consideration of unconventional reactor technologies which afford improvements in product separation, overall energy efficiency and operational safety. An understanding of the physicochemical properties and behaviour of diverse solid catalysts and associated factors influencing catalyst selection for specific chemical transformations, catalyst compatibility with different reactor designs, and mechanistic insight accessible through time-resolved in-situ spectroscopic tools, will aid industrial and academic researchers in addition to undergraduate students taking courses in sustainable or green chemistry. We hope this text will serve as a central resource for catalytic scientists and engineers across the clean technology community, providing information on next-generation catalyst formulations, process operation, and online monitoring. Newcomers to the field of heterogeneous catalysis, particularly undergraduate and postgraduate students, will also be exposed to the fundamental physical principles underpinning an array of spectroscopic methods, and synthetic strategies adopted to prepare high performance nanocrystalline and nanoporous catalysts and to valorise bio-derived, multi-functional feedstocks through atom- and energy economical processes.

This book would not have been possible without the collective work of a number of scientists and engineers spanning catalysis, materials, spectroscopy, process intensification and green chemistry. We would like to express our gratitude to all the contributors, whose time, efforts, and expertise have helped to deliver what we hope will become a valuable scientific resource for beginners and experienced practitioners of clean and sustainable chemistry. We are also grateful to Drs. Elke Maase and Lesley Belfit at Wiley-VCH for their support and useful advice in preparing this book.

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1
Introduction to Clean Technology and Catalysis

James H. Clark

1.1
Green Chemistry and Clean Technology

Traditional chemical manufacturing is resource demanding and wasteful, and often involves the use of hazardous substances. Resources are used throughout the production and including the treatment of waste streams and emissions (Figure 1.1).

Green chemistry focuses on resource efficiency and on the design of chemical products and processes that are more environmentally benign. If green chemistry is used in a process, it should be made simpler, the inputs and outputs should be safer and more sustainable, the energy consumption should be reduced and costs should be reduced as yields increase, and so separations become simpler and less waste is generated [1]. Green chemistry moves the trend toward new, clean technologies such as flow reactors and microwave reactors, as well as clean synthesis. For instance, lower temperature, shorter reaction time, choice of an alternative route, increased yield, or using fewer washings at workup improve the ''cleanness'' of a reaction by saving energy and process time and reducing waste [2].

At present, there is more emphasis on the use of renewable feedstocks [3] and on the design of safer products including an increasing trend for recovering resources or ''closed-loop manufacturing.'' Green chemistry research and application now encompass the use of biomass as a source of organic carbon and the design of new greener products, for example, to replace the existing products that are unacceptable in the light of new legislation (e.g., REACH) or consumer perception.

Green chemistry can be seen as a tool by which sustainable development can be achieved: the application of green chemistry is relevant to social, environmental, and economic aspects.

To achieve sustainable development will require action by the international community, national governments, commercial and noncommercial organizations, and individual action by citizens from a wide variety of disciplines. Acknowledgment of sustainable development has been taken forward into policy by many governments including most world powers notably in Europe [4], China [5], and the United States [6].

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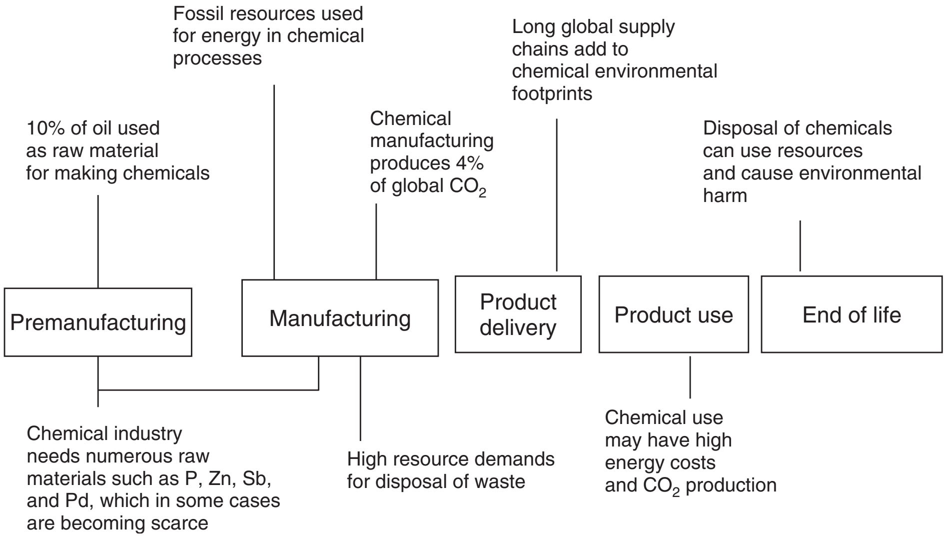

Figure 1.1 Resource demands of traditional chemical manufacturing.

1.1.1
Ideals of Green Chemistry

In Figure 1.2 and Figure 1.3, the ideals of green chemical synthetic design are shown.

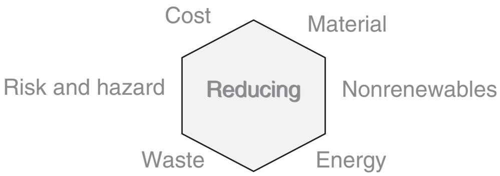

Figure 1.2 Factors for reduction in syntheses.

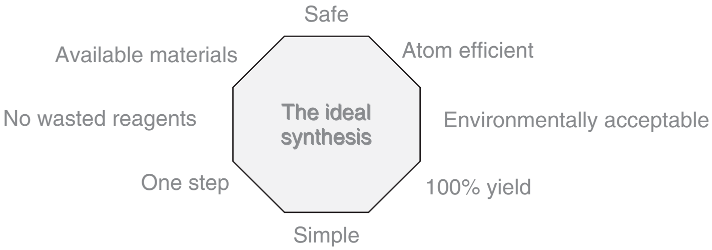

Figure 1.3 The eight parts of an ideal synthesis.

It is important to note that these green chemistry goals are most effectively dealt with and are easier to apply if they are considered at the design stage rather than retrospectively – green chemistry is not an end-of-pipe solution.

Chemical plants have traditionally concentrated on mechanical safety devices, reducing the probability of accidents. However, mechanical devices are not infallible and safety measures cannot completely prevent the accidents that are happening. The concept of inherently safer design (ISD) was designed with the intention of eliminating rather than preventing the hazards and led to the phrase ''What you don't have can't harm you'' [7]. ISD means not holding significant inventories of hazardous chemicals or not using them at all.

This approach would have prevented the accident at Bhopal, India in 1984, where many thousands of people were killed or seriously injured. One of the chemicals used in the process at the Union Carbide factory was highly water sensitive, and when a watertight holding tank was breached, the accident occurred, releasing the chemicals into the air, affecting the villages surrounding the factory. The chemical is nonessential and the ISD approach would have been used an alternative, thus eliminating the risk altogether.

Green chemistry research has led to the invention of a number of clever processing technologies to save time and energy or reduce waste production, but these technologies mostly exist in academia and, with very few exceptions, industry has been slow to utilize them. Green chemical technologies include heterogeneous catalysis (well established in some sectors but much less used in fine chemicals and pharmaceuticals, see the subsequent text), use of supercritical fluids (as reaction and extraction media), photochemistry, microwave chemistry, sonochemistry, and synthetic electrochemistry. All these replacements for conventional methods and conductive heating can lead to improved yields, reduced reaction times, and reduced by-product formation. Engineered greener technologies also exist, including a number of replacements for the stirred tank batch reactor, such as continuous stirred tanks, fluidized bed reactors, microchannel reactors, and spinning disc reactors as well as microwave reactors, all of which increase the throughput, while decreasing the energy usage and waste. Unfortunately, despite these many new processes, industry is reluctant to use these hardware solutions because of the often massive financial expenditure involved in purchasing these items and the limited number of chemistries that have been demonstrated with them to date. There is also a reluctance to change well-established (and paid for) chemical plant so that newer, cleaner technologies may well have more success in the developing (e.g., the Brazil, Russia, India, and China (BRIC)) nations, where the chemical industry is growing and new plant is required to meet the increasing expectations of local and increasingly affluent markets.

1.2
Green Chemistry Metrics

It is important to be able to quantify the change when changes are made to chemical processes. This enables us to quantify the benefit from the new technology introduced (if there are benefits). This can aid in in-house communication (to demonstrate the value to the workforce) as well as in external communication. For yield improvements and selectivity increases, simple percentages are suitable, but this simplistic approach may not always be appropriate. For example, if a toxic reagent is replaced by a less toxic one, the benefit may not be captured by conventional methods of measuring reaction efficiency. Equally, these do not capture the mass efficiency of the process – a high-yielding process may consume large amounts of auxiliaries such as solvents and reagents, as well as those used in product separation and purification. Ideally, we also need to find a way to include energy and water, both of them have been commonly used in a rather cavalier way but they are now subject to considerable interest that they can vary depending on the location of the manufacturing site.

Numerous metrics have been formulated over time and their suitability discussed at great length [8–12]. The problem observed is that the more accurate and universally applicable the metric devised, the more complex and unemployable it becomes. A good metric must be clearly defined, simple, measurable, objective rather than subjective, and must ultimately drive the desired behavior. Some of the most popular metrics are

- E factor (which effectively measures the amount of product compared to the amount of waste – the larger the E factor is, the less product-specific is the process; the fine chemical and pharmaceutical manufacturing sectors tend to have the highest E factors) [13];
- effective mass yield (the percentage of the mass of the desired product relative to the mass of all nonbenign materials used in its synthesis – this includes an attempt to recognize that ‘‘not all chemicals are equal’’ – important and very real but very difficult to quantify);
- atom efficiency/economy (measures the efficiency in terms of all the atoms involved and is measured as the molecular weight of the desired product divided by the molecular weight of all of the reagents; this is especially valuable in the design ‘‘paper chemistry’’ stage when low atom efficiency reactions can be easily spotted and discarded);
- reaction mass efficiency (essentially the inverse of E factor).

Of course, the ultimate metric is life cycle assessment (LCA); however, this is a demanding exercise that requires a lot of input data, making it inappropriate for most decisions made in a process environment. However, some companies do include LCA impacts such as greenhouse gas production in their in-house assessment, for example, to rank solvents in terms of their greenness. It is also essential that we adopt a ‘‘life cycle thinking’’ approach to decision making so that we do not make matters worse when greening one stage in a manufacturing process without appreciating the effects of that change on the full process including further up and down the supply chain.

1.3
Alternative Solvents

Most chemical processes involve solvents – in the reactions and in the workups as well as in the cleaning operations [14, 15]. The environmental impact of a chemical process cannot be properly evaluated without considering the solvent(s). For some time there has been a drive toward replacing or at least reducing the use of traditional volatile organic solvents such as dichloromethane, tetrahydrofuran, and *N*-methylpyrollidone – commonly used solvents in, for example, catalytic processes.

Ionic liquids, fluorous biphasic systems, and supercritical fluids have all been studied as alternatives to conventional organic solvents. However, because of their nature, some of these novel systems require additional hardware for utilization. For example, some suppliers have designed advanced mixing systems to enable polyphasic systems to be intimately mixed at the laboratory scale. There has also been considerable rethinking of the green credentials of some of these alternative solvents in recent years and many ionic liquids are no longer considered suitable because of their complex syntheses, toxicity, or other unacceptable properties, or difficulty in separation and purification. Fluorous solvents (which are based on heavily fluorinated usually aliphatic compounds) are not considered to be environmentally compatible (as they persist in the environment).

Supercritical solvents are difficult to manipulate because of the high pressures and temperatures often employed. In the case of supercritical water, equipment had to be designed, which could contain the highly corrosive liquid. Vessels for creating supercritical solvents such as supercritical CO_2 (scCO_2) are now available and are capable of fine adjustments in temperature and pressure to affect the solvents' properties. Very high pressure and temperatures are not required to produce scCO_2 and it is becoming an increasingly popular reaction medium as its properties are controllable by varying the temperature and pressure or by the use of a cosolvent [16]. The main environmental benefit of scCO_2 lies in the workup, as the product mixture is obtained free from solvent by simply returning to atmospheric conditions. Additionally, carbon dioxide is nontoxic, nonflammable, recyclable, and a by-product of other processes. However, there are energy and safety concerns associated with the elevated temperatures and pressures employed and in particular, there are high capex costs to install a plant. These must be balanced against the benefits of its use.

scCO_2 can be a good medium for catalysis, although its low polarity means that either catalysts are heterogeneous or they have to be modified to enable them to dissolve (e.g., by introducing solubilizing substituents on the catalyst ligands).

Ionic liquids are molten salts and are liquid at relatively low temperatures: room-temperature ionic liquids are the most widely studied. Their lack of vapor pressure has been their biggest selling point but the enormous flexibility of choice of ions enables ionic liquids to be designed as catalysts as well as solvent. In particular, they can be powerful combined solvent–acid catalysts. The use of ionic liquids has been reported in various synthetic transformations such as Friedel–Crafts reaction, Diels–Alder reaction, and metal-catalyzed asymmetric synthesis. The problems with their use include toxicity (in some cases), cost of manufacture, and difficulties in separation/purification (they cannot be distilled), and these have hampered their industrial uptake, although they are certainly interesting at least for niche applications [17, 18].

Biphasic systems can be an effective method by which catalyst, substrates, and products can be easily separated into different liquid phases and therefore simplifying and ‘‘greening’’ reaction workup. Fluorous biphasic solvent systems, where the homogeneous catalyst is soluble within the fluorous phase and reactants are soluble within an immiscible conventional solvent, have been extensively studied. Heating leads to the two solvents becoming miscible, enabling the reaction to occur. On completion of the reaction, when cooled, the phases return to being immiscible with the product partitioning into the conventional solvent phase for isolation. However, there have been serious concerns expressed over the ‘‘green’’ credentials of these heavily fluorinated molecules as they persist in the environment and can be hazardous to operators. Phase transfer catalysts (PTCs) have been used for many years in biphasic systems for transferring species into a phase they would not normally be soluble in. They aid the reaction by improving the availability of the substrates [19]. PTCs are commonly quaternary ammonium or phosphonium compounds; they mostly do not present major environmental concerns and continue to be popular for greening organic reactions. Perhaps, the biggest concern is with regard to their recovery from reactions as they are usually very soluble in both phases of the biphasic system, although heterogeneous PTC, involving, for example, silica-supported onium compounds have been reported.

1.4
Heterogeneous or Homogeneous

While homogeneous catalysis generally offers good activity and a homogeneous distribution of active sites, as explained earlier, it is not without problems notably with regard to separation and reuse. Here, heterogeneous catalysis has clear advantages. There are in fact a number of advantages of heterogeneous catalysis compared to homogeneous [20, 21].

- *Safety* – heterogeneous catalysts are often environmentally benign and safe to handle because of the active species being bound to a support material (e.g., silica-supported sulfonic acid for acid catalysis compared to sulfuric acid).
- *Separation and reusability* – the solid catalyst can either be used in a fixed bed configuration or simply filtered or centrifuged from a stirred tank reaction and then, in many cases reactivated for reuse (e.g., zeolites used in petroleum refining can be reactivated and reused for years before disposal).
- *Activity* – while homogeneous catalyst are commonly the most active, there are many cases where perhaps counterintuitively, the heterogeneous analog is more