

Clean Synthesis

using Porous Inorganic Solid Catalysts
and Supported Reagents

J. H. CLARK and C. N. RHODES

series editor JAMES H. CLARK



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ISBN 0-85404-526-0

A catalogue record for this book is available from the British Library

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Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road
Cambridge CB4 0WF, UK

For further information see our web site at www.rsc.org

Typeset by Paston PrePress Ltd, Beccles, Suffolk
Printed and bound by MPG Books Ltd, Bodmin, Cornwall

Clean Synthesis Using Porous Inorganic Solid Catalysts and Supported Reagents

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CHAPTER 1

Introduction

1 Waste Minimisation

Waste minimisation techniques can be grouped into four categories:

- Inventory management and improved operations
- Equipment modification
- Changes in the production processes
- Recovery, recycling and reuse

The waste minimisation approaches as largely developed by the Environmental Protection Agency (EPA) are given in Table 1.1. They can be applied across a wide range of industries including chemicals manufacturing.

2 Clean Synthesis

The hierarchy of waste management techniques has prevention as the most desirable option ahead of minimisation, recycling and, as the least desirable option, disposal. The term *cleaner production* embraces principles and goals that fall comfortably within the waste prevention–minimisation range. It has been described within the United Nations Environmental Programme as:

The continuous application of an integrated preventative environmental strategy to processes and products to reduce risks to humans and the environment. For production processes, cleaner production includes conserving raw materials and energy, eliminating toxic raw materials, and reducing the quantity and toxicity of all emissions and wastes before they leave a process.

Cleaner processes fall under the umbrella of *waste reduction at source* and along with retrofitting, can be considered to be one of the two principal relevant technological changes. Waste reduction at source also covers good house-keeping, input material changes and product changes.¹ Within chemistry and the handling of chemicals the term *green chemistry* has become associated with

Table 1.1 *Waste minimisation approaches and techniques*

<i>Approach</i>	<i>Techniques</i>
Inventory management and improved operations	Inventory for all raw materials Use fewer toxic raw materials Produce fewer toxic chemicals Improvements in storage and handling Improve employee training
Equipment modification	Redesign production equipment so as to produce less waste Improve equipment operating efficiency Redesign equipment to aid recovery, recycling and reuse
Changes in the production process	Replace hazardous raw materials Optimise reactions Consider alternative low-waste routes Eliminate leaks and spills Consider product substitution
Recovery, recycling and reuse	Install closed-loop systems Recycle on site for reuse Properly segregate waste

the methods of waste reduction at source and more generally with reducing the environmental impact of chemicals and chemical processes.^{2,3}

Within the context of cleaner production, terms such as *environmentally benign chemical synthesis* and *clean(er) synthesis* have often proven popular to help define the scope of national or trans-national programmes on waste minimisation. There is no widely accepted definition of clean synthesis but there is reasonable international agreement that the cleaner synthesis of chemicals, *i.e.* that involving a reduction in the toxicity and quantity of emissions and waste through changes to the process, is likely to be achieved through:⁴

- better use of catalysis
- alternative synthesis routes that avoid the need to use toxic solvents and feedstocks
- reduction in the number of synthetic steps
- elimination of the need to store or transport toxic intermediates or reagent
- novel energy efficient methods

It should be noted that catalysis features very highly on any list of preferred/relevant technologies to help achieve a reduction in waste from chemical processes through the use of cleaner synthetic methods.

3 Catalysts and Catalysis

Catalysts are species that are capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction. They cannot change the thermodynamic equilibrium of reactions.⁵

The performance of a catalyst is largely measured in terms of its effects on the reaction kinetics. The *catalytic activity* is a way of indicating the effect the catalyst has on the rate of reaction and can be expressed in terms of the rate of the catalytic reaction, the relative rate of a chemical reaction (*i.e.* in comparison to the rate of the uncatalysed reaction) or *via* another parameter, such as the temperature required to achieve a certain conversion after a particular time period under specified conditions. Catalysts may also be evaluated in terms of their effect on the *selectivity* of reaction, specifically on their ability to give one particular reaction product. In some cases, catalysts may be used primarily to give high reaction selectivity rather than high activity. *Stability* is another important catalyst property since catalysts can be expected to lose activity and selectivity with prolonged use. This then opens the way to *regenerability* which is a measure of the catalyst's ability to have its activity and/or selectivity restored through some regeneration process.

Catalytic processes are the application of catalysts in chemical reactions. In chemicals manufacture, catalysis is used to make an enormous range of products: heavy chemicals, commodity chemicals and fine chemicals. Catalytic processes are used throughout fuels processing, in petroleum refining, in synthesis gas ($\text{CO} + \text{H}_2$) conversion, and in coal conversion. More recently some aspect of clean technology or environment protection has driven most of the new developments. Many emission abatement processes are catalytic. An increasing number of catalytic processes employ *biocatalysis*. Most of these are fermentations classically carried out in stirred reactors using enzyme catalysts, which are present in living organisms such as yeast. Immobilised enzymes processes are becoming more common.

Catalysis is described as *homogeneous* when the catalyst is soluble in the reaction medium and *heterogeneous* when the catalyst exists in a phase distinctly different from the reaction phase of the reaction medium.

Almost all homogeneous catalytic processes are liquid phase and operate at moderate temperatures ($< 150^\circ\text{C}$) and pressures ($< 20\text{ atm}$). Corrosion of reaction vessels by catalyst solutions, and difficult and expensive separation processes are common problems. Traditionally the most commonly employed homogeneous catalysts are inexpensive mineral acids, notably H_2SO_4 , and bases such as KOH in aqueous solution. The chemistry and the associated technology is well established and to a large extent well understood. Many other acidic catalysts such as AlCl_3 and BF_3 are widely used in commodity and fine chemicals manufacture *via* classical organic reactions such as esterifications, rearrangements, alkylations, acylations, hydrations, dehydrations and condensations. More recently there have been significant scientific and technological innovations through the use of organometallic catalysts.

Normally, heterogeneous catalysis involves a solid catalyst that is brought

into contact with a gaseous phase or liquid phase reactant medium in which it is insoluble. This has led to the expression *contact catalysis* sometimes used as an alternative designation for heterogeneous catalysis. The situation can be rather more complicated with *phase transfer catalysis* (PTC) systems. Here the reactants themselves are present in mutually distinct phases, typically water and a non-aqueous phase (usually a hydrocarbon or halogenated hydrocarbon which has a very low solubility in water). The catalyst, which is normally a quaternary ammonium or phosphonium compound or a cation complexing agent such as a crown ether, is believed to operate at the interfacial region⁶ and strictly need not be soluble in either the aqueous or non-aqueous phases. This is demonstrated by the activity of immobilised onium compounds (see Chapter 4). In practice, simple onium compounds such as tetraarylphosphonium compounds, which are insoluble in hydrocarbons, are inactive in corresponding hydrocarbon–water PTC systems, presumably because the low surface area of the salt provides little effective interfacial area for the catalysis to occur.

4 Heterogeneous Catalysts

Most of the large-scale catalytic processes take place with gaseous substrates contacting solid catalysts. The engineering advantages of these processes compared to homogeneous processes are:

- solid catalyst are rarely corrosive
- a very wide range of temperatures and pressures can be applied to suit the process and the plant (strongly exothermic and endothermic reactions are routinely carried out using solid catalysts)
- separation of substrates and products from catalysts is easy and inexpensive

Many solid catalysts are based on porous inorganic solids. The important physical properties of these materials are surface area (often very large and measured in hundreds of square metres per gram), pore volume, pore size distribution (which can be very narrow or very broad), the size and shape of the particles and their strength. The solid catalyst provides a surface, usually largely internal, for the substrates to adsorb and react on. Thus the surface characteristics of the surface (roughness, functional groups, organophilicity, hydrophobicity, *etc.*) are also vital to performance.

Typical heterogeneous catalysts used in large-scale industrial processes are complex materials in terms of composition and structure. Catalytically active phases, supports, binders and promoters are common components. They typically are activated in some way before use, often by calcination. Heterogeneous catalysts have been prepared for many years and often the preparation procedure used in industry is based more on operator experience and tradition than on sound science. Generally the support is prepared or activated before use with the actual catalytic species and any promoters are added later, often as aqueous solutions of precursor compounds, which are then converted into their

final active forms by a final treatment step (*e.g.* calcination). The active sites in heterogeneous catalysts are often metal centres. At the surface these can be very different to those in the bulk, due to differences in ligand environment and coordination geometry. Generally metal surfaces offer the advantage over metal complexes of higher thermal stabilities. Supported palladium, for example, has largely replaced soluble palladium compounds in the manufacture of vinyl acetates.

Metal oxides are widely used as catalyst supports but can also be catalytically active and useful in their own right. Alumina, for example, is used to manufacture ethene from ethanol by dehydration. Very many mixed metal oxide catalysts are now used in commercial processes. The best understood and most interesting of these are zeolites that offer the particular advantage of shape selectivity resulting from their narrow microporous pore structure. Zeolites are now used in a number of large-scale catalytic processes. Their use in fine chemical synthesis is discussed in Chapter 2.

5 Heterogeneous Catalysis

The catalytic mechanism of reaction on solids can be broken down into five consecutive steps:

1. Substrate diffusion
2. Substrate adsorption
3. Surface reaction
4. Product desorption
5. Product diffusion

Substrate molecules must diffuse through the network of pores to reach the internal region and the product molecules must diffuse out of the pore network. Smaller pores provide the advantage of large surface areas and high particle mechanical strengths but lead to problems with slow molecular diffusion. This can lead to concentration gradients where the substrate concentration is at a maximum at the external surface of the particle while the product concentration is at a maximum at the centre of the particle. Large concentration gradients will mean poor catalyst effectiveness.

In the case of a solid catalyst operating in a liquid phase reaction system the problems of diffusion and concentration gradients can be particularly severe. Substrate diffusion can be further broken down into two steps, external diffusion and internal diffusion. The former is controlled by the flow of substrate molecules through the layer of molecules surrounding catalyst particles and is proportional to the concentration gradient in the bulk liquid, *i.e.* the difference in the concentrations of the substrate in the bulk medium and at the catalyst surface. The thickness of the external layer in a liquid medium is dependent on the flowing fluid and on the agitation within the reaction system; typically it is 0.1–0.01 mm thick. Internal diffusion of substrate molecules is a complex process determined not only by the resistance to flow due to the

medium but also by the constraints imposed by the pore structure. As stated earlier, the latter is especially important with microporous solids, *i.e.* when the pore geometries are comparable to molecular geometries. Diffusional limitation, be it due to external, or more commonly, internal, resistance to motion means that the actual (observed) rate of reaction will always be lower than that predicted on the basis of the intrinsic activity of the available surface of the catalyst. Furthermore, the actual rate of reaction can never be faster than the maximum rate of diffusion of the substrate molecules. Apart from mass transfer considerations, heat transfer also becomes of considerable importance in commercial scale processes. Since reaction is either endothermic or exothermic, and reaction occurs at the (internal or external) surface of the catalyst, a temperature gradient will be established between the catalyst particle surface and the external medium. This will depend on the heat of reaction, the activity of the catalyst and the thermal properties of the solid and other phases. Since temperature affects the rate of reaction, heat transfer calculations can become extremely complex and the data that are calculated can be unreliable.

6 Adsorption by Powders and Porous Solids

Adsorption is the enrichment of material or increase in the density of the fluid close to an interface. Under certain conditions this results in an appreciable enhancement in the concentration of a particular component which is dependent on the surface or interfacial area. Thus all industrial adsorbents and the majority of industrial heterogeneous catalysts have large surface areas of $> 100 \text{ m}^2 \text{ g}^{-1}$ based on porous solids and/or highly particulate materials.⁷ In the simplest case for spherical particles of density r and all of diameter d , the specific surface area s , can be defined as:

$$s = 6/rd$$

Thus for a powder made up of smooth particles of diameter 10^{-6} m and density 2 g cm^{-3} , the specific surface area would be $3 \text{ m}^2 \text{ g}^{-1}$. In reality powder particles are irregular and are clustered together in aggregates. These aggregates may be broken down by grinding. The aggregate can itself be regarded as a secondary particle, which contains some internal surface often larger than the external surface. Thus the aggregate possesses a pore structure. The size of the pores in porous solids can be classified as micro, meso or macro based on their width as measured by some defined method. It is often difficult to distinguish between porosity and roughness or between pores and voids, although a useful distinction is to reserve porosity for materials with irregularities deeper than they are wide.

Adsorption is brought about by the interactions between the solid and the molecules in the fluid phase. The forces involved are classified as chemisorption (chemical bonding) or physisorption (non-chemical bonding). Some of the main distinguishing features are:

- physisorbed molecules keep their identities and desorb back to the fluid

phase unchanged, whereas chemisorbed molecules can be expected to change as a result of adsorption and are not recovered unchanged on desorption

- chemisorption is generally restricted to a monolayer whereas at high enough pressures, physisorption can produce multilayers
- physisorption is exothermic (commonly tens of kilojoules per mole) but tends to involve energies below those typical of chemical bond formation, whereas chemisorption involves energies of the same magnitude as chemical bond formation

Some of the principal terms and properties of adsorption, powders and porous solids are given in Table 1.2.

7 Reactor Types

Solid catalysts can be used in all of the major reactor types, *batch*, *semibatch*, *continuous stirred tank* and *tubular*. In the first three cases particulate (powder) catalysts would be appropriate, whereas with the tubular reactor the catalyst would often need to be formed into pellets.^{8,9}

Batch reactors using particulate catalysts need to be well stirred in order to give uniform compositions and to minimise mass transport limitations. They are likely to be preferred for small-scale production of high-priced products or

Table 1.2 *Definitions associated with adsorption, powders and porous solids*

<i>Term</i>	<i>Definition</i>
Adsorption	Enrichment in an interfacial layer
Adsorbate	Substance in the adsorbed state
Adsorbent	Solid material on which adsorption occurs
Adsorption isotherm	The relation at constant temperature between the amount adsorbed and equilibrium pressure or concentration
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding
Monolayer	Amount required to cover the entire surface
Powder	Discrete particulate material (particle dimension < ca. 1 mm)
Surface area	Available surface as defined by a particular method
External surface area	Area of surface outside of pores
Internal surface area	Area of pore walls
Porous solid	Solid with cavities or channels which are deeper than they are wide
Void	Space between particles
Micropore	Pore of internal width of < 2 nm
Mesopore	Pore of internal width of 2–50 nm
Macropore	Pore of internal width of > 50 nm
Pore size	Pore width
Pore volume	Volume of pores (defined by stated method)
Porosity	Ratio of total pore volume to apparent volume of particle

when continuous flow is difficult. The separation of the catalyst from the organic components in a batch reactor may not be simple. If the particles settle well, then the liquid can be removed by decantation and the vessel can be subsequently recharged with fresh substrate(s). Otherwise, it may be necessary to separate *via* filtration or centrifugation, which requires additional equipment and adds to process time. Batch reactors are commonly used in fine/speciality chemicals manufacturing companies and it is important that solid catalysts can be amenable to such reactor configurations so as to make the catalyst technology accessible and attractive to these companies. Smaller and more specialised companies are unlikely to be prepared to invest in new equipment so as to exploit new chemistry unless the whole technology is clearly proven and there is a secure long-term profitable market for the products.

The semibatch reactor with the continuous addition or removal of one or more of the components offers an added degree of sophistication, which can benefit the process through greater stability and safer operation. This method may also lend itself to liquid–particulate solid reactions where a bulk substrate is continuously being converted over a catalyst into a product. For example, in aerial oxidations of substrates, continuous removal of the reaction mixture (through a suitable frit to prevent transfer of solid catalyst) followed by recycling of the unreacted (lower boiling) substrate will enable large total amounts of product to be produced from one catalyst batch and in one reactor.

The continuous stirred tank reactor (CSTR) adds a further degree of sophistication and is generally preferred to single batch operations for the larger scale or more frequent manufacture of products due to lower operating costs and overall investment. In practice, mechanical or hydraulic agitation is required to achieve uniform composition and temperature.

The tubular reactor is a vessel through which the flow is continuous. There are several configurations of tubular reactors suitable for multiphase work, *e.g.* for liquid–solid and gas–liquid–solid compositions. The flow patterns in these systems are complex. A fixed bed reactor is packed with catalyst, typically formed into pellets of some shape, and if the feed is single phase, a simple tubular plug-flow reactor may suffice (Figure 1.1). Mixed component feeds can be handled in modifications to this.

The moving bed reactor can be used when catalyst deactivation is a major factor (*i.e.* when the lifetime of the fixed bed catalyst is low); here spent catalyst is slowly removed from the reactor while fresh material is slowly added at the top (Figure 1.2).

Low feed rates are suitable for trickle bed reactors where for gas–liquid–solid mixing, the gas and the liquid are fed into the top of the reactor. This gives long gas residence times but short liquid residence times. Such a configuration is often used in hydrogenation reactions. When the gas–liquid is fed into the bottom of the reactor, it is known as a bubble reactor. Here the gas residence times are short but the liquid residence times are relatively long. This is commonly used in oxidation reactions. Heat transfer can be a major problem with both trickle and bubble reactors and in such cases a slurry bubble column reactor can be employed.

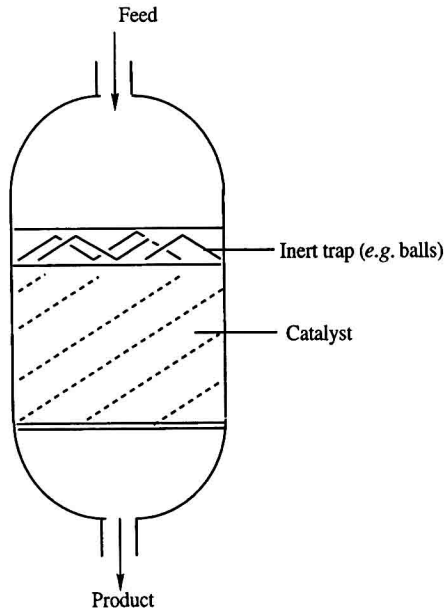


Figure 1.1 *Fixed bed reaction (adiabatic)*

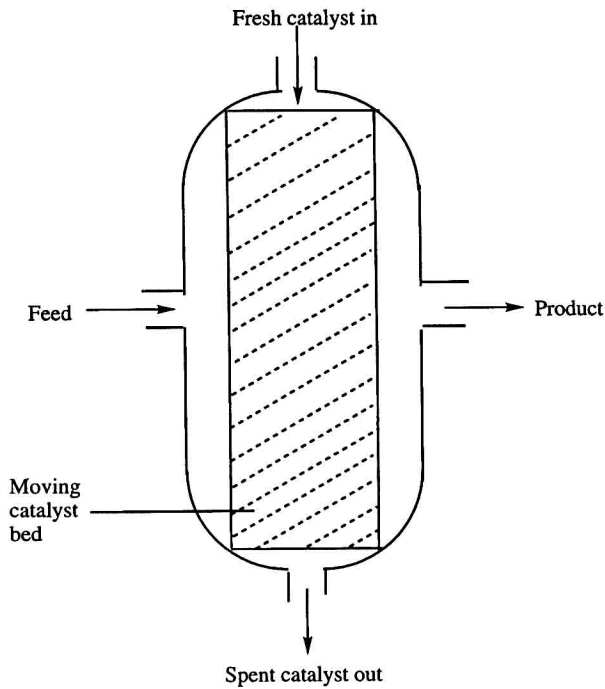


Figure 1.2 *Moving (radial) fixed-bed reactor*

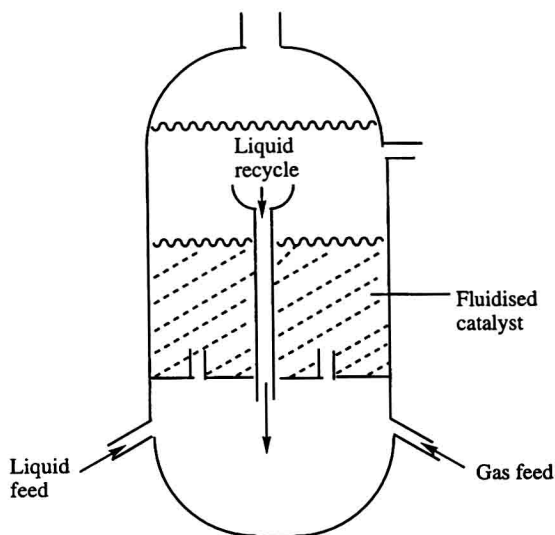


Figure 1.3 *Gas-liquid-solid fluidised reactor*

It is possible to use solid catalysts in particulate forms in tubular reactors through the use of fluidised or fluid bed reactors, where the upward flow of the feed is sufficient to suspend the particulate catalyst in such a way that it seems to behave like a liquid (Figure 1.3). It is however preferable to use more structured catalysts, since better flow characteristics can be achieved, thus minimising hydrodynamic uncertainties and maximising volumetric reaction rates.

8 Commercial Heterogeneous Catalytic Processes

Catalysts played a major role in establishing the economic strength of the chemical and related industries in the first half of the 20th century and an estimated 90% of all of the chemical processes introduced since 1930 depend on catalysis. This has resulted in the build up of an enormous worldwide market for catalysts, which is valued today at some \$5000 million per annum with the product value dependent upon them being a staggering \$250 000 million.

Heterogeneous catalysis is especially important in industry. Some of the major industrial processes that use solid catalysts include the synthesis of inorganic chemicals such as NH_3 , SO_3 and NO , the various reactions used in the refining of crude petroleum such as cracking, isomerisation and reforming, and many of the major reactions of the petrochemical industry, such as the synthesis of methanol, the hydrogenation of aromatics and various controlled oxidations. Some of the major industrial processes to be catalysed by inorganic solids are shown in Table 1.3.

In the long-established manufacturing process of ammonia, for example, 100 megatonnes of ammonia requires some 40 megatonnes of hydrocarbons, 85 megatonnes of water and 80 megatonnes of nitrogen from the air, through 7–8