# CHAPTER 1 HOMOGENEOUS CATALYSIS – ADVANTAGES AND PROBLEMS

D. J. COLE-HAMILTON[a] AND R. P. TOOZE[b]
[a]*EaStCHEM, School of Chemistry, Univesity of St. Andrews, St. Andrews, Fife, KY19 9ST, Scotland*
[b]*Sasol Technology UK, Ltd., Purdie Building, North Haugh, St. Andrews, Fife, KY19 9ST, Scotland*

## 1.1 Catalysis

Catalysts speed up chemical reactions but can be recovered unchanged at the end of the reaction. They can also direct the reaction towards a specific product and allow Chemistry to be carried out at lower temperatures and pressures with higher selectivity towards the desired product. As a result they are used very extensively in the Chemical Industry. Chris Adams, writing for The North American Catalysis Society estimates that "35% of global GDP depends on catalysis, although this excludes the emergent genetic business. Confining the analysis to the chemicals industry, with global sales of perhaps $\$1.5 \times 10^{12}$ the proportion of processes using catalysts is 80% and increasing. The catalyst market itself is US$\$10^{10}$, so that catalysis costs are much less than 1% of the sales revenue from the products which they help create. Small wonder that the catalyst market is increasing at 5% per annum" [1]

TABLE 1.1 Comparison of homogeneous and heterogeneous catalysts

| | Heterogeneous | Homogeneous |
|---|---|---|
| Catalyst form | Solid, often metal or metal oxide | Metal complex |
| Mode of use | Fixed bed or slurry | Dissolved in reaction medium |
| Solvent | Usually not required | Usually required – can be product or byproduct |
| Selectivity | Usually poor | Can be tuned |
| Stability | Stable to high temperature | Often decompose < 100°C |
| Recyclability | Easy | Can be very difficult |
| Special reactions | Haber process, exhaust clean up etc. | Hydroformylation of alkenes, methanol carbonylation, asymmetric synthesis etc |

There are two kinds of catalysts. Heterogeneous catalysts are insoluble in the medium in which the reaction is taking place so that reactions of gaseous or liquid reagents occur at the surface, whilst homogeneous catalysts are dissolved in the reaction medium and hence all catalytic sites are available for reaction. Some of the properties of catalysts are collected in Table 1.1, where heterogeneous and homogeneous catalysts are compared.

*D. J. Cole-Hamilton and R. P. Tooze (eds.), Catalyst Separation, Recovery and Recycling,* 1–8.

Heterogeneous catalysts are generally metals or metal oxides and they tend to give rather unselective reactions. They are very stable towards heat and pressure, so can be used at high temperature. Only the surface atoms are available for reaction. Homogeneous catalysts, on the other hand are usually complexes, which consist of a metal centre surrounded by a set of organic ligands. The ligands impart solubility and stability to the metal complex and can be used to tune the selectivity of a particular catalyst towards the synthesis of a particular desirable product. By varying the size, shape and electronic properties of the ligands, the site at which the substrate binds can be constrained in such a way that only one of a large number of possible products can be produced. As an example, Figure 1.1 shows a range of products that might be produced from a mixture containing an alkene, carbon monoxide, hydrogen and an alcohol. All of the products have their uses, but it is a triumph of homogeneous catalysis that any one of the products can now be made with > 90 % selectivity by careful selection of the metal centre, ligands, reaction conditions and in some cases substrate [2]

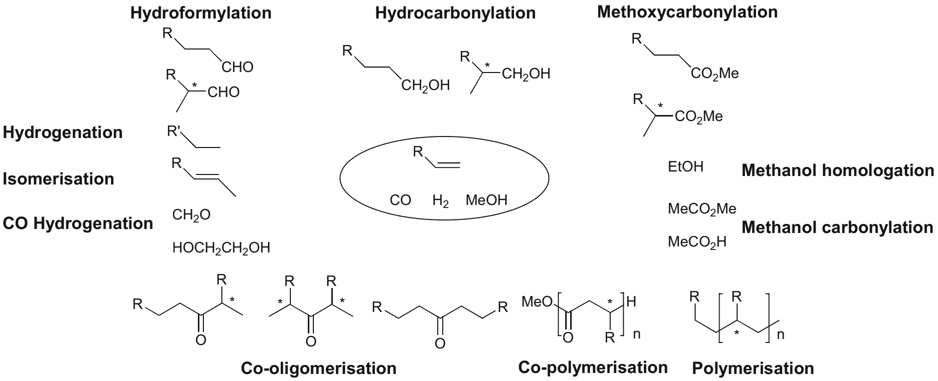

*Figure 1.1.* Some of the products that can form from an alkene, carbon momoxide, hydrogen and methanol. The asterisks represent asymmetric centres in chiral molecules

Various different kinds of selectivity are represented in Figure 1.1. These include:

- Chemoselectivity, the production of one product type such as alcohols rather than aldehydes
- Regioselectivity, the production of a linear ester rather then one with a branching methyl group
- Stereoselectivity, the production of one enantiomer of a chiral compound (chiral products are marked with an asterisk in Figure 1.1)

In general, heterogeneous catalysts do not show the selectivity shown by chiral catalysts, although current research on surface modifiers has shown that even enantioselective reactions, albeit for a restricted range of substrates is becoming possible [3, 4]

Despite this selectivity advantage of homogeneous catalysts, almost all of the industrial catalytic processes use heterogeneous catalysts, because of their one major advantage, their ease of separation form the reaction product. Being insoluble in the reaction medium, heterogeneous catalysts can often be used as fixed beds over which the substrates flow continuously in the liquid or gaseous form. This means that the catalyst can be contained within the reactor at all times. Not only does this mean that the separation of the products from the catalyst is built into the process, but also, the catalyst is always kept under the conditions of temperature, pressure, contact with the substrate and products, for which it has been optimised.

For homogeneous catalysts, which are dissolved in the reaction medium containing the substrates, products and dissolved gases, the separation can be extremely energy intensive and time consuming. Only rarely, when the product can be evaporated under the reaction conditions, can homogeneous catalytic reactions be carried out under continuous flow conditions, where the substrates are introduced continuously into the reactor whilst the products are continuously removed. More often, commercial processes are carried out under what we shall refer to as batch continuous conditions. Part of the liquid catalytic solution containing the product(s), unreacted substrates and catalyst is removed continuously from the reactor to a separator, which is usually a distillation system operating at lower pressure than the reactor. The products and unreacted substrates are then separated from the catalyst and lower boiling byproducts by fractional distillation before the fraction containing the catalyst is returned to the reactor. Since the separation is carried out under conditions that are far removed from those for which the catalyst has been optimised, there is a danger that the catalyst may precipitate, thus clogging pipework or, worse still, decompose in the recyling loop.

In general homogeneous catalysis has only been commercialised when there is no heterogenous catalyst that is capable of promoting the desired reaction or when selectivity to a higher added value product is possible using a homogeneous catalyst. Creative chemists and process engineers have then joined forces to provide a cost effective solution to the separation problem.

Increasing environmental concerns and dwindling supplies of raw materials and energy sources mean that there is now a significant pressure to introduce cleaner processing in the chemical and pharmaceutical industries.
Ideally reactions should have as many as possible of the following properties:

- Use renewable feedstocks
- Make a single product
- Have 100 % atom efficiency (all the atoms in the starting materials end up in the products, although expulsion of water might be acceptable)
- Operate under mild conditions (preferably ambient temperature and pressure)
- Be tolerant of the presence of air
- Produce no waste or other byproducts (these are often quantified using the *E*-Factor, which is the mass (kg) of waste produced per kg of product formed. For a fuller discussion see Chapter 5, Section 5.3.4)
- Have a very long-lived catalyst if, as is very likely, one is required
- Have a simple separation method for the catalyst from the products
- Operate under continuous flow conditions

The catalysts that come closest to meeting these requirements are enzymes, but in general, the products of biological process are not separated from the medium in which they are formed, rather being used in situ. The demand for high selectivity and low environmental impact suggests that there will be a desire to commercialise more processes using homogenous catalysis and hence the problem of separating, recovering and/or recycling the catalysts must be addressed, perhaps using innovative solutions [5, 6]

There are, then, three critical requirements of any catalyst if it is to be exploited on a commercial scale; these are activity, selectivity and stability. It has been widely demonstrated and generally accepted that homogeneous catalysts are superior to their heterogeneous counterparts in terms of both activity (certainly under mild reaction conditions) and selectivity (the classical example is chiral catalysis).

The fatal weakness that has prevented the predicted proliferation of homogeneous catalysts is lack of stability. This further illustrates that all of the above criteria need to be fulfilled.

## 1.2 Catalyst Stability

Catalyst stability can be defined in terms of turnover number (TON). A textbook definition of this is:

$$\text{TON} = \frac{\text{mol of feed consumed before activity ceases}}{\text{mol of catalyst utilised}}$$

In reality the limiting case it not complete loss of activity but rather reduction of activity below a critical threshold determined by the economics of any given process and reactor design.

The TON can be reduced in a number of ways

- Thermally induced decomposition.
- Chemically induced decomposition, of which two further categories can be considered namely substrate induced decomposition and poisoning by impurities or products.
- Physical loss from the process.

These will now be considered briefly in turn

### 1.2.1 THERMALLY INDUCED DECOMPOSITION

As mentioned above one of the fundamental attributes ascribed to homogeneous catalysts is superior activity at low temperature. However, even within classes of such catalysts, improvements in catalyst activity can be made allowing operation at lower temperatures, thus reducing or avoiding completely this mode of catalyst decay. One such example can found in recent advances in palladium catalysed ethene carbonylation (Equation 1.1).

$$CH_2{=}CH_2 + CO + ROH \longrightarrow H\text{-}\{CH_2CH_2C(O)\}_n\text{-}OR$$

*Equation 1.1.* Ethene carbonylation leading to alkyl (R) propionates (n = 1) or to ethene carbon monoxide copolymers (n is large)

This reaction to give methyl propanoate can be catalysed by a combination of palladium acetate, triphenylphosphine and methanesulphonic acid [7]. However in order to obtain acceptable rates the reaction must be carried out at over 100 $^{o}$ C. At this temperature catalyst life is short due to a variety of side reactions [8, 9] and very expensive palladium is lost. Advances in catalyst design have identified alternative phosphine ligands such as 1,2-*bis*(ditertiarybutylphosphinomethylbenzene) that can give much increased activity even at 30$^{o}$ lower temperatures and thus avoid thermal decomposition [10]. Whilst this and other examples show that increased understanding can lead to improvements in catalyst design such that reactor operating conditions can be changed so as to avoid decomposition, no such activity enhancement will impact on the separation process which is governed by the physical properties of all products and reactants. An example here would be the hydroformylation of alkenes. Scientific advances have resulted in phosphine modified rhodium catalysts that exhibit much greater activity than for example unmodified cobalt catalysts, but when this technology is applied to higher molecular weight alkenes (C10+) the separation of products from catalyst in such a way as to avoid extensive decomposition of expensive catalyst is a formidable technological challenge. Different possible separation methodologies for long chain aldehydes formed by hydroformylation reactions are explored in more detail in the subsequent chapters of this book.

### 1.2.2 CHEMICALLY INDUCED DECOMPOSITION

No catalyst has an infinite lifetime. The accepted view of a catalytic cycle is that it proceeds via a series of reactive species, be they transient transition state type structures or relatively more stable intermediates. Reaction of such intermediates with either excess ligand or substrate can give rise to very stable complexes that are kinetically incompetent of sustaining catalysis. The textbook example of this is triphenylphosphine modified rhodium hydroformylation, where a plot of activity versus ligand:metal ratio shows the classical “volcano plot” whereby activity reaches a peak at a certain ratio but then falls off rapidly in the presence of excess phosphine, see Figure 1.2 [11]. On occasion these over ligated complexes are materials that can be identified in solution or perhaps more tellingly isolated from catalytic reactions. Such reactions can often be reversed by removal of the excess reagent. Such processes are not considered in the context of this book as resulting in loss of overall turnover number.

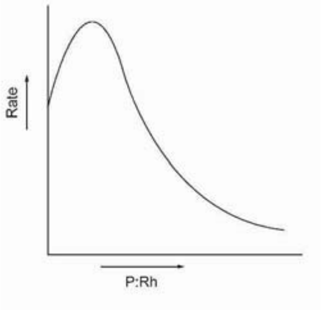

*Figure 1.2.* Typical plot of the effect of rate on the P:Rh ratio for a Rh/$PPh_3$ hydroformylation catalyst. The exact position of the maximum depends on [Rh], $p_{CO}$ and T

A more serious but potentially soluble problem is that of poisoning by impurities in the feed to a catalytic reaction. Homogeneous catalysts are again believed to be more susceptible to this mode of decomposition than their heterogeneous counterparts. This problem may be solved by the development of more robust catalysts, but a more usual solution is feedstock purification. An example where this purification is carried out *in situ* involves the addition of large quantities of aluminium reagents (such as methylaluminoxane, MAO) to polymerisation and oligomerisation reactions. The ratio of aluminium to transition metal can be very high (>500) and part of the purpose of this large excess is believed to be removal of oxygenates from alkene feeds [12].

### 1.2.3 PHYSICAL LOSS FROM THE PROCESS

The loss of expensive catalyst from the reactor system can be fatal for any process. Physical loss involves the removal of active catalyst from the closed loop of the process. This can include the plating out of metal or oxides on the internal surfaces of the manufacturing plant, failure to recover potentially active catalyst from purge streams and the decomposition of active catalyst by the process of product recovery. The first two can be alleviated to some extent by improvements in catalyst or process design, the last is an intrinsic problem for all manufacturing operations and is the subject of this book.

Catalysts are traditionally designed and optimised based on their performance in the reactor and not for their ability to withstand traditional separation processes. However, on taking any system from the laboratory to the pilot plant and beyond, this need to isolate product whilst efficiently recovering the catalyst often becomes the most important single issue. The best option is selection of a product isolation method that maintains the integrity of the catalyst and requires no further treatment of the catalyst prior to reintroduction into the reactor, or leaves the catalyst in the reactor at all times.

A compromise solution can be that, although a catalyst may not be in its active form in the separation unit, it can be recovered and regenerated easily at the production facility. A final option is that spent catalyst can be recovered, concentrated and returned to the original supplier for reprocessing. Whilst this is an expensive and inelegant option, it remains the most pragmatic solution until technologies described in this book reach maturity.

## 1.3 Layout of the Book

In this book, we report on the state of the art of methods for catalyst separation recovery and recycling, not just describing the chemistry, but also discussing the process design that would be required to put the processes into practice.

Conventional processes involving distillation of the product directly from the reactor or batch continuous operation where the distillation is carried out in a separate chamber (Chapter 2) provide the backdrop for the many alternative processes that are being discussed.

These alternative processes can be divided into two main categories, those that involve insoluble (Chapter 3) or soluble (Chapter 4) supports coupled with continuous flow operation or filtration on the macro – nano scale, and those in which the catalyst is immobilised in a separate phase from the product. These chapters are introduced by a discussion of aqueous biphasic systems (Chapter 5), which have already been commercialised. Other chapters then discuss newer approaches involving fluorous solvents (Chapter 6), ionic liquids (Chapter 7) and supercritical fluids (Chapter 8).

No attempt is made to provide comprehensive coverage of all the work carried out in these different media, but rather to give a flavour of the kind of systems for which the different approaches may be appropriate. In all the chapters, a more detailed discussion of the rhodium catalysed hydroformylation of 1-octene to nonanal, as a representative example of the synthesis of a long chain aldehyde with relatively low volatility, is provided [13, 14]. This reaction has been chosen because:

- It is a reaction demonstrating 100 % atom economy
- It is a reaction which uses both gas and liquid substrates
- The rate of the reaction is crucial for successful commercialisation
- There are important issues relating to chemoselectivity (aldehydes or alcohols may be the products and alkene isomerisation is a competing side reaction, which must be reduced to a minimum) and regioselectivity (linear aldehyde is much preferred over branched)
- It is a commercially important reaction as a step in the synthesis of nonanol, an important plasticizer alcohol. Other long chain alcohols, derived from product aldehydes by hydrogenation are used as the basis of soaps and detergents,
- Currently the reaction is carried out using cobalt based catalysts with severe penalties in terms of harsh operating conditions (80 bar $CO/H_2$, 200°C). In addition, substantial loss of substrate (*ca.* 10%) to hydrogenation makes the overall selectivity to the linear alcohol *ca.* 80% [15]. Rhodium based systems are capable of giving higher selectivities (>90%) to the desired linear aldeyde product under milder conditions (20 bar, 100°C) [13]
- The reaction has been studied using all of the different possible separation methods and represents a system where advantages and disadvantages of the various processes can be compared [5]
- Despite the very attractive properties of the rhodium-based system, no commercial plants used it because the low stability of the catalyst meant that the catalyst separation problem prevented commercialisation. Very recently, this situation has changed with the introduction of rhodium-based plant by Sasol in South Africa which uses technology developed by Kvaerner Process Technology (now Davy Process Technology). This batch continuous plant produces medium - long chain aldehydes and the separation is carriedout by low pressure distillation [16-18]

In the final Chapter of the book (Chapter 9), all the different processes are compared with a discussion of the various areas where further research will be required to improve the new processes to a point where they may be commercially attractive.

## 1.4 References

[1] C. J. Adams, *The North American Catalyst Society*, http://www.nacatsoc.org/edu_info.asp?edu_infoID=1.

[2] 'Applied Homogenous Catalysis with Organometallic Compounds', ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996.

[3] Q. H. Xia, H. Q. Ge, C. P. Ye, Z. M. Liu, and K. X. Su, *Chem. Rev.*, 2005, **105**, 1603.

[4] T. Burgi and A. Baiker, *Accounts Chem. Res.*, 2004, **37**, 909.

[5] D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.

[6] C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, and R. Haag, *Angew. Chem.-Int. Edit.*, 2002, **41**, 3964.

[7] E. Drent, *Eur. Pat.*, 1984, 0106.

[8] R. P. Tooze, K. Whiston, A. P. Malyan, M. J. Taylor, and N. W. Wilson, *J. Chem. Soc.-Dalton Trans.*, 2000, 3441.

[9] W. G. Reman, G. B. J. Deboer, S. A. J. Van Langen, and A. Nahuijsen, *Eur. Pat.*, 1991, 0411.

[10] W. Clegg, G. R. Eastham, M. R. J. Elsegood, R. P. Tooze, X. L. Wang, and K. Whiston, *Chem. Commun.*, 1999, 1877.

[11] K. L. Oliver and F. B. Booth, *Hudrocarbon Process.*, 1970, **49**, 112.

[12] E. Y. X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391.

[13] 'Rhodium catalysed hydroformylation', ed. P. N. W. M. Van Leeuwen and C. Claver, Kluwer, Dordrecht, 2000.

[14] C. D. Frohling and C. W. Kohlpaintner, in 'Applied Homogeneous Catalysis with Organometallic Compounds', ed. W. A. Herrmann, VCH, Weinheim, 1996.

[15] B. Cornils, in 'New synthesis with Carbon Monoxide', ed. J. Falbe, Springer Verlag, Berlin, 1980.

[16] J. A. Banister and G. E. Harrison, *US Patent*, 2004, 0186323.

[17] *Chem. Eng. News.*, 1999, **77**, 19.

[18] *Chem. Eng. News.*, 2004, **82**, 29.