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Catalysis and sustainable (green) chemistry

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Abstract

Catalysis is a key technology to achieve the objectives of sustainable (green) chemistry. After introducing the concepts of sustainable (green) chemistry and a brief assessment of new sustainable chemical technologies, the relationship between catalysis and sustainable (green) chemistry is discussed and illustrated via an analysis of some selected and relevant examples. Emphasis is also given to the concept of catalytic technologies for scaling-down chemical processes, in order to develop sustainable production processes which reduce the impact on the environment to an acceptable level that allows self-depuration processes of the living environment.

Keywords: Catalysis; Sustainable chemistry; Green chemistry; Catalytic processes; Environment protection

1. Introduction

1.1. The concept of sustainable (green) chemistry

The “green chemistry” concept was introduced in the early 1990s in the scientific community and soon adopted by mass-media as the new approach of chemistry in opposition to the pollute-and-then-clean-up approach considered the common industrial practice. The concept rapidly became popular and various research institutes, books and journals use this definition, although not always with the same meaning. A good definition of “green chemistry” is that of the US Environmental Protection Agency (EPA): use of chemistry for pollution prevention, and design of chemical products and processes that are more environmentally benign (http://www.epa.gov/greenchemistry/whatis.htm). EPA identifies the following main areas for green chemistry:

- Use of alternative synthetic pathways (examples, are natural processes such as photochemistry and biomimetic synthesis or alternative feedstocks that are more innocuous and renewable such as biomass).
- Alternative reaction conditions (examples are use of solvents that have a reduced impact on human health and the environment), or increased selectivity and reduced wastes and emissions.
- Design of eco-compatible chemicals (less toxic than current alternatives or inherently safer with regard to accident potential).

“Sustainable chemistry” is the concept sometimes opposed and sometimes confused with “green chemistry” [1]. There is a key difference in the definition: while green chemistry indicates that a not risky and polluting chemical production process may exist, the sustainable chemistry concept links eco-efficiency, economic growth and quality of life in terms of a cost/benefit analysis. The sustainable chemistry approach emphasizes the concept of sustainable risk, i.e. that there does not exist a good

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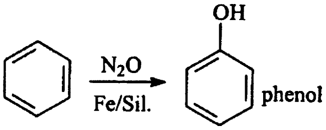
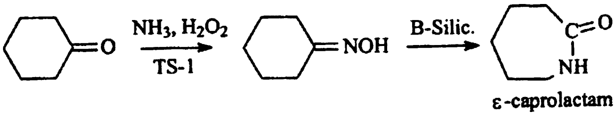
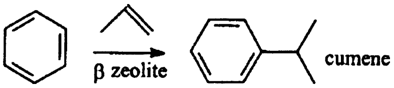
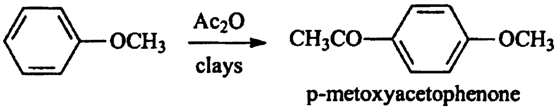
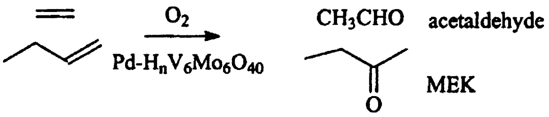
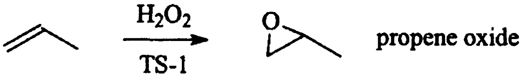
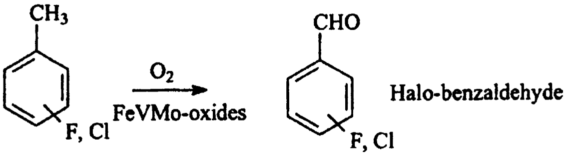
"green chemistry" opposite to a dirty chemistry, but simply that each chemical process has a risk associated with production. The role of chemists and engineers is to minimize this risk and reduce the impact on the environment to a level sustainable by the environment, assuring a good quality of life. If one looks at the changes that have occurred in the chemical industry over the last two decades, it can be seen that all new processes introduced were motivated by a need to reduce the environmental impact or hazardous risks, and achieve better use of resources. None of the changes were possible however without better process economics, including environmental and social aspects in the cost evaluation. Some examples of eco-efficient alternative processes to the conventional ones are listed in Table 1 together with the key aspects of the processes in terms of eco-compatibility.

Protection of the environment is not necessarily in contrast with economic growth, but certainly the use of new improved chemical technologies is required to combine these two factors otherwise in contrast. R&D is thus the key for sustainable development. Recent examples, furthermore, indicate that new eco-efficient processes can give companies the opportunity to gain new market positions.

1.2. Assessment of sustainable (green) chemical processes

Another aspect to consider is that often the label "green chemistry" is used to indicate technologies for

Table 1
Examples of new eco-efficient catalytic processes

Process	Key characteristics
	Solutia process Reduction of N_2O emissions (greenhouse gas) by reuse as reactant
	EniChem process Reduction of ammonium sulfate waste Avoids use of toxic hydroxylamine
	EniChem process Reduction of polyalkylate waste
	Rhodia process Avoids use of hazardous catalysts such as $AlCl_3$, BF_3 Reduced waste formation
	Catalytica process Reduced formation of chlorinated waste
	EniChem process Avoids chlorinated organic by-products (with respect to the chlorohydrin process)
	Aventis process Reduced waste formation Reduced corrosion problems

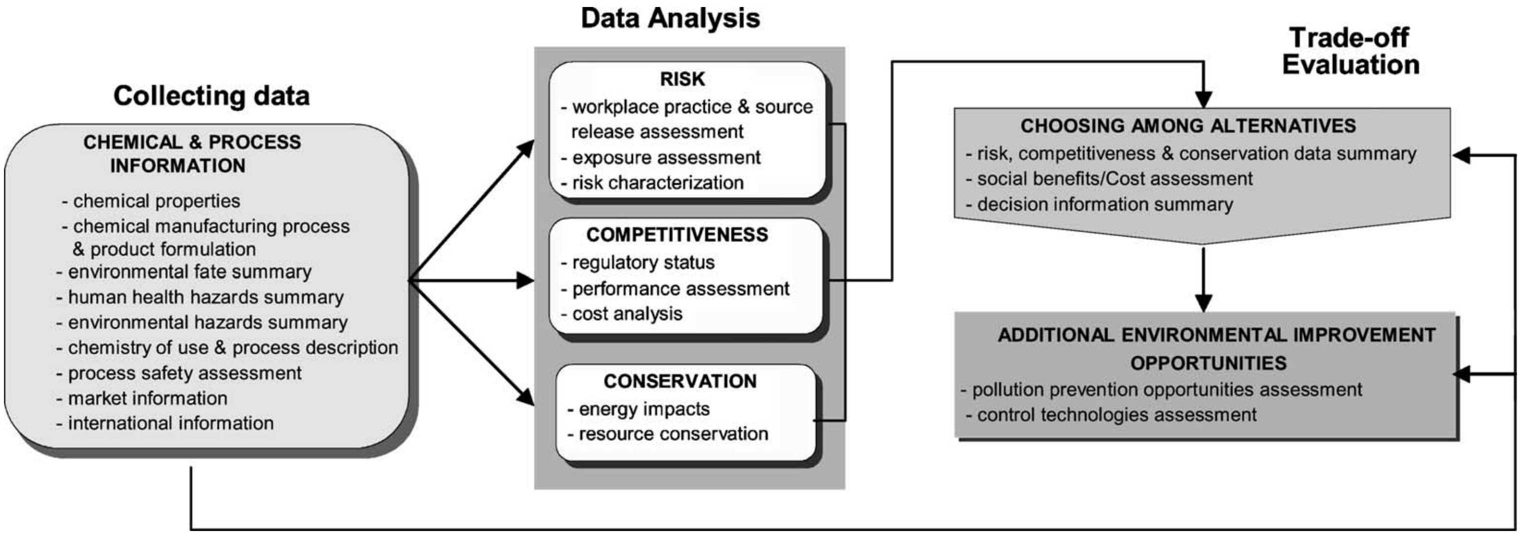


Fig. 1. Overview of the CTSA procedure (see text).

which a careful cost/benefit or assessment study has not been made. The EPA has defined a procedure for the assessment of cleaner technologies (Cleaner Technologies Substitutes Assessment—CTSA), based on the comparative evaluation of risk, performance, cost, and resource conservation with respect to currently used chemicals/technologies [2]. Key aspects of the assessment procedure are shown in Fig. 1.

A more complete analysis should also include life cycle assessment, a complex and more costly procedure. The central aspect of these procedures remains the quantitative assessment of costs and social and environmental benefits. Considerable effort is also being directed to evaluating the relationship between the environment and health [3].

"Sustainable (green) chemistry" is thus the natural trend of chemistry, but not an independent factor from economic growth, quality of human life and health care. The evaluation of new "green" chemical processes and products should follow a rigorous assessment in terms of eco-efficiency, risk minimization and socio-environmental impact which quantitatively evaluates the costs and benefits of the new process and alternative solutions.

2. Discussion

2.1. Catalysis and sustainable (green) chemistry

Catalysis is a necessary and critical tool for achieving social and economic objectives. Table 2 summarizes the principles of "green chemistry" [4–6] and compares them with the objectives of industrial catalysis; some examples are also given.

Atom economy (introduced by Trost) is the first principle of green chemistry and is a parameter of synthetic efficiency. The concept of E factor (environmental factor) proposed by Sheldon would be preferable. Defining waste as everything except the desired product, the E factor is the ratio (kg/kg) of by-products to products. Typical values are: oil refining (about 0.1), bulk chemicals (1–5 range) and pharmaceuticals (up to 100). By multiplying the E factor with an environmental quotient (Q) which depends on the nature of the waste, it is possible to obtain a weighted factor which allows the degree of "green chemistry" content of a chemical product to be classified. This concept is popular in the "green chemistry" community, but not very precise. It is preferable to use more rigorous approaches such as the CTSA procedure mentioned above.

Industrial processes from the beginning have moved towards more efficient use of resources and improvement in selectivity, because both aspects correspond to an improvement in the process economics. An example of this process is the synthesis of maleic anhydride [7,8]. The catalytic process starting from benzene was substituted with that using butane about 15–20 years ago for the following reasons:

- The loss of two carbon atoms (as starting from benzene) is avoided.
- The only by-products are carbon oxides and a minor amount of acetic acid. With benzene the selectivity is higher, but several by-products are formed requiring expensive separation.
- The toxicity aspects related to the use of benzene is avoided, reducing costs related to safety systems and benzene handling.

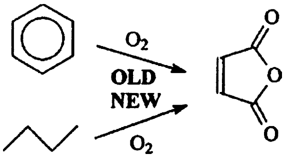
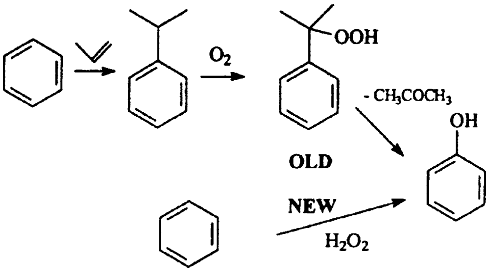
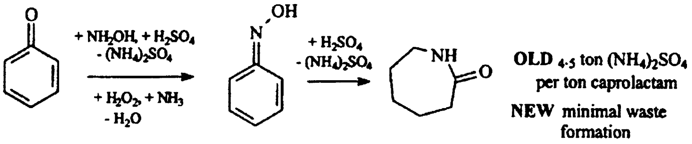
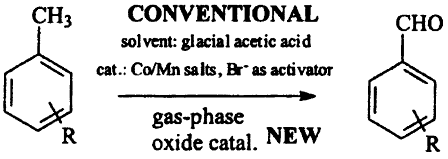
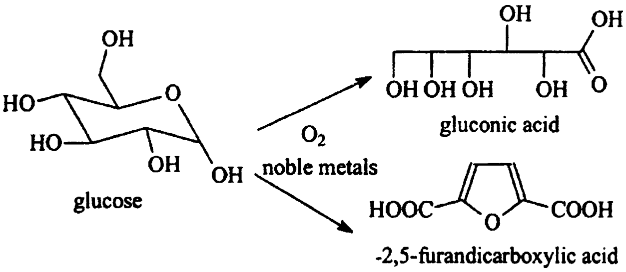
The butane process fully implements the principles of green chemistry:

(i) Use of non-toxic reactants.
(ii) Improved atom economy.
(iii) A complex multistep transformation (the reaction is a 14 e^- oxidation, with abstraction of eight H atoms from the butane molecule and insertion of three O atoms) is realized in one single step, without using solvents.
(iv) Waste formation is minimized.

More than 95% of maleic anhydride plants use the butane process today. The reason, however, is not an early conversion of companies to "green chemistry" philosophy. The use of the new process derives instead from the following economic reasons:

(i) Butane is cheaper than benzene, and requires in addition less costly safety equipment.
(ii) The molar yield starting from butane instead of benzene is lower, but the weight yield (the relevant industrial parameter) is higher.
(iii) When a selective catalyst is available, reduction of process complexity means a reduction in both fixed costs and variable costs (utilities, labour, etc.).

Table 2
Comparison of the principles of green chemistry and objectives of industrial catalysis

Principles of "green chemistry"	Objectives of industrial catalysis	Examples
Atom economy ("how much of the reactants end up in the product?")	Avoid side reactions (maximize selectivity), rational use of hydrocarbons	
Simple and safe process	Reduce process complexity and formation of intermediates by making in a single step over a solid catalyst complex multistep reactions	
No waste	Reduce or avoid waste formation	
Avoid toxic chemicals or solvents	Avoid solvents using heterogeneous catalysis	
Use of renewable resources	Use of natural resources for production of chemicals	

(iv) Gas-phase reactions reduce the costs of separation.
(v) The formation of by-products and waste, besides a loss in selectivity, also implies higher costs of separation.

The butane process has now being adopted worldwide due to the better economics; in this case the change also is in the direction of environment protection. This is not an exception, but rather a common feature of most of the new chemical processes developed over the last two decades.

The process to obtain maleic anhydride from butane was possible only after the discovery of vanadyl pyrophosphate catalysts which possess unique characteristics of activity and selectivity [8] unmatched in all other types of mixed oxides that have been studied for this reaction. Catalyst innovation indeed is a key step in the development of new eco-efficient but also cost effective processes.

2.2. Downsizing the production of chemicals

The development of sustainable production of chemicals not only requires the development of less polluting and risky production processes, but also requires a more general change in the approach to production of chemicals in terms of the global impact on the environment. During the development of the petrochemical industry in the middle of the last century the keywords were process integration and upsizing plants in order to reduce the cost of production. Typically the cost of production (not considering environmental costs) increases by a factor of less than one with respect to production. The concentration of various chemical processes in one large petrochemical centre reduces the costs of utilities and services, transport, etc. However, these large petrochemical centres have a massive impact on the environment and health, even when each single process has been improved to reduce its impact on the environment. It is thus necessary to change the philosophy and go in the direction of downsizing and decentralizing the production of chemicals to a level acceptable for the environment.

A change in vision for the production of chemicals is required. For example, steam cracking is the main source of olefins for petrochemical and polymer use, but large plants are necessary and different olefins form. As a consequence, typically various processes using these olefins are located near the steam cracking process. Producing olefins by alkane dehydrogenation (or oxidative dehydrogenation) may instead allow a single type of olefin to be produced in a dedicated plant which can be integrated with a downstream petrochemical process. By designing new catalytic solutions (for example, catalytic membranes) it may even be possible to develop new economic alkane dehydrogenation processes on a small to medium scale. Therefore, instead of horizontal integration as in the past, vertical integration may be possible in which, for example, starting from an alkane a polymer or chemical may be produced directly in a single integrated line, and in the amount needed for local use. This avoids costs and risks of transport and storage of chemicals and in addition decentralizing the production of chemicals may make it possible to maintain the impact on environment at a sustainable level. The concept of on-site production is already used in some new production processes to avoid the storage of toxic or dangerous chemicals (for example, on-site production of HCN) in the production of toluene diisocyanate. This development was made possible by the combined development of new catalysts and new reactor engineering solutions which allowed an economic production even in a small size plant. Therefore, innovation in catalyst and catalytic reactor engineering was the key element towards minimization of risks and environmental impact.

Another interesting example is the use of H_2O_2 as a clean reactant. Hydrogen peroxide in combination with catalysts such as TS-1 (Ti-silicalite) or related materials can give rise to a range of highly interesting reactions, some of them listed in Tables 1 and 2. They include the ammoximation of cyclohexanone, the epoxidation of propene and other small alkenes, the hydroxylation of aromatics and of linear alkanes, plus other reactions of less industrial importance. With respect to present commercial processes the new processes considerably limit the formation of waste, and the use of hazardous chemicals (for example, alkyl hydroperoxide) and reduce process complexity.

However, the key parameter for industrial development is the cost of H_2O_2. H_2O_2 is produced by only a few companies, and very large investments are required, because H_2O_2 synthesis (alkylanthraquinone route) is economic only when large quantities are produced. The cost of H_2O_2 today is higher than allowable for the commercialization of the above listed reactions, even taking into account the environmental advantages. The introduction of these new processes requires the development of new processes for the synthesis of H_2O_2, which should meet two requirements: lowering the cost of production and be applicable to small to medium size plants.

The new H_2O_2 synthesis can be vertically integrated with a line of production of propene oxide (PO) from propene (perhaps produced from propane as indicated above) and downstream to a line of PO used in the production of polyurethane foams or polyester resins. Such integration requires medium to small plants ($<$100–200 kt PO per year) for which the chlorohydrin process is currently the only viable option from the economic point of view (epoxidation using alkyl hydroperoxides is economic only for large scale processes ($>$250 kt PO per year)). The chlorohydrin process, however, forms large quantities of waste water (40 t waste water/t PO) containing inorganic salts (ca. 1 t $CaCl_2$/t PO produced) and significant amounts of chlorinated organic by-products (formed in ca. 10% yield based on the propene consumption). The new route of synthesis of PO by epoxidation of propene with H_2O_2 on a TS-1 catalyst is thus preferable to reduce this relevant environmental impact, but requires the production of H_2O_2 on-site (to avoid risks related to its storage and transport), at a low cost and with a level of production compatible with its complete use on-site.

A possible route meeting these requirements is based on the synthesis of H_2O_2 from $H_2 + O_2$ mixtures using Pd-based catalysts. There are, however, a series of problems related to reactor design (especially to assure safe operation), the H_2O_2 productivity and concentration which can be obtained, and catalyst optimization to maximize selectivity towards H_2. The solution of these problems, which requires an integrated reactor and catalyst approach, is the critical step to enable the new concept of on-site eco-efficient PO synthesis discussed above. Catalytic membranes are a solution under investigation to eliminate the problems indicated above.

This example evidences the complexity of problems encountered in developing processes of sustainable chemistry. *Scaling-down* chemical processes is a future requirement to develop sustainable production processes which reduce the impact on the environment to a level acceptable for autopurification processes. It must be noted, however, that the eco-indexes to evaluate this acceptable level of eco-compatibility must be related to environment parameters (for example, maintain the eco-diversity of species) and not only to chemical parameters (like the presence of pollutants, metal ions, etc.), differently from the common approach. Legislative limits, which are the driving force for innovation towards R&D for sustainable chemistry, must also be related to these eco-indexes. A step forward with respect to the current situation where limits are applied mainly on the basis of the “precaution” concept is thus necessary.

Catalysis plays a central role in this process of scaling-down, because new solutions are required in terms of both process miniaturization and use of more sophisticated technologies (for example, catalytic membranes).

2.3. Towards a catalytic sustainable (green) chemistry

Although the environmental budget is rapidly becoming larger than the R&D budget in several chemical companies, the R&D industrial objectives have been progressively moved from the medium to the short term, without corresponding compensation by public investments on long-term research. Process innovation, especially when it involves complete process redesign, is a long-term investment. The industrial research effort on “green chemistry” has thus been mainly focused on finding short-term solutions, like substitution of hazardous chemicals, solvents, etc. which can revamp plants, more than on developing completely new solutions which require much higher investments. In addition, the largest part of the environmental budget is related to cleanup technologies to make sure that all emissions meet legislative regulations.

It is thus possible to identify two main directions in catalysis research related to sustainable (green) chemistry:

- A long-term approach (breakthrough approach), based on innovation in catalytic materials chemistry and use of unconventional reaction conditions which will provide the driving force for developing new solutions (catalysts, technologies and processes). Renewed effort is also necessary in multidisciplinary approaches and in technologies which allow making reactions under mild conditions (electro- and photo-catalysis, reactions in plasma and with dielectric barrier discharges, etc.).
- A short–medium-term approach (evolutionary approach), mainly focused on the improvement of current catalytic technologies and processes.

The largest part of industrial effort is focused on the second direction. Combinatorial catalysis is often classified in the first area, being aimed at discovering new catalytic materials by a fast screening procedure. However, breakthrough catalytic technologies and processes may derive only from the identification of problems and the testing of unconventional ideas, due to the complexity of the catalytic and sustainable chemistry problems. Fast, but automatic, catalyst screening procedures assume a linearity of effects which is not effectively true.

2.4. *Catalysis, green chemistry and organic syntheses*

The discussion in the previous sections has shown that the concept of "green chemistry" may be applied with severe limitations in the production of base chemicals, because even though the concepts are already well established, the next generation processes involve different problems from those suggested by "green chemistry" principles. Indeed, the latter were especially designed with reference to the synthesis of organic chemicals, for which there is an effective need also in today's commercial production to pass from stoichiometric reactions to catalytic ones, to use cleaner solvents, to reduce waste, and to maximize atom efficiency [9,10]. A "green chemistry" expert system to help in surveying the field and choosing the preferable solvent, reaction conditions and synthetic methodologies is also available online (http://www.epa.gov/greenchemistry/tools.htm).

Catalysis is also in this case a fundamental component of the innovation towards cleaner production processes. A few examples are given below to highlight new possibilities for catalysis in eco-compatible organic syntheses. In most of the cases however process economics and catalyst stability have not been demonstrated:

- Noble and non-noble metals are widely used in selective hydrogenation of organic molecules, but selectivity is not complete. Charged transition metal complexes (ferrocenyl-rhodium, for example) may be immobilized on alumina or silica by functionalizing the latter by grafting a heteropolyanion which then anchors the charged transition metal complex. This catalyst allows quantitative hydrogenation reactions (Fig. 2a) [11] and good turnover numbers. This example shows the possibility offered by anchoring or tethering metal complexes to solids. A series of interesting behaviours has also been found by tethering metal complexes to the walls of mesoporous materials (like MCM-41). Encapsulated metal complexes (often defined ship-in-a-bottle samples) may also be included in the same general class of complexes in constrained environments [12].
- The hydroxylation of benzene to phenol is an interesting industrial reaction (see Tables 1 and 2), but also a model reaction for the synthesis of a variety of substituted phenols of large interest as intermediates in the production of fine chemicals. However, phenol is more reactive than benzene towards hydroxylation and therefore the problem is how to stop reactivity to maximize selectivity. One solution is to use biphasic systems, where the products due to the partition coefficient are rapidly taken away from the catalyst. By using biphasic $FeSO_4$ with a pyrazine carboxylic acid ligand and trifluoroacetic acid as cocatalyst in a benzene–water–acetonitrile biphasic system it is possible to achieve 97% selectivity to phenol at about 8% conversion (Fig. 2b) [13]. Due to the nature of the chemical used, it is difficult to consider the applicability of this process and solution to large scale products (like phenol), but it may be an interesting solution for the synthesis of substituted phenols.
- Ionic liquids represent a new class of highly interesting and versatile solvents. Based around imidazolium salts, these solvents are liquid over a wide range of conditions, but have a minimal vapour pressure. They also possess interesting properties which are a combination of the characteristics of water and organic solvents. They can be used as non-usual solvents which allow interesting reactions. For example, enzyme *Candida Antartica* catalyzes the oxidation of octanoic acid by H_2O_2 to form a peroxo acid which then is able to oxidize alkenes with good yields (Fig. 2c) [14].

New catalytic organic synthesis methodologies thus offer several possibilities for a relevant improvement in the eco-compatibly of fine chemicals production, allowing a drastic decrease in the *E* factor. It should be noted, however, that there is a factor of around 100 between the waste produced in the production of fine chemicals and base chemicals, for example, but a factor much higher between the volume of base chemicals produced (as well as refinery products) and fine chemicals. Therefore, in terms of global impact it is the production of refinery and base chemicals which should be primarily addressed, but this requires a longer term approach.

2.5. *The use of alternative reaction media*

The use of alternative reaction media is a concept particularly emphasized in green chemistry, because the problem is seen from the organic chemistry

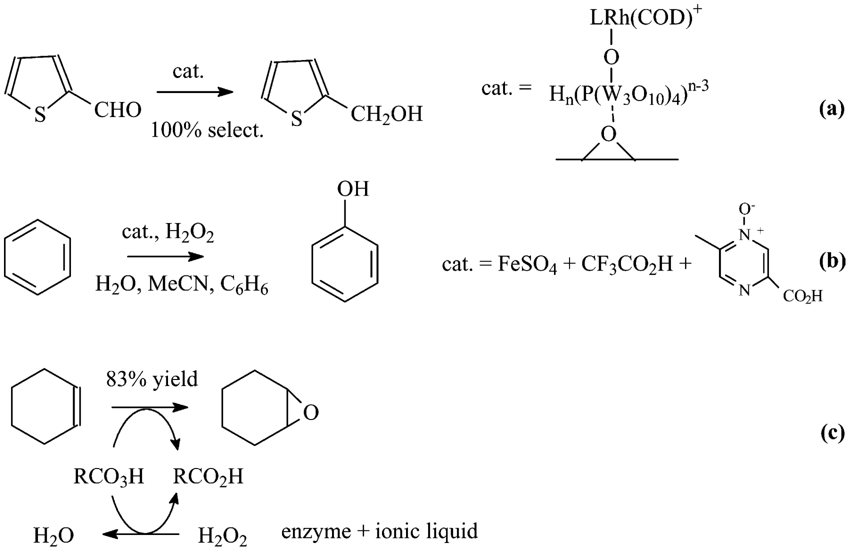


Fig. 2. Examples of new catalytic reactions of green chemistry.

perspective (as discussed above) and thus there is a need to substitute toxic solvents with non-toxic solvents, as well as to decrease the amount of waste (mainly related to the large volumes of solvents for the reactions). Emphasis is thus given to novel solvent systems (for example, ionic liquids and biphasic systems), non-solvent reactions and supercritical solvents (CO_2, in particular).

Supercritical fluid technology has been around for many years, but has found commercial application mainly for extraction processes. The recent progress in engineering and equipment technology for operations under pressure (which parallel a reduction in cost) has made affordable the use of supercritical fluids of new reaction media.

Supercritical fluids, SCFs, are gases compressed until their density approaches that of liquids. Such compression can occur only above the "critical temperature" of the fluid, since at lower temperatures the fluid liquefies on compression. Therefore, an SCF is a gas which displays some of the properties of a liquid. The advantages of using supercritical fluids are related to the absence of toxic residues, relatively low temperature needed for the extraction process, and higher solvent power of SCFs.

SCFs also offer interesting opportunities for chemical syntheses with solid catalysts. SCFs are characterized by high diffusivity, low viscosity, and intermediate density. This may give rise to considerable improvements in chemical reactions, since all phenomena which are related to mass-transfer phenomena and which can limit the rate of reaction may be overcome by exploiting these properties. Health and safety benefits include the fact that most SCFs, $scCO_2$ and scH_2O, are non-toxic, non-carcinogenic, and non-flammable, a clear advantage with respect to conventional organic solvents.

Specific further advantages might be exploited for catalytic applications in the field of petrochemical and fine chemicals synthesis:

- The extraction properties of SCFs may be exploited to separate products from by-products, or to recover homogeneous catalysts, replacing conventional organic solvents and improving performances with respect to the latter. An application of this might be the in situ regeneration of heterogeneous catalysts which deactivate due to the formation of heavy residues.
- Easy separation of the SC solvent from the products allows obtaining pure products without solvent residues.
- The rate of reaction may be considerably increased with respect to reactions carried out with

Table 3
Examples of catalytic reactions in supercritical fluids[a]

Type of reaction	Reaction	Catalyst	Reaction conditions	Effect[b]
Alkylation	Isobutane + isobutene	H–Y (dealuminated)	Solvent: isobutane, $T = 50$–$140\,^{\circ}$C, $P = 3$–$5\,$MPa	Increase activity, increase lifetime
Esterification	Oleicacid + methanol	Ion-exchange resins	Solvent: CO_2, $T = 40$–$60\,^{\circ}$C, $P = 0.9$–$1.3\,$MPa	Increase activity
Hydrogenation	Fats and oil	Supported Pd	Solvent: propane, $T = 50$–$100\,^{\circ}$C, $P = 7$–$12\,$MPa	Increase activity, increase selectivity
Isomerization	1-Hexene	Supported Pt	Solvent: CO_2 (cosolvent: pentane), $T = 250\,^{\circ}$C, $P = 18\,$MPa	Increase activity, selectivity and lifetime
Oxidation	Toluene to benzaldehyde	Co/alumina	Solvent: CO_2, $T = 100$–$200\,^{\circ}$C, $P = 8\,$MPa	Increase selectivity

[a] Elaborated from [15].
[b] Effect of using supercritical conditions with respect to subcritical conditions.

conventional solvents. This is may be due to several different effects:
  - Higher diffusivity in the SC solvent of reactants; in heterogeneously catalyzed reactions, often inter-particle mass-transfer may be the rate-limiting step for very rapid reactions. With SC solvents, this problem is overcome due to the fact that the boundary layer is considerably reduced in thickness.
  - High miscibility of the SCF with other gaseous reactants.
  - Presence of a single homogeneous phase instead of a gas–liquid biphasic system again may be helpful to overcome the problems associated with mass-transfer.
  - The SCF may take directly part in the reaction, and all the above mentioned advantages may contribute in enhancing the rate of reaction.
- The selectivity of the process may be affected as a consequence of modification of relative reaction rates associated with the mass-transfer phenomena.

Table 3 reports some examples of catalytic reactions studied in supercritical conditions [15]. Although such studies can be considered as being only in the initial stages, data indicate that supercritical fluids provide several opportunities to enhance and control heterogeneous catalytic reactions, and at the same time provide new paths for sustainable chemistry.

3. Conclusions

Catalysis is a key technology to achieve the objectives of sustainable (green) chemistry, but an innovative effort is necessary in the design of new catalysts and catalytic technologies (including reactor engineering) and also in reconsidering all chemical production processes with the objective of developing small and delocalized plants for on-site production. This long-term objective requires an even more innovative effort in the direction of using catalysis in unconventional conditions.

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