

# Past and Present Challenges in Catalysis: Developing Green and Sustainable Processes

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## Abstract

This article is based on a lecture by one of the four recipients of the Royal Society of New South Wales Scholarships for 2013, delivered at the Union, University and Schools Club, on Wednesday, 5 February 2014. It briefly discusses the role of societal, political, and environmental drivers on the development of catalysts in the 20<sup>th</sup> century, which led to the technological advances that enabled the modern lifestyle we enjoy today. Three challenges of catalysis in the 21<sup>st</sup> century will then be discussed in more detail, with a focus on changing feedstocks from fossil resources to biomass resources, and the growing emphasis on lower energy, 'greener' processing.

**Keywords:** Catalysis, biomass, green chemistry, sustainability.

## Introduction

Catalysts play a central role in chemistry, and are used in approximately 90% of all industrial chemical processes (Thomas and Williams 2005, Armor 2011, Thomas 1994). In the last 250 years, especially during the 20<sup>th</sup> century, catalysts were involved in many technological developments that contributed to the lifestyle and standard of living that we enjoy today. Many of these developments emerged due to the convenience and abundance of fossil feedstocks. However, with global energy demands expected to double within the next forty years, peak oil being reached soon or even past, the growing concerns surrounding carbon dioxide emissions, and the political instability related to geographical restrictions of oil reserves, there is a growing need for greener processing and to develop alternative resources. Just as

catalysts played an important role in the 20<sup>th</sup> century, they are expected to have an ever more crucial role in the 21<sup>st</sup> century, as will be discussed in the subsequent sections.

## Historical Perspective

The first use of catalysts can be traced back approximately 10 000 years, with depictions of brewing on archaeological remains (Adams 2009). Even back then, catalysts had an important role for humankind! However, it was not until the 19<sup>th</sup> century that the concept of catalysis was understood. Jöns Jacob Berzelius introduced the term *catalysis* in 1835 before Wilhelm Ostwald provided a scientific definition in 1895 (Zaera 2012). Over the next century, catalysts played a significant role in the development of industrial processes that have greatly influenced modern society. Arguably the most important catalytic

development was the Haber–Bosch process, which is promoted by iron-based catalysts. Motivated by the need for fertiliser during the anticipated Chilean embargo on saltpetre, this process has had an enormous impact on the development of modern society. On the one hand, it was responsible for between 100 and 150 million deaths in the 20<sup>th</sup> century because of its role in the production of explosives and chemical weapons used in armed conflicts (Erisman et al. 2008). Indeed, the demand for explosives based upon nitric acid had a huge impact on the growth of the industrial production of bulk chemicals during World War One (Lindstroem and Petterson 2003). On the other hand, the Haber–Bosch process is responsible, through the production of agricultural fertiliser, for feeding approximately 48% of the world’s population in 2008 (Fig. 1) (Erisman et al. 2008). As will be shown briefly in this section, major catalytic developments rarely occurred in isolation. Rather, they required societal, political, or environmental motivations as drivers. Equally important was the accessibility to raw materials, and in turn, new technology created new demands.

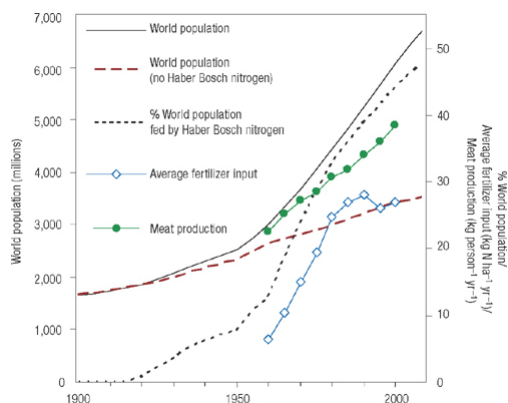


Figure 1: Trends in human population and nitrogen use in the 20<sup>th</sup> century. Reprinted by permission from Macmillan Publishers Ltd: NATURE GEOSCIENCE. Erisman et al. *Nature Geoscience*, 1, 10 (2008), copyright 2008.

Although the first crude oil was drilled in 1859, the main feedstock for chemicals at the onset of the 20<sup>th</sup> century was coal, based mainly on coal liquefaction, distillation of coal tar, acetylene, and coal gasification (Armor 2011). As the demands for explosives diminished, the focus after World War One moved to synthetic fuels. Among the most important catalytic developments in this period was the use of iron and copper catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen (obtained from coal) by Franz Fischer and Hans Tropsch in 1923. The Fisher–Tropsch synthesis of fuels is just as relevant today as it was nearly a century ago. Nonetheless, the widespread use of crude oil as a feedstock began when Eugène Houdry developed the catalytic cracking of petroleum in 1936. Lewis and Gillian modified the process with the introduction of fluid catalytic cracking (FCC) in 1941, and this improvement enabled the supply of the vast quantities of high-octane aviation fuel needed to supply the Allied Forces in World War Two.

With the end of the war, needs again changed with society, and the automobile market accelerated in Europe. The increased demands for gasoline created the petrochemical industry, as petroleum refining enabled the production of plastics, pharmaceuticals, and specialty chemicals. Crude oil became entrenched as a convenient and accessible feedstock. The most important development during this period was the use of a modified X zeolite catalyst in the FCC of petroleum, and one of the most important concepts in zeolite catalysis was the discovery of shape-selective catalysis in zeolites (Masters and Maschmeyer 2011). With these advances, zeolites revolutionised the catalytic cracking and hydrocracking of the crude oil feedstocks, dramatically improving yield and process efficiencies.

Indeed, the use of zeolite catalysts is estimated to save the petroleum industry 10 billion dollars a year (Weitkamp 2000).

As the transportation industry and chemical processes expanded, research into new catalysts was required to meet the regulations regarding vehicle and stationary engine emissions. Hydrodesulfurisation was developed in the 1960s for the removal of sulfur in fuels. In 1974, the first oxidation catalytic converter for automobiles was developed, followed by the three-way catalytic converter in 1978, and the Pd three-way converter in the 1990s. By 1990, the catalytic converter had reduced emissions from hydrocarbons, NO<sub>x</sub>, and CO from vehicles by 90% compared to levels in 1965 (Armor 2011).

Although emissions control catalysts are among the exceptions, the fundamental studies on catalysts in the 20<sup>th</sup> century were mostly focused on achieving high turnover rates. There is now a growing need to develop alternative resources and lower energy, 'greener' processing. Catalysts are expected to play a huge role as many of the challenges of the previous century will be revisited with changing feedstocks, as will be discussed in the subsequent sections.

## Catalysts in the 21<sup>st</sup> Century

### The Need for Green and Sustainable Processes

The U.S. Energy Information Administration anticipates that worldwide energy use will grow by 56% between 2010 and 2040, which is equivalent to global energy demand increasing by approximately 1.5% a year (EIA 2013). More than 85% of this increase occurs due to the strong economic growth and expanding populations in developing nations. However, this rapid increase in energy

demand is problematic as finite fossil resources (coal, oil and gas) currently provide 85% of the world's energy (IPCC 2011). Of the three, oil is the most concerning, as worldwide reserves of oil are sufficient for only another 55 years (IEA 2012). Indeed, a recent article in *Nature* argues that 'peak oil' (the time when global production of oil reaches a peak before declining) was passed in around 2005 (Murray and King 2012). Access to the worldwide oil reserves is also compromised due to political instability (*e.g.* in the Middle East, an area which accounts for almost 50% of proven oil reserves at the end of 2012) (BP 2013), causing problems of energy security to developed countries. Moreover, the level of carbon dioxide in the atmosphere has increased by approximately 40% compared to pre-industrial levels, largely because of the surge in fossil fuel consumption and land use changes (Edenhofer et al. 2012). This increased carbon dioxide has serious consequences for global warming, with the International Panel on Climate Change affirming human influence as "extremely likely" (*i.e.* 95–100% probability) to be the dominant cause of climate change (IPCC 2013).

### Green Chemistry and Catalysis

The last thirty years has seen a significant move towards green chemistry, as it is recognised that the challenges of sustainability will be met with new technologies that provide society with energy and materials in an environmentally responsible manner (Anastas and Kirchhoff 2002). The Brundtland commission defined sustainable development in 1987 as "Meeting the needs of the present generation without compromising the ability of future generations to meet their own needs" (Brundtland 1987). Four years later, Anastas defined green chemistry as "the utilisation of a set of principles that reduces or eliminates

the use or generation of hazardous substances in the design, manufacture and application of chemical products” (Anastas and Warner 1998). These Twelve Principles of Green Chemistry, listed in Figure 2, are the means to achieving sustainable development.

The Twelve Principles of Green Chemistry
1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all the materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible, and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Figure 2: *The Twelve Principles of Green Chemistry*  
(Anastas and Warner 1998).

The Twelve Principles comprise of three main aspects, identified by Sheldon. The first aspect aims to minimise waste through the efficient utilisation of raw materials (Sheldon 2014). Waste is defined as any material that is generated in a process that does not have realised value and includes the loss of unutilised energy (Anastas and Eghbali 2010). With the need to double energy production

within the next forty years (without increasing carbon dioxide emissions), the need to develop more energy efficient processes is essential. Secondly, avoiding the use of toxic and/or hazardous substances is important to circumvent health, safety and environmental issues. This aspect includes avoiding the use of solvents, which often account for the majority of mass wasted in syntheses and processes (Anastas and Beach 2007). Finally, the third aspect identified by Sheldon is the use of renewable biomass feedstocks instead of non-renewable fossil feedstocks. Biomass conversion has become an important area of research due to the need for new technologies to obtain energy and chemical feedstocks in a sustainable manner (Huber et al. 2006, Corma et al. 2007), and it is a major aim of green chemistry (Anastas and Beach 2007).

The motivations and drivers in the 21<sup>st</sup> century have changed. With the need for alternative resources, catalysts are expected to play an ever more crucial role in the technological developments for biomass conversion, enabling pathways previously unavailable in processing alternative feedstocks. Catalysts are also fundamental to improving the efficiency of reactions by lowering energy input, by avoiding the need for stoichiometric quantities of reagents, by decreasing the use of processing and separation agents, and by offering greater product selectivity (Anastas and Eghbali 2010, Anastas et al. 2001). Over the next few decades, catalytic processes will be developed to convert biomass to fuels and chemicals, but no developments will be made that are not informed by the thinking of green chemistry and that do not fulfil their role in a sustainable manner.

### Current Challenges in Catalysis

For the remainder of this paper, three different but related novel applications of

catalysis to address the challenges of the 21<sup>st</sup> century will be discussed. This paper will focus on biomass as a renewable feedstock for fuels and chemicals, and the move towards lower energy, ‘greener’ processing. It is by no means a comprehensive investigation of all the challenges facing catalysis, but comprises of three niche areas of particular interest to the author. A brief context will be given highlighting the current challenges in each area, and an example of how these problems can be met based on the PhD research of the author will be provided.

### **Designing Sulfur Resistant Catalysts for Biomass Processing**

With oil supplies diminishing significantly over the next few decades, there is an increasing need to develop liquid transport fuels from biomass. Due to the chemical, thermal and functionality differences between biomass and petroleum feedstocks, new chemical pathways need to be developed for biomass processing (Demirbas 2007, Huber and Dumesic 2006). The current technologies for the conversion of biomass include gasification, pyrolysis, hydrothermal liquefaction, delignification followed by saccharification and fermentation, and aqueous phase reforming (APR). Many of these processes involve catalysts, such as APR, which is a promising technology that uses supported metal catalysts to convert biomass-derived feedstocks into either hydrogen or alkanes (Cortright et al. 2002, Chheda et al. 2007).

An important challenge in developing catalysts for biomass conversion, including APR, is operating the catalysts in the presence of sulfur in real biomass feedstocks (e.g., wood: approx. 56 ppm), due to the presence of sulfur-containing amino acids and from the uptake of nutrients in the soil (Robinson et al. 2009). This sulfur is a problem because sulfur

is known to poison noble metal catalysts (Bartholomew et al. 1982, Rodriguez 2006). (Bartholomew et al. 1982, Rodriguez 2006) Although the sulfur tolerance of catalysts was widely investigated in the 20<sup>th</sup> century, both for the petrochemical and fine chemical industries (Bartholomew et al. 1982, Rodriguez and Goodman 1991, Somorjai 1994), there has been little research into improving the sulfur resistance of catalysts for use with biomass feedstocks. Thus, developing sulfur resistant catalysts for biomass processing is one of the catalytic challenges of the 20<sup>th</sup> century that is being revisited in the 21<sup>st</sup> century as feedstocks change from fossil resources to biomass resources.

We have recently designed supported bimetallic Pt-Ru catalysts that exhibit improved sulfur resistance and show promising potential for APR of model compounds, using the hydrogenation of cyclohexane as a screening reaction (Stanley et al. 2011). Thiophene was used as the model sulfur source. In all cases, the bimetallic catalysts achieved higher turnover frequencies than their monometallic counterparts in both the absence and presence of the sulfur-containing species. Indeed, the bimetallic catalysts remained active even in reactions having *ten times* the concentration of sulfur expected in woody biomass feedstocks, suggesting the operation of a sulfur/hydrogen spillover equilibrium. In contrast, the monometallic catalysts were completely poisoned.

Powder X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) experiments were used to probe changes to the Pt unit cell and Pt/Ru bonding environments induced by sulfur poisoning for the bimetallic catalysts (Stanley et al. 2011, Stanley et al. 2014). The results

from these investigations are consistent with increasing concentrations of sulfur-containing species coordinating to the ruthenium atoms during sulfur poisoning, leading to a partial separation of the alloy. However, after regenerating the poisoned catalysts under pure hydrogen to remove the sulfur species, the alloy is reformed, showing that this process is reversible. Thus, these results are consistent with an *in-situ* self-regeneration mechanism, which we propose is occurring to enable the bimetallic catalysts to remain active. That is, during poisoning the catalyst partially dealloys, but a sulfur spillover and a hydrogen spillover take place to regenerate the catalyst *in-situ*, and the metals are then re-alloyed. The catalysts are sulfur-resistant.

### **Hydrogenation of Aromatics and Hydrogen Storage**

The second catalytic challenge facing the 21<sup>st</sup> century fits in with the drive towards lower energy, 'greener' processing. In the previous century, the focus of fundamental studies was largely on achieving high turnover rates. Now, the main drivers for technological developments have changed, and a greater focus is on reducing energy requirements. The hydrogenation of aromatics is an important reaction both for small-scale synthesis and for industrial reactions, including the production of cyclohexane, which is an important precursor for the manufacturing of nylon-6,6 (Mevellec et al. 2006, Park et al. 2005, Roucoux et al. 2003). These reactions are traditionally carried out using elevated temperatures and pressures, which often exceed 100 °C and 50 atm H<sub>2</sub> (Augustine 1995). Furthermore, aromatic compounds are responsible for undesired particle emissions in exhaust gas, leading to a tightening of fuel legislation (Stanislaus and Cooper 1994, Cooper and Donnis 1996). Thus, being able to perform the hydrogenations under mild conditions is an

important challenge in terms of energy efficiency and environmental concerns.

Additionally, the reversible toluene/methylcyclohexane couple has the added interest of being a safe and feasible hydrocarbon combination for the storage of hydrogen (Alhumaidan et al. 2011). Cyclic hydrocarbons have a relatively high hydrogen storage capacity, produce no carbon dioxide or carcinogenic products, and their volatility range makes them compatible with existing infrastructure such as refuelling stations and oil tankers for the storage and transportation of the liquid hydrocarbons (Kariya et al. 2002, Kariya et al. 2003, Hodoshima and Saito 2009, Alhumaidan et al. 2011). Thus, the cyclic hydrocarbon combinations have a distinct advantage over other solid hydrocarbons for hydrogen storage.

Over the last ten years, there has been an increased focus on effecting the hydrogenation of toluene under mild conditions, particularly at room temperature. However, the catalyst preparations are often challenging, and the resulting catalysts often have poor activity and/or poor stability (Park et al. 2005). Several groups have demonstrated that metal nanoparticles can perform the reactions with highly water-soluble surfactants used to stabilise these particles in aqueous solution (Schulz et al. 2002, Schulz et al. 1999, Schulz et al. 2000, Fonseca et al. 2003, Mevellec et al. 2004, Hubert et al. 2009a, Hubert et al. 2009b, Roucoux et al. 2003), while others have investigated the use of ionic liquids for nanoparticle stabilisation (Fonseca et al. 2003, Scheeren et al. 2003, Silveira et al. 2004, Rossi and Machado 2009). Further still, a range of solid supports has been used in an attempt to overcome the problems of stability (Bianchini et al. 2003, Park et al. 2005, Mevellec et al. 2006, Park et al. 2007b, Park et al. 2007a,

Takasaki et al. 2007, Barthe et al. 2009a, Barthe et al. 2009b, Pan and Wai 2009, Pélisson et al. 2012, Song et al. 2009, Zhou et al. 2009, Jahjah et al. 2010, Fang et al. 2011, Hubert et al. 2011, Zahmakiran et al. 2010). However, in many cases the reaction and/or catalyst manipulations required air-free conditions and, where special precautions were not required, elevated hydrogen pressures were again used.

To overcome these challenges, we have developed robust bimetallic supported Pt-Ru catalysts that, remarkably, operate under one atmosphere to rapidly catalyse the room temperature hydrogenation of toluene (and tetralin) at 1 atm H<sub>2</sub> (Stanley et al. 2013a). Higher turnover frequencies were achieved with the bimetallic catalysts compared to their monometallic counterparts, suggesting a synergistic effect between platinum and ruthenium. These easily handled, air-stable catalysts are amongst the most active catalysts for aromatic hydrogenations under ambient conditions reported to date.

### **Green Catalytic Processing of Lignin**

Returning to renewable feedstocks, the third challenge is the need to develop the catalytic technologies to obtain chemicals from alternative resources. As already mentioned, biomass is the only renewable source for carbon-based materials. Lignin (which constitutes approx. 15–30% by weight and 40% by energy content of lignocellulosic biomass (Perlack et al. 2005)) is particularly valuable, as its unique structure as an amorphous, highly substituted, aromatic polymer makes it the major renewable source of aromatics (Zakzeski et al. 2010). However, synthetic approaches for the conversion of lignin to chemicals are markedly less developed compared to the cellulosic components of biomass, partly due to the recalcitrant nature of lignin that provides

plants with their strength (Zakzeski et al. 2012). Much effort is currently being devoted to the development of new technology to process low value lignin into higher value-added chemicals. Although aggressive depolymerisation of lignin yields chemicals such as benzene, toluene, and xylene, as well as phenols and aliphatic hydrocarbons used in conventional chemical processes, the selective depolymerisation of lignin could yield monomeric lignin aromatics which are not accessible by traditional petrochemical routes. For example, these monomeric lignin aromatics could be obtained from the pretreatment streams of the pulp and paper industries, which alone produced 50 million tons of extracted lignin in 2004 (Zakzeski et al. 2010). Extraordinarily, the vast majority of this type of lignin is burned as a low value fuel – only 2% is used commercially (Gosselink et al. 2004).

Now, analogous to the petroleum refinery, a biorefinery could use biomass feedstocks to produce a range of products. As outlined earlier, the petroleum refinery developed over many decades in the 20<sup>th</sup> century, as crude oil emerged as a convenient and readily available feedstock. It began with only few products, but as the needs changed with those of society and new catalytic technology was developed, it expanded to produce plastics, pharmaceuticals, and speciality chemicals. With the growing need to obtain these products from renewable resources, the biorefinery is emerging. In the early stages, the biorefinery will need to produce large volumes of more chemically accessible, lower value fuels. Later, higher value chemicals produced in smaller quantities will be required to offset the costs (Bozell and Petersen 2010). Finally, it is expected that all components of biomass will need to be used for a biorefinery to be economically viable. Catalysts are critical to the development of the new

technology for enabling the conversion of biomass. The catalytic challenges for performing the chemical transformations, which were overcome for crude oil over many decades in the 20<sup>th</sup> century in the petroleum refinery, are being revisited with biomass-derived feedstocks in the 21<sup>st</sup> century in the biorefinery.

Currently, there are two approaches for converting biomass-derived resources into higher-value added fuels. The first is a drop-in strategy, where the biomass feedstocks are transformed into existing platform chemicals, to directly replace well-established chemicals currently produced from fossil feedstocks (Vennestrom et al. 2011, Dapsens et al. 2012). The other approach, which we favour, is a curiosity driven broad-based strategy that exploits the existing structure and functionality of biomass. In this approach, renewable platform chemicals based on the structure of biomass could lead to the development of new chemistry and, in the longer term, a plethora of chemical products with as yet unknown applications (Zakzeski et al. 2010).

Fundamental to establishing the required catalytic technology for converting biomass-derived feedstocks into chemicals is an understanding of the reactivity trends and reaction pathways. It has been recognised that many of the building blocks obtained from the disruption of lignin into monomeric aromatics resemble *p*-coumaryl, coniferyl, and sinapyl alcohol. We have recently shown that model compounds based on the *p*-coumaryl structure, specifically cinnamyl alcohol and 4-(3-hydroxypropyl)phenol, can be selectively transformed into different products by catalytic methodologies based on dimethyl carbonate (DMC) as a green solvent/reagent (Stanley et al. 2013b). This selectivity can be tuned by varying the reaction temperature

and the nature of the catalyst. In general, basic catalysts promote selective transesterification of the aliphatic hydroxyl group at 90 °C. On the other hand, amphoteric solids such as alkali metal-exchanged faujasites selectively produce the corresponding alkyl ethers at higher temperatures (165–180 °C). Phenolic hydroxyl groups can be similarly methylated with the faujasites at high temperatures. Thus, these results indicate that efficient and selective catalytic upgrading of lignin-derived chemical building blocks is possible with DMC, and the preliminary screening for selectivity illustrates the reactivity trends and the most promising synthetic pathways.

## Conclusions

Catalysts will play a crucial role in the 21<sup>st</sup> century in moving away from fossil resources. Although oil will still be the main source of fuels and chemicals in the earlier part of this century, there is a great need to improve our current processes to make them more energy efficient. The development of robust catalysts that perform reactions at lower temperatures and pressures is one way to achieve this aim. However, biomass is the only sustainable source of liquid transportation fuels and aromatic chemicals, and the development of new catalytic technology and chemical pathways for use in the biorefinery is essential. Nonetheless, there is no one solution to addressing the challenges of sustainable development. The 21<sup>st</sup> century will require a combination of solar, geothermal, wind, biomass, hydrogen, and nuclear to meet our energy needs.

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