

Nobel Prize for green chemistry: Stance for a future

By awarding this year's Nobel Prize for metathesis, the Royal Swedish Academy of Sciences has rewarded the efforts to make the world more habitable and supports the stance for good and environment-friendly chemical practices. Yves Chauvin (France), Robert Grubbs (USA) and Richard Schrock (USA) shared the prize for their contribution to the development of metathesis (meaning 'change places'), an energetically favoured and less hazardous method in organic synthesis, which has immense industrial applications. Apart from its applications in the polymer industry (for making stronger plastics), metathesis has also found an important role in biotechnology in recent years. 'It represents a great step forward for "green chemistry", reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been for the benefit of man, society, and environment', the prize committee commented.

The discovery of olefin metathesis dates back to the 1950s, when some industrial chemists working in the petrochemical industry observed the unexpected formation of new olefins with random swapping of molecular parts, when gaseous alkenes were passed over Mo catalyst. A major breakthrough in the understanding of the mechanism of the process came in 1971 from Chauvin, who identified that olefin metathesis is initiated by the formation of a metal carbene. This work was monumental in that, in due course of time, it paved the way for metathesis in pre-designed pathways, leading to selective formation of the desired molecular systems. Born in 1930, Chauvin is currently the Honorary Director of the French Petroleum Institute in Rueil-Malmaison near Paris. Schrock was born in Berne, Indiana in 1945. He received his Ph D from Harvard University and later joined the Department of Chemistry at MIT. Grubbs, 63, received his Ph D from Columbia University in 1968 and is currently a professor of chemistry at the California Institute of Technology, Pasadena. Schrock and Grubbs played a significant role in the development of the right catalysts for metathesis, which revolutionized its industrial applications. Another important contributor to the early development of metathesis was Thomas J. Katz of Columbia University.

Green chemistry is smart chemistry

Many, both in the academia and industry, often doubt the commercial viability of green chemistry. This mindset is a major hurdle that the industry and policy-makers have to overcome while enforcing environment-friendly practices in the chemical industry. In fact, green chemistry is smart chemistry and the success of metathesis shows that it can cut down manufacturing costs significantly and remain environment-friendly. Green chemistry has essentially two parts. The first, and the most fundamental part, is the development of a principled and environmentally conscious approach to chemistry. The other is the innovative build-up of greener strategies in the chemists' tools kit. The former aspect is not new, although it has found more support only recently. Also, there is a revolutionary concept of introducing a systematic greenness evaluation into the scheme of chemistry. It is perceived widely that the most important reason for the neglect so far has been the lack of awareness about the toxicity of several materials and the environment damage it can cause. Greed also has played its role when the industry compromised on environment safety for profit. It is time to change this attitude now, since awareness among scientists, lawmakers and even the layman has immensely increased and they insist that those who generate toxic waste should clean it up and also pay for it.

Another important concern is our excessive dependence on petroleum products for the manufacture of materials for daily use. With these resources dwindling rapidly, there is a question on how to sustain such production. There is a growing feeling that we should learn more from nature on how it sustains production and should depend more on plant-based bio-degradable materials. Nature makes materials in the lowest energy route without generating any waste and in fact, recycles every bit it produces.

Prevention is better than cure

Although the chemical industry has been central to the material prospects of mankind by making new materials and molecules for several applications ranging

from transportation to telecommunication, and from clothing to food and medicines, it is also faced with accusations of causing large-scale damage to our environment from the toxic waste it dumps into the surrounding land, water and air. The sustainability of such development is often under question and the gravity of environmental degeneration projected into the future points to a doomsday. With the environmental regulatory agencies and social groups in developed countries toughening their stance with punitive action, several companies find the settlement costs for environmental clean-up unbearable to handle. Look at some data to get an idea about the heat that they feel. DuPont in the US, which has a monopoly in making *Teflon* and *Gore-tex*, recently had to agree to pay as much as 600 million US dollars as clean-up costs for the environmental damage it caused while making these materials. General Electric will have to spend several hundred million dollars to clean up the Hudson river of the PCBs it discharged into it. If the clean-up costs exorbitantly rise like this, the manufacturing costs will become too high for many chemical industries to survive. Now they are on a rethink mode. The new mantra is to green-up the manufacturing technologies rather than the conventional approach of waste clean-up. It is time to go back to the classrooms looking for greener alternative products and processes.

Green chemistry aims towards the design of environment-friendly products and processes using environment-friendly materials and solvents, with no or minimal amount of waste generation. Complete conversion of the reactant molecules to useful products (atom economy) is the first step in green chemistry. This cuts waste at its roots. The use of renewable materials, environment friendly alternatives for the volatile organic solvents (VOCs, the reckless use of which causes serious damage to the air), bio-inspired chemical strategies, the principled design and use of non-toxic materials and processes, wherever it is possible, and optimization of the chemical functionality versus its toxicity (as in the case of pesticides) are among the 12 principles^{1,2} of green chemistry (see Box 1). Metathesis is a classic example of green chemistry.

Box 1. Twelve principles of green chemistry.

1. It is better to prevent waste than to treat or clean it up after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all 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. Use of auxiliary substances (e.g. solvents, separation agents, etc.) should be avoided whenever 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 feedstock should be renewable rather than depleting, whenever technically and economically practical.
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.

Has the industry begun to see the benefits? It is too early to judge the profit in terms of cash. But there are several novel green innovations that have been already implemented by the industry. While processes like metathesis have revolutionized the advance of green chemistry, there is a concerted effort in several other areas to reduce environment pollution caused by the chemical industry. For example, researchers have shown that compressed carbon dioxide can be used as an environmentally benign medium for dry-cleaning. This can replace the use of a toxic chemical named *perc*, which is recognized to pose serious long-term hazards to the environment. There are several dry-cleaning units in the US now using carbon dioxide technology and the microelectronics industry too finds a lot of promise in this approach. Another major industry that finds CO₂ a suitable medium is fluoropolymer manufacturing. DuPont has invested US\$ 275 million for a plant that produces *Teflon* in compressed carbon dioxide medium (this replaces the use of chlorofluorocarbons), a technology that originated from the University of North Carolina. Since carbon dioxide is abundant, inexpensive, non-toxic and non-flammable, it offers an excellent alternative

medium for several industrial applications, including pharmaceutical applications.

There are several such examples showing how healthy industry-academia partnerships can result in sustainable research, and researchers have joined hands across geographical barriers in this new endeavour. Although the recent green chemistry mission was originally initiated by the US Environmental Protection Agency (USEPA), there are now several research networks that share information and enhance cooperation in the area. The Green Chemistry Research Network (Europe), Green Chemistry Institute (US), Green and Sustainable Chemistry Network (Japan), etc. are some of the recent collective, initiatives. Most universities around the world have agreed to incorporate green chemistry principles into their curriculum. Governments and the industry have increased funding for the innovation of greener technologies. In India also, the Department of Science and Technology, New Delhi has a funding programme exclusively for green chemistry projects. Various chemical societies have recognized green chemistry as a core research area for their journal. The Royal Society, UK even has a journal named *Green Chemistry*, exclusively to cover research in

this area. The USEPA has also instituted the Presidential Green Chemistry Challenge Awards for both academic researchers and industries that excel in the discovery and practice of environment-friendly chemistry.

With the chemical industry expanding at an enormous pace, it is the first priority of the governments and the various academic societies to set the right course of action. The Nobel Prize for green chemistry will definitely help boost the efforts for a sustainable chemistry. Starting from our undergraduate education, we have miles to go if this mission has to bear fruits for the coming generations.

1. Anastas, P. T. and Warner, J. C., *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
2. Matlack, A. S., *Introduction to Green Chemistry*, Marcel Dekker, NY, 2001.

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