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Green chemistry in China*

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Abstract: The principles of green chemistry provide a framework for rational design of environmentally friendly chemicals and chemical processes having reduced intrinsic hazard. In China, the academic community has made advances in key areas, developing new catalysts, solvents, polymers, plastics additives, and biomass transformations that add to the "toolbox" of alternative, more benign, and transformative technologies. Educational and outreach activities have also flourished in recent years. This perspective highlights examples of green chemistry breakthroughs in China, focusing on literature reports from 2008 to 2010. While we cannot hope to be comprehensive, we aim to provide examples that demonstrate the scope of the current research field.

Keywords: biomass; catalysis; flame retardants; degradable polymers; green chemistry; ionic liquids.

INTRODUCTION

For the past 12 years, the 12 principles of green chemistry published by Anastas and Warner have provided a cohesive set of design guidelines for integrating sustainability in the chemical industry [1]. The principles call on chemists to recognize inherent hazard (whether physical, toxicological, or global) as a design flaw and develop products that minimize hazard across all stages of a chemical lifecycle from raw materials to manufacturing and end-of-life. The mission of green chemistry is to avoid economic, social, and environmental costs by designing products and processes to be inherently nonpolluting, so that there is no danger from chemical exposures and risk is intrinsically minimized. The 12 principles of green chemistry provide a comprehensive framework to clarify what is meant by "green" and offer a way to analyze, create, and evaluate chemicals and chemical processes according to sustainable goals. Since the 1990s, the field of green chemistry has flourished and the creativity of researchers worldwide has led to success in pollution prevention, creating a "toolbox" of alternative methods.

Green chemistry is poised to play a transformative role in the growth of chemical enterprises in developing countries. In China, the booming economy has correlated with rapid growth in chemical manufacturing from commodity to pharmaceutical and custom chemicals [2]. This has come at some cost, as evidenced by high-profile reports of toxins in toothpaste, pet food, children's toys, and other consumer products. Nevertheless, ongoing development in China presents an opportunity for creative, forward-looking technology. As new laboratories and factories are being built, implementing green chemistry principles at the onset will help avoid issues of environmental pollution and toxic products that threaten the sustainability of China's recent gains.

The principles of green chemistry are far from unknown in China—indeed, it is the aim of this review to show that green chemistry and green engineering are thriving in Chinese laboratories, where

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academic researchers have made advances in key areas. As early as 1994, green chemistry received attention in Chinese journals; these early reports were typically translations of English-language manuscripts reporting green chemistry updates in other countries, usually the United States. In 1996, the Chinese Academy of Science organized a "Green Chemistry and Technology Symposium", which marked the beginning of green chemistry research in China, and also spurred national and provincial funding for research. As of 2010, there are a number of established institutes and national laboratories that contribute to China's green chemistry research effort; a selection of these is highlighted in Fig. 1. In the past decade, almost every year has seen green chemistry or green engineering conferences hosted in China. Many of these events, such as the First China-USA Green Chemistry Workshop in 2005, were intended to catalyze international collaboration [3]. There remains a need for continued effort in this respect due to inefficiencies in translation and communication.

Fig. 1 Locations of national- and provincial-level "key" labs for green chemistry and green engineering in China.

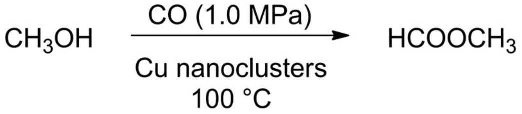
This perspective provides a brief review of state-of-the-art green chemistry research in China, focusing on the literature and conference proceedings from 2008 to 2010, including Chinese-language publications. While it is impossible to comprehensively summarize all research developments, we will highlight advances in the fields of catalysis, alternative solvents, polymer chemistry, and biomass utilization, to demonstrate the scope of current research activity.

CATALYSIS

Catalysts have been called a “foundational pillar of green chemistry” because they provide a means of achieving multiple green principles [4]. Selective catalysts can reduce the generation of unwanted side products from a reaction, thus preventing waste at its source on the molecular level. When catalysts lower the temperature necessary for a reaction to take place, the energy savings can be significant in an industrial setting. Recent research in China has focused on development of metal nanoparticle catalysts, which hold promise as highly active and selective catalysts for many reactions of practical importance.

An example of the high efficiency that can be gained by using nanoparticle catalysts is a system developed at the Chinese Academy of Sciences in Beijing in which Rh nanoparticles were immobilized with ionic liquid on a clay surface and used to promote hydrogenation reactions. Under conditions of mild temperature and pressure, the turnover frequency of the new catalysts was 3 times higher than a conventional supported Rh catalyst, and 30 times higher than Pd dispersed in ionic liquid, while achieving 99 % conversion of substrate in every case [5]. A similar approach was used to develop transformations of glycerol, an abundant co-product of biodiesel manufacturing. Ru and Cu nanoparticles supported on a functional-ionic-liquid-modified clay led to hydrogenolysis of glycerol to 1,2-propanediol. At 100 % conversion, the selectivity was 85 %, representing an advance in performance compared to earlier methods, and the catalyst system could be recovered and reused at least five times without loss of activity [6].

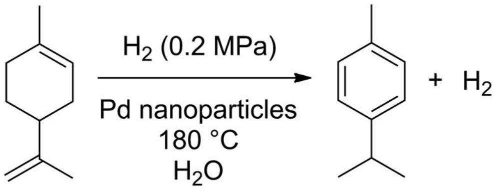
Nanoparticle catalysts have also shown promise in replacing conventional hazardous reagents. The Green Chemistry Center at Peking University developed a soluble Pt nanoparticle for aerobic oxidation of a nonactivated aliphatic primary alcohols, obviating the need for stoichiometric, toxic metal oxides or strong base [7]. Similarly, caustic alkoxides can be avoided in the synthesis of methyl formate by using soluble Cu nanocluster catalysts, which promote the carbonylation of methanol with high activity and 100 % selectivity with good atom economy and energy efficiency (Scheme 1) [8]. The Center for Green Chemistry and Catalysis at the Chinese Academy of Sciences in Lanzhou has developed Au/Fe nanocluster catalysts that use carbon monoxide to selectively reduce aromatic nitro compounds to the corresponding amines. The effiency is an order of magnitude higher than previously reported systems, in some cases, and the new system does not rely on toxic metal carbonyl compounds or highly caustic conditions. The temperature and pressure are also reduced [9]. The catalyst itself is prepared at room temperature, whereas previous methods involved calcining at temperatures up to 400 °C [10].



$$CH_3OH \xrightarrow[\text{Cu nanoclusters, 100 °C}]{\text{CO (1.0 MPa)}} HCOOCH_3$$

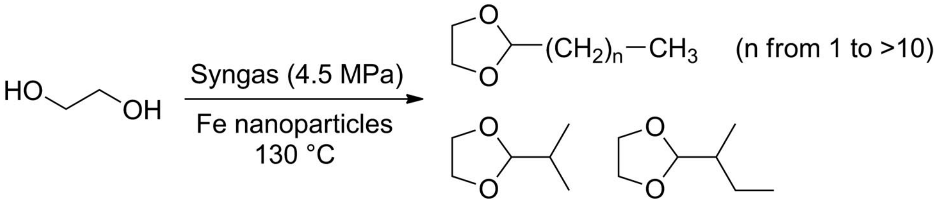
Scheme 1 Carbonylation of methanol via a soluble Cu nanocluster catalyst.

Nanoparticle catalysts have also been used to promote biomass utilization and chemical transformations. Limonene, a waste product of the fruit juice industry, can be converted into *p*-cymene, a more valuable aromatic compound, using soluble Pd nanoparticles. The dehydroaromatization reaction takes place under biphasic conditions in the presence of water (Scheme 2), making it straightforward to separate the product and recover and reuse the catalyst, which is wholly retained in the aqueous layer [11].



Scheme 2 Dehydroaromatization of limonene to *p*-cymene.

There have also been efforts to use less expensive and more abundant metals as catalysts. Inexpensive Fe nanoparticles promote the direct reaction of ethylene glycol with syngas under mild conditions to yield 2-alkyldioxolanes, which are of interest as alternative fuel additives (Scheme 3) [12]. The syngas may be derived from biomass or municipal waste, making this the first report of dioxolanes generated from renewable sources of carbon. The Fe catalyst can be easily recovered with a permanent magnet and reused.



Scheme 3 One-step synthesis of 2-alkyldioxolanes from ethylene glycol and syngas.

Further work in the area of catalysis will need to focus not only on improved performance but also consider the full lifecycle of the catalyst including the impacts of the raw materials and energy needed for its production and also potential toxic effects. This can be achieved by expanding collaboration between chemists, physicists, and engineers to include industrial ecologists and environmental health scientists. Particularly where nanomaterials are involved, a better understanding of the relationships between nanoparticle properties and toxic effects will be critical in rational design of chemical reactions that are not only material- and energy-efficient but safe for chemical workers and surrounding communities as well.

IONIC LIQUIDS

Since ca. 1999–2000, exponential growth has been seen in publications on ionic liquids. *Chemical Abstracts* data shows that the topic now results in more than 2000 scholarly articles per year, and the number continues to grow. Ionic liquids have attracted interest because of their high thermal and electrochemical stability and unique solvent properties. From a "green" point of view, their extremely low volatility and low flammability has led them to be promoted as alternatives to conventional organic solvents. Since the first issue of *Green Chemistry* appeared in 1999, nearly 25 % of all articles appearing in the journal through 2007 were related to ionic liquids. In recent years, however, the environmental benefits of ionic liquids have been called into question after reports that many specific compounds, and sometimes classes of compounds, can harm the growth and reproductive ability of different organisms, including algae [13], earthworms [14], fish [15], and mice [16].

Research in China has been aimed not only at understanding the toxicity of existing ionic liquids, but developing safer alternatives. To promote biodegradability and reduce toxicity, researchers at

Peking University invented a series of ionic liquids based on amino acids and their derivatives, sparking numerous research groups to investigate structure–activity relationships and potential applications [17]. Choline chloride in combination with malonic acid, oxalic acid, and citric acid has been used as an ionic liquid system derived from natural, abundant, and renewable materials. These bio-based solvents were shown to be very efficient for the conversion of biomass-derived inulin to 5-hydroxymethylfurfural (HMF), a useful intermediate for fine chemical and polymer synthesis [18,19]. Ongoing efforts to predict the physical properties of bio-based ionic liquids will help improve their prospects as replacements for more toxic solvents.

Besides improving the environmental profile of ionic liquid solvents, research in China has also explored whether ionic liquids can help offset greenhouse gas emissions by CO_2 capture. A system based on mixtures of ionic liquids, ionic liquid precursors, water, and piperazine was shown to be able to absorb up to 16 % CO_2 by weight. Low viscosity and lower energy consumption in regeneration compared to conventional amine absorbents were among the reported benefits [20].

Acceptance of ionic liquids in industry and the marketplace will depend on further understanding of their full health and safety profiles. Practical aspects such as separation from other chemicals, particularly water, remain to be fully solved and may depend on advances in other technologies, for example, membrane separation [21].

FLAME RETARDANTS

Plastics additives such as polybrominated diphenyl ethers (PBDEs) have become a health concern because of their tendency to leach out of products and their properties of environmental persistence, bioaccumulation, and toxicity [22]. The majority of commodity plastics, however, are flammable in the ambient atmosphere and require technology for fire safety. Strategies for alternative flame retardants generally fall into two categories: (1) small-molecule drop-in replacements for PBDEs and other problematic chemicals; and (2) modification of the polymer backbone itself with flame-retardant functionality. The former approach is attractive because it is straightforward and compatible with existing infrastructure. The latter also has benefits in that leaching is strongly attenuated, and in some cases the amount of flame retardant needed can be an order of magnitude lower [23].

In China, research on small-molecule alternative flame retardants has led to many novel nonhalogenated additives. These replacements usually rely on phosphorus and/or nitrogen content for their performance. Although the mechanism is different from halogen-based chemicals, the lack of halogen is seen as a safety feature in that toxic gases like HCl and HBr will not be formed during a fire and the molecules may be less persistent and bioaccumulating in the environment. One example of a nonhalogenated additive comes from the Center for Degradable and Flame-Retardant Polymeric Materials at Sichuan University, who have developed a phosphonate charring agent (Fig. 2) that shows a synergistic effect with melamine and ammonium polyphosphate. For polypropylene plastic, the new system was shown to achieve the highest safety ratings, without dripping, whereas in the absence of the charring agent combinations of the conventional flame retardants failed [24,25]. Similarly, the Heilongjiang Key Laboratory for Flame-Retardant Materials has developed a spirophosphoryldicyandiamide additive that works synergistically with ammonium polyphosphate to protect polypropylene. The additive system did not harm the mechanical performance of the plastics [26]. In both of these examples, the researchers showed that the new additives improve fire safety, but the “green” benefits remain to be clarified in terms of leaching, persistence, and toxicity. However, the more alternatives that are put forward, the more likely it is that one with a combination of favorable economic, environmental, and performance characteristics will emerge.

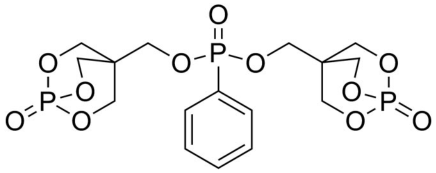


Fig. 2 Nonhalogenated flame retardant and charring agent for polypropylene plastic.

Imparting flame resistance through modification of the polymer itself is more likely to limit harmful environmental impacts, if the flame-retardant functionality is covalently bound to the polymer and therefore less likely to migrate out of the material. An example of this approach is new derivatives of polyethylene terephthalate (PET) which show enhanced flame resistance. Neopentyl glycol (NPG) and 3-(hydroxyphenylphosphinyl)propionic acid (HPPPA) were used as comonomers with terephthalic acid and ethylene glycol to synthesize phosphorus-containing polyesters (Fig. 3). These modified PETs passed the highest safety ratings and reduced the heat release rate during burning with just 5–10 % of the phosphorus comonomer, compared to loadings of 30 % or more for the small-molecule systems described earlier [27]. Branched PETs with phosphorus-containing end caps also have shown significant improvements in flame retardancy compared to ordinary PET. Less than 2 % of branching agent and <10 % of the phosphinyl end caps led to increased limiting oxygen index (LOI), faster char formation, and reduced dripping [28]. Further success of the backbone-modification approach will depend on minimal disruption of mechanical properties compared to conventional polymers, and straightforward synthetic approaches.

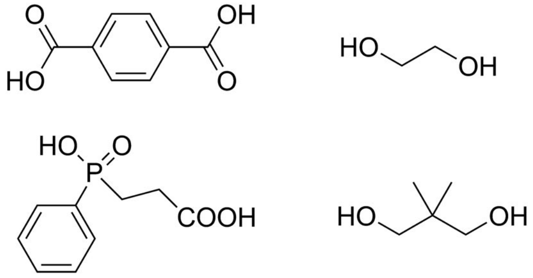


Fig. 3 Monomers used to prepare phosphorus-containing poly[(ethylene terephthalate)-*co*-(neopentyl terephthalate)] flame-retardant polymers.

BIODEGRADABLE PLASTICS

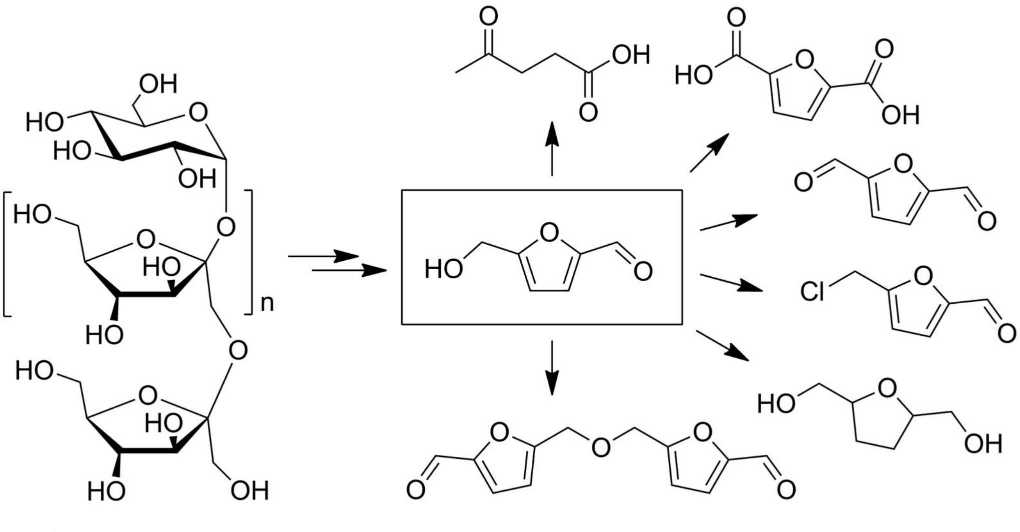
Besides health and environmental impacts of additives, the other major concern related to polymer technologies is persistence in the environment. Nondegradable plastic products place a burden on landfills and pose a littering problem, leading China to impose restrictions on ultrathin, giveaway plastic bags in 2008. Green chemists are offering science-based rather than policy-based solutions to the problem. One of the most fruitful approaches to functional, degradable polymers has been the use of biomass-derived monomers. For example, poly(5-hydroxylevulinic acid) (PHLA) is made from levulinic acid, which is in turn derived from starch or simple sugars. Researchers at Zhejiang University reported that levulinic acid reacts with α,ω-diols to generate cross-linked polymers. These exhibited modest elasticity, tunable glass transition temperatures depending on which diols were used, and degradability via a hydrolytic mechanism [29]. Lactides have also been a major research focus. Copolymers of L-lactide and epoxidized soybean oil (ESO) were shown to have lower glass transition temperature and improved elongation-at-break compared to pure poly(lactic acid) [30]. New aliphatic polycarbonates based on DL-lactide, carbon dioxide (CO_2), and propylene oxide have also shown improvements over poly(lactic acid) and poly(glycolic acid) in medical applications [31]. Other recently reported starting materials for degradable polymers include caffeic acid and *p*-hydroxybenzoic acid [32] and cyclodextrin and glutamic acid derivatives [33]. A unique application of degradable plastics has been conversion of microbially produced poly(hydroxyalkanoates) (PHAs) into ester fragments that can be blended with gasoline. The researchers estimated that production costs would lead to a market price about 50 % higher than gasoline, but fluctuations in the price of petroleum might improve the prospects of PHA-derived biofuels [34,35].

Although poly(lactic acid) and several other degradable plastics have already appeared on the market, the range of application areas and economics are not yet competitive with petroleum-based polymers [36]. Further development of the biorefinery concept and wider acceptance of biofuels will lead to increased abundance of bio-based co-products suitable for use as monomers.

BIOMASS UTILIZATION

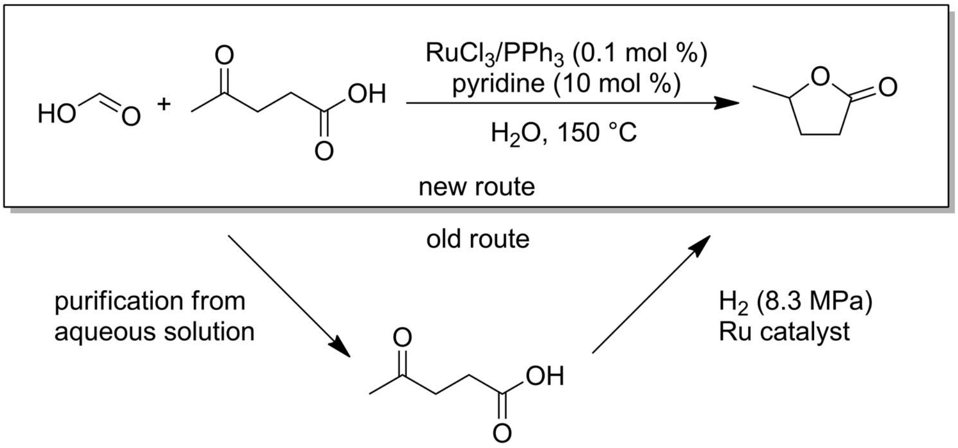
The advantages of using renewable feedstocks in chemistry are many: petroleum has a long-term tendency to become more expensive; renewable resources are becoming cheaper; many developing countries lack petroleum infrastructure; quality and availability of bio-based feedstocks has increased due to breakthroughs in enzymatic and catalytic chemistry; to an extent renewable resources offer better compatibility with natural systems; and there are more opportunities to valorize waste streams (from agriculture and wood pulping, for example) [37]. Biomass is now providing a larger variety of renewable platform chemicals, and there are increasingly more substitutes for petrochemical feedstocks. In China, a great deal of effort has been devoted to using locally abundant natural crops and waste streams to produce valuable chemicals.

Among these resources are roots of plants like chicory, which can yield inulin, an indigestible oligosaccharide, on the order of tons per hectare. Researchers at the Chinese Academy of Sciences in Beijing have developed a direct method for conversion of inulin to HMF [19]. HMF is a major biomass platform chemical that provides access to a variety of structures (Scheme 4), including levulinic acid and 2,5-furandicarboxylic acid, two of the chemicals from the U.S. Department of Energy's list of 12 "Top Value Added Chemicals from Biomass" [38].



Scheme 4 Inulin can be directly converted to HMF, a valuable chemical intermediate.

Other research on biomass conversion in China has focused on cotton stalk, the most abundant agricultural byproduct in Xinjiang Province. It has been used to produce activated carbon using a microwave-assisted technique that reduces energy consumption compared to conventional heating methods [39]. Bagasse and paddy straw have also been used as the starting material to produce levulinic acid via pressure liquefaction. In China, millions of tons of this biomass waste are discarded or incinerated. If this biomass waste was instead used for chemicals production, the cost of levulinic acid could be greatly reduced compared to conventional methods that rely on furfuryl alcohol [40]. One of the potential uses of levulinic acid is as a precursor to γ-valerolactone (GVL), which has promising characteristics as a drop-in replacement for conventional liquid fuels [41]. Production of GVL has been simplified by the development of an inexpensive, recyclable catalyst system that improves the atom economy of the process and also avoids the need for added hydrogen. Instead, the new approach uses formic acid as the reductant. Formic acid and levulinic acid are usually co-produced in aqueous solution, and by working with this mixture directly, an energy-intensive intermediate step is avoided (Scheme 5) [42].



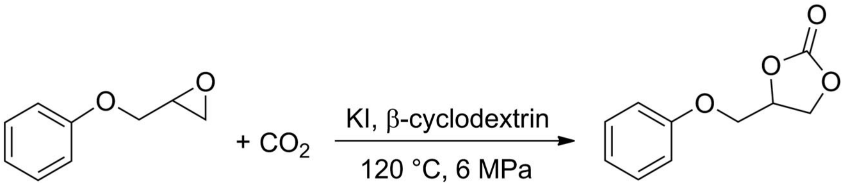
Scheme 5 Direct conversion of an aqueous formic acid/levulinic acid mixture to GVL.

The Key Laboratory of Green Chemistry and Technology at Sichuan University has been active in researching pyrolytic transformations of biomass into bio-oils. Bio-oils are promising renewable fuels because of their high energy density and compatibility with existing liquid fuel infrastructure. A variety of raw materials can be liquefied with suitable catalysts, including rice husks, algal residue, bamboo, and waste polyethylene. These feedstocks would ordinarily be waste streams, but pyrolysis offers a way to extract value [43–46]. The Anhui Province Key Laboratory of Biomass Clean Energy has also explored biomass pyrolysis in supercritical solvents to reduce condensation reactions and avoid formation of tar [47,48]. Other researchers have aimed to improve production methods for conventional biodiesel, developing new catalysts for transesterification of vegetable oils. Heterogeneous base catalysts or ionic liquids have reduced side reactions and improved recoverability and reusability compared to homogeneous catalysts [49–51]. Scientists at the Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology at Tsinghua University have also employed solid acid catalysts prepared from waste biomass. The sulfonated, vegetable-oil-derived material allows producers to produce biodiesel from free fatty acids without being deactivated by water, and avoiding the safety and operational problems associated with liquid acid catalysts [52,53]. As one of the top countries in terms of crop cultivation and arable land, China will continue to be a major source of biomass and agricultural waste streams. Further advances in biomass transformation to fuel and chemicals will help relieve pressures on fossil resources.

CARBON DIOXIDE

CO_2 is an abundant, nonhazardous carbon-containing raw material for synthesis of small molecules and polymers. Use of CO_2 as a C_1 feedstock is not expected to mitigate global greenhouse gas emissions, but if it can be harvested from waste streams of industrial or natural processes, it can be considered a sustainable “building block” chemical.

One of the most successful carbon–carbon bond-forming reactions involving CO_2 is the synthesis of cyclic carbonates. Inexpensive, efficient, and stable catalytic systems are necessary to promote the cycloaddition reaction between CO_2 and epoxides. One such system is KI/β-cyclodextrin, in which the metal salt and cyclodextrin work synergistically under solvent-free conditions to couple CO_2 with propylene oxides to form propylene carbonates (Scheme 6) [54]. Similar reactivity was demonstrated with a heterogeneous zinc oxide/terephthalic acid catalyst that could be easily recovered from the product mixture and reused without any decrease in activity [55].



Scheme 6 Coupling of CO_2 with glycidyl phenyl ether to form a cyclic carbonate.

Besides chemical synthesis, CO_2 is also widely employed as an alternative solvent due to its easily accessible supercritical point. Supercritical CO_2 has low viscosity and high diffusivity, and solvent power is tunable depending on temperature and pressure. Besides its utility as a medium for extraction and recovery of interesting natural products [56], it also can provide unique benefits in chemical syntheses and processes. For example, various carbon nanotube (CNT) composites with metals, metal oxides, and polymers were prepared in supercritical CO_2 with unusual morphologies that are difficult to obtain by conventional methods [57,58]. Supercritical CO_2 has also been employed as a loosening treatment in the sheepskin fiber tanning industry, to avoid producing caustic aqueous wastewater high in lime, sulfides, biological and chemical oxygen demand, nitrogen salts, and other contaminants [59]. CO_2 has proven useful in biomass chemistry, for example, in conversion of cellulose to HMF, a binary system based on subcritical water and CO_2 operates without any acid catalysts or enzymes [60].

CONCLUSION AND PERSPECTIVE

It was noted at the First China-USA Green Chemistry Workshop in 2005 that despite good funding and strong relationships between academia and industry in China, the misuse of “green” concepts was a stumbling block [3]. In the past five years, however, green chemistry education in China has grown remarkably as evidenced by the publication of a variety of scholarly volumes focusing on developments in the field (Table 1). Sichuan University is also one of the few institutions in the world that offers graduate degree programs specifically in green chemistry.

Table 1 Selection of green chemistry books published in China since 2005.

Title	Publisher	Year
Green Chemistry and the Environment	Tsinghua University Press	2005
Green Oxidation and Reduction	China Petrochemical Press	2005
Green Organic Catalysis	China Petrochemical Press	2005
Supercritical Fluid Science and Technology	China Petrochemical Press	2005
Modern Green Chemistry Technology	China Environmental Science Press	2005
Clean Production, Principles and Practice of Green Chemistry	Chemical Industry Press	2006
Green Chemistry in Oil Refining and Fundamental Organic Chemical Synthesis	China Petrochemical Press	2006
Green Production Technology for Fine Chemicals	Guangdong Technology Press	2006
Atom Economic Reactions	China Petrochemical Press	2006
Assessment and Principles of Green Chemistry	China Petrochemical Press	2006
Properties, Preparation and Applications of Ionic Liquids	China Petrochemical Press	2006
Green Process System Integration	China Petrochemical Press	2006
Green Chemistry	University of Science and Technology of China Press	2007
Principles and Practice of Green Chemistry	China Petrochemical Press	2007
Green Organic Chemistry Experiments	Chemical Industry Press	2008
Principles of Green Chemistry and Design of Green Products	Chemical Industry Press	2008
Experiments in Green Chemistry	Huazhong University of Science and Technology Press	2008
Green Chemistry	China Environmental Science Press	2009
Ionic Liquids and Green Chemistry	Science Press	2009
Principles and Experiments in Green Chemistry	Chemical Industry Press	2010

The future of green chemistry in China, and also worldwide, will depend on innovations that embrace all of the 12 principles as inseparable, mutually reinforcing components of a sustainable design framework. If “green” improvements are only incremental and focus only on a single principle of sustainable chemistry, there will be greater danger of replacing an existing problem with a new one. Examples of this have been seen in recent years, such as biofuels that compete with food crops, clean water that relies on toxic chemicals for purification, increased crop yields using persistent pesticides, and life-saving pharmaceuticals that generate hundreds or thousands of kilograms of waste for every kilogram of product. Greater attention to entire chemical or process lifecycles will help avoid these situations. Innovations that focus on providing a service or function without artificial constraints of existing technologies will provide chemists and engineers with easier choices in designing the chemical enterprise of the 21st century.

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