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Introduction: Recoverable Catalysts and Reagents—Perspective and Prospective

Throughout society in general, one sees rapid increases in recycling initiatives that affect many aspects of day-to-day living. However, numerous questions remain about the optimum processes, the ultimate yields, and the true contributions to "sustainability". Chemists deserve to be regarded as trendsetters in recycling, and the 21 articles in this special issue of *Chemical Reviews* showcase various aspects of the broad interdisciplinary subject, "Recoverable Catalysts and Reagents". This area is attracting increasing attention and cachet under the umbrella of "green chemistry", and the articles admirably illustrate both the outstanding progress achieved to date, and the many questions and challenges that remain.

In the case of catalysis, recycling does not have the sense of trapping and reprocessing a waste product, making new paper from old paper, or collecting and refilling empty soda bottles. Rather, one is seeking to sequester and harness anew the vis vitalis of a chemical reaction, a species—molecular or nonmolecular—that should have the same hallowed status as the enzymes that are essential in vivo to life processes. However, despite the high turnover numbers that naturally occurring enzymes achieve, all cellular machinery is subject to degradation and must be regenerated by biosynthesis. This poses to chemists the irresistible challenge of doing one better than Nature, namely, "immortal" catalysts that do not deactivate and can be recovered with efficiencies of 100%. While this is clearly an unattainable goal, the following articles show that valiant attempts are being made to asymptotically approach it.

Some of the complications in formulating sensible recycling policies in the public sector include layperson misconceptions and poor baseline data. However, there are analogs of these problems in the chemistry sector, intensifying the need for the expert perspectives collected below. For example, chemists often only loosely distinguish between a catalyst precursor and the active catalyst. The former is added at the beginning of a reaction, and additional steps are usually needed to enter the catalytic cycle. One of the easiest to visualize is a ligand dissociation. Other catalyst precursors exhibit induction periods, which generally indicate some type of fundamental and irreversible change. Regardless, what is always being recycled is the catalyst rest state. This is seldom equivalent to the catalyst precursor. As emphasized in the articles in this issue, many different properties can be exploited for catalyst recovery. However, this property must always be associated with the rest state. The situation is similar for recoverable reagents. Here, properties associated with the spent reagent or coproduct are key to recycling.

Another issue of critical importance is the quantitative evaluation of recycling efficiency. Unfortunately, there is much substandard work in the catalysis literature. In particular, product yield as a function of cycle is a poor criterion. The time selected for the initial cycles is often arbitrary, and consider the case of an "overnight run" (15 h) that is in fact finished within 0.5 h. Suppose half the catalyst is lost in each cycle. If measurements are always made after 15 h, quantitative yields will still be observed for a number of cycles before any deterioration is evident. In contrast, if reaction rates are assayed, the loss of activity becomes glaringly apparent in the second cycle. Accordingly, rate measurements are good criteria for recovery. The direct determination of the amount of recovered catalyst is also desirable, as are leaching measurements. However, these can be complicated, nontrivial undertakings, as further analyzed elsewhere (Gladysz, J. A. *Pure Appl. Chem*. **2001**, *73*, 1319).

It should be noted that for many catalytic processes, only rough mechanistic models are available. When the nature of the active catalyst and rest state is uncertain, the rational design of recoverable catalysts can be more difficult, or (optimistically expressed) of a "sporting" nature. Indeed, the success or failure of the recoverable version can often be taken as evidence regarding the accuracy of the mechanistic model. For example, a number of palladacycle catalyst precursors are known for the Heck and Suzuki reactions. Several have recently been immobilized on polystyrene or in liquid phases. However, the recycling results were very poor. Further experiments demonstrated that leached colloidal palladium metal was the active species. Hence, the nonrecoverable versions of these palladacycles likely operate by a similar mechanism.

Given the broad constituency of scientists interested in recoverable catalysts and reagents, there are a variety of possible ways to organize the literature. One obvious approach, optimum for many synthetic chemists, is by the type of reaction. Another useful classification, which often serves specialists better, is according to the recycling method (e.g., a support type, a solvent or phase system, a physical attribute, etc.). The synthesis of recoverable catalysts and reagents is also a special subject in itself, as are various theoretical, engineering, and analytical aspects. It is therefore not surprising that the articles

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in this issue offer a diverse mixture of perspectives, and some of the common denominators and relationships are as follows.

Five articles treat complementary aspects of recoverable polymer-bound catalysts and reagents. Leadbeater and Marco focus on syntheses of polystyrene-supported ligands and metal complexes, for which special techniques are often required. In contrast, McNamara, Dixon, and Bradley emphasize applications of polystyrene-supported systems, including the critical role of cross-linking with respect to performance characteristics. Barrett, Hopkins, and Köbberling describe a variety of reagents and catalyst precursors generated via ring opening metatheses of strained functionalized monomers, with an emphasis on applications in parallel syntheses. Articles by Dickerson, Reed, and Janda and Bergbreiter offer two different perspectives on soluble polymers. The former highlights polyethylene glycol and non-cross-linked polystyrene systems that can be recovered by precipitation. The latter accentuates transition metal catalyst precursors, and additional supports and recovery strategies. These include pH- and temperature-induced precipitations, and liquid/liquid biphase separations.

Three articles are concerned with recoverable catalysts for enantioselective organic synthesis. An impressive treatise by Fan, Li, and Chan offers analysis of 13 types of transformations from the standpoint of different catalyst recovery strategies. Rechavi and Lemaire select six transformations catalyzed by metal complexes of heterogenized bis(oxazoline) ligands, and critically compare the factors that affect enantioselectivities. Song and Lee treat chiral catalysts that have been supported on inorganic materials, especially silica, and summarize applications in reduction, oxidation, and carbon–carbon bond forming reactions.

Silicon-containing catalyst supports play prominent roles in other articles. For example, Duchateau reviews the use of incompletely condensed silsesquioxanes as platforms for immobilized olefin polymerization catalysts. Lu, Lindner, and Mayer describe the fascinating concept of interphase catalysis, with a focus on sol-gel-derived microenvironments. Kakkar covers thin film methodologies for the heterogenization of homogeneous catalysts. These include Langmuir-Blodgett films, and the direct functionalization of glass, quartz, and single crystal silicon.

Three articles further expand the treatment of inorganic oxide catalyst supports. Wight and Davis review strategy and design in the preparation of hybrid organic–inorganic catalysts, where the latter derives from a porous inorganic oxide (amorphous silica, zeolites). In a complementary tractate, De Vos, Dams, Sels, and Jacobs describe a number of organic reactions catalyzed by metal fragments immobilized on zeolites or ordered mesoporous molecular sieves. Okuhara portrays the state-of-the-art in water-tolerant solid acids, including zeolites, heteropoly compounds, oxides and mixed oxides, phosphates, and polymer resin–silica composites.

Of course, there are many strategies for catalyst and reagent recovery that do not require a support. In this category, Dupont, de Souza, and Suarez review the burgeoning area of organometallic catalysts that can be recycled with ionic liquids. Yoshida and Itami analyze the use of "tags" that allow catalysts and reagents to partition into aqueous or fluorous media that are orthogonal to the product-containing media. Heerbeek, Kamer, van Leeuwen, and Reek detail the rapidly developing use of dendrimers as platforms for recoverable catalysts and reagents. Roucoux, Schulz, and Patin delve into the transcendental realm between the homogeneous and heterogeneous—specifically, soluble colloidal metal nanoparticles, which can be recovered by several methods.

Engineering plays a critical role in recovery, and Vankelecom reviews the use of polymeric membranes in catalytic reactors. This subject includes both membrane-bound catalysts and inert membranes that exclude higher molecular weight species such as dendrimer-bound catalysts. Light constitutes another important tool in chemistry, and Maldotti, Molinari, and Amadelli insightfully compare a variety of reusable systems for the photocatalytic oxyfunctionalization of hydrocarbons. Finally, Corma and Garcia offer an epic treatment of recoverable homogeneous and heterogeneous Lewis acids catalysts for oxidation reactions.

The many topics outlined above naturally lead to yet another question, one that many beginning students pose to professors, namely, "which recovery method is best?" The following articles make it clear that there is no general solution. Each protocol has advantages and disadvantages, and an ongoing friendly competition, involving uniform, objective evaluation criteria, is healthy for the field. From the standpoint of a synthetic or process chemist, a portfolio of methods is optimum. Of these, one will be uniquely suited or superior for the need at hand. Nonetheless, all researchers in this field keep striving towards the holy grail of "ideal recoverable catalysts or reagents". These would, among other attributes, have outstanding performance characteristics (rates, stereoselectivities, etc.), not be subject to degradation, leaching, etc., and be easily recovered (as the catalyst rest state or spent reagent) in quantitative yields. This very challenging quest will clearly keep chemists busy for generations to come.

In conclusion, this thematic issue covers a fast-moving field that encompasses principles from nearly all areas of chemistry. It presages an era in which syntheses of all types may be conducted in toto with recoverable catalysts and reagents. Indeed, the dawn of this epoch was recently evinced by a multistep total synthesis of an amaryllidaceae alkaloid that used only supported reagents and scavengers (Baxendale, I. R.; Ley, S. V.; Piutti, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2194)—no less than 13 immobilized systems! Yet another exciting and gratifying aspect of this field is that commercial and environmental driving forces are operating in synergy. Together these are prompting outstanding advances in fundamental chemistry, and defining fascinating challenges for future research, as so beautifully illustrated in the articles on the following pages.

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