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What Should be Done in the Future

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Polymer-bound catalysts offer various attractive properties in combination with membrane separation techniques:

- Catalyst recovery can be performed in an energy-efficient way by reducing the volume of distillation streams.
- Temperature-sensitive catalysts can be recovered at relatively mild temperatures from high boiling compounds.
- By enabling continuous operation, reactions can be run under steady-state conditions, e.g., at limited conversions.
- Catalysts based on expensive metals or ligands can be recovered effectively.

A broad range of organic reactions catalyzed by polymer-bound catalysts have been described since the mid-1990s. Selectivities and activities can generally compete with those of the analogous catalysts that are not polymer-bound. Synthetic routes to a multitude of polymeric ligands are well worked out on a laboratory scale. Beyond these various proofs of principle, basic issues remain open in most instances, however. For example, in repeated recycling runs often the reaction is not followed over time but only a final conversion is given, telling little about changes in catalyst performance. The metal content in the filtrate from catalyst separation is usually taken as an indication of recovery efficiency, but the polymer content of the filtrate is rarely reported. Thus, catalyst decomposition or other reactions resulting in low molecular weight species containing metals cannot be differentiated from insufficient recovery of the polymer itself. On a more sophisticated level, a mechanistic understanding on a molecular level of catalyst deactivation is a decisive and also a scientifically attractive topic. When recycling the catalyst by means of binding to a soluble polymer, its stability over time becomes a much more critical issue by comparison to batch reactions without recycling. Moreover, deactivation reactions can also be specific to polymer-bound catalysts, due to the high local concentrations of the polymer-bound metal centers, and also due to different concentrations of reagents and products in continuously operated reactions by comparison to traditional batch mode.

Membrane filtration techniques are effective in the recovery of polymer-bound soluble catalysts. This is contrasted by the scarceness of published systematic data on membrane properties and stability in organic solvents. Even the composition of the commercially available membranes used is often unclear. The nominal molecular weight cutoffs for solvent-stable membranes are usually given for aqueous or methanol solutions, although it is evident that membrane swelling and other properties in different solvents can affect the retention characteristics by orders of magnitude. Phenomenological studies of the retention in different organic solvents

for a range of model solutes varying in molecular weight, chemical composition (and thus affinity for the membrane surface), and molecular architecture (e.g., linear versus branched) would already be helpful to describe a given membrane systematically. In particular, the comparison between different membranes calls for a precise definition of experimental conditions concerning solvent flow rates, solute concentrations, transmembrane pressure, and experimental setup. With polymer-bound catalysts, interactions with the membrane such as adsorption on or in the separating layer have received little attention, although they can strongly affect membrane performance. In the larger scheme of things, the development of organic as well as inorganic membranes with a high mechanical stability and stability of separation characteristics in organic solvents is a decisive issue. This applies to the development of flat sheet membranes as well as modules with their seals and other elements. Finally, engineering of the overall separation unit in combination with the reaction space is just as crucial for separation performance. Working with gaseous reagents in continuous mode adds to these challenges.

Commercial applications have advanced to the pilot plant scale so far. It can be speculated that in the overall scheme the aforementioned issues of catalyst stability and membrane stability and performance are critical issues. In the particular case of rhodium-catalyzed hydroformylation (for higher alkenes or functional olefins) for the synthesis of fine chemicals it can be assumed that, as a nonscientific and nontechnical driver, the price of rhodium will contribute to the commercial success.

An attractive aspect which has received little attention so far is the aforementioned possibility of running reactions in continuous mode under steady-state conditions concerning reactant concentrations by means of membrane techniques. The potential for directing reactions by suppressing side reactions or otherwise controlling selectivities has attractive potential. It must be realized that for applications in the synthesis of fine chemicals such a concept requires additional development (costing time and money) by comparison to established conventional batch processes, and therefore will only be realistic for well-chosen problems with sufficient reward.

Overall, by comparison to the state-of-the-art in two-phase techniques, polymer-bound catalysts are at an earlier stage. Combining expertise in catalysis, polymer synthesis, and characterization, membrane technology and particularly engineering are required to advance this attractive field.