7.3

Homogeneous Catalysis with Soluble Polymer-Bound Catalysts as a Unit Operation

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7.3.1

Overview and General Considerations

Homogeneous catalysis with soluble polymer-bound catalysts has been carried out by a variety of academic and industrial research groups. These investigations have been performed on a laboratory scale in a batchwise fashion for the most part. In several cases, reactions have also been performed on a pilot plant scale, however (cf. Section 7.5). From the published data, no general systematic differences from catalysis with conventional catalysts that are not polymer-bound are evident regarding the reaction conditions of catalysis. The increased solution viscosity of polymer solutions by comparison to solutions of low molecular weight compounds should usually not be a major issue in view of the rather limited concentrations required for catalysts. The high local concentration of metal centers in polymer-bound catalysts represents a difference from non-polymer-bound homogeneous catalysts. This can result in an enhancement of undesirable bimolecular deactivation reactions in polymer-bound catalysts [1]. Differences in the catalytic properties by comparison to non-polymer-bound analogues, which were observed in some cases, have also been ascribed to the polymer coil representing a local different “solvent” composition.

Thus, the unit operations most characteristic of catalysis with soluble polymer-bound catalysts apply to the separation and recycling step rather than to the actual catalytic reaction (as a special case, both can be carried out at the same time, e.g., in a continuously operated membrane reactor; vide infra). As mentioned previously, the separation of polymer-bound catalysts makes use of properties specific to macromolecules, in order to differentiate between the polymer-bound catalyst and the low molecular weight reaction products of the catalytic reaction and unreacted substrates in the recycling step. The miscibility of polymers with low molecular weight compounds, i.e., the solubility in the reaction solvent (which can also be the neat substrate), is such a property. For most polymer/solvent combinations, a non-solvent can easily be identified which precipitates the polymer-bound catalyst when added in sufficient amounts, while the reaction products of catalysis stay in solution. For example, the common support poly(ethylene glycol) is insoluble in diethyl ether, and polystyrene can be precipitated with methanol. However, while this approach may be useful on a laboratory scale, from a chemical engineering point of view it is not very elegant and practical, requiring the recycling and fractionation by distillation of large amounts of solvent. Alternatives are the utilization of the temperature [2–4] or pH dependence [5, 6] of the solubility of polymers. The miscibility of many polymer/solvent combinations is strongly dependent upon temperature [7]. Thus polyethylenes are soluble in aromatic hydrocarbons only at elevated temperatures.

Whereas mostly systems rely on an upper critical solution temperature, some, such as aqueous solutions of poly(ethylene glycol) or poly(*N*-alkylacrylamide)s, also separate upon the increasing temperature [8]. This unusual temperature dependance has been termed “smart behavior”. A restriction of temperature-dependent solubility is that the solvent (containing the dissolved substrate and product)/polymer combination must be chosen individually for each substrate. pH-dependent solubility is focused on catalytic conversions of water-soluble substrates with aqueous solutions of polymer-bound catalysts, a rather specific case given that most organic substrates are not water-soluble. As a sideline it is worth noting that, for technical viability, all these separation methods require the polymer to separate in a physical form suitable for filtration. Separation as a highly viscous goo, which is not uncommon, poses problems. All these separations utilizing polymer-specific solubility behavior rely on general standard unit operations, which will not be discussed further here.

A different approach of major practical importance is the separation of polymer-bound catalysts from low molecular weight products and substrates by means of appropriate nano- or ultrafiltration membranes. For porous membranes, the larger “size” of the dissolved macromolecules, which prevents permeation through the pores, can be regarded as the underlying principle. In nonporous membranes, the solubility of the macromolecules in the membrane material in combination with the diffusion coefficient can be considered as the physical basis. The unit operations for membrane separation are discussed in the Section 7.3.2.

7.3.2

Membrane Ultrafiltration Techniques

Membrane separation techniques are employed on a large scale today, the most important applications being in the food industry and in water desalination [9]. According to the driving force of the separation step and the size of the retained species, membrane separations can be classified into osmosis and dialysis (driving force: osmotic pressure and concentration gradient respectively), microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (driving force: external hydraulic pressure). The latter, hydraulic pressure driven processes, which are of particular importance for industrial applications, can be divided according to the size of the retained species, as outlined in Figure 1. Ultrafiltration retains macromolecules, i.e., species with sizes greater than about 1–20 nm, corresponding to molecular weights of 10^3 – 10^6 g mol⁻¹. Thus it is of interest for the separation of polymer-bound soluble catalysts. Only moderate pressures are required, ranging from a slight overpressure to ca. 3–4 MPa as the upper limit. It should be noted that the terms between ultrafiltration, nanofiltration, and even reverse osmosis are not strictly differentiated in use in the literature, and they are often used interchangeably.

Conventional filtration processes are usually performed in a “dead-end” mode. By contrast, membrane separations are designed to be operated in a cross-flow mode (Figure 2). Such a turbulent cross-flow prevents an undesired concentration–polarization of the membrane, i.e., a concentration of solutes at the membrane

Figure 1 Pressure-driven membrane separation techniques.

Figure 2 Cross-flow vs. dead-end mode filtration.

surface, and reduces membrane fouling. The most common membrane designs are flat sheet membranes, or hollow fibers. In industrial applications membranes are integrated in modules which possess a high membrane surface per module space. Common designs are hollow fiber bundles, or spiral-wound modules (cf. Figure 7). Laboratory-scale exploratory research on catalyst recovery usually requires a frequent replacement of the membranes to avoid possible contamination upon

Figure 3 Simple laboratory-scale ultrafiltration setup.
(a) Schematic setup; (b) ultrafiltration cell.

changing to other substrate feeds, to exclude any possible damage to the membranes which would lead to misinterpretation of experimental results, etc. Therefore, flat sheet membranes are usually used as such in simple test filtration setups (Figure 3) [10], rather than much more costly membrane modules.

Most ultrafiltration, nanofiltration, or reverse osmosis membranes possess an asymmetric structure. A thin layer with an extension of the order of $1\text{ }\mu\text{m}$ on the surface of the membrane is responsible for the separation characteristics. It is supported by an underlying layer which may contain larger voids. Depending on the method of membrane preparation, the thin surface layer may be porous, as depicted in Figure 4, or it can be nonporous. The entire structure can be supported by further, thicker layers providing mechanical stability to form a multilayer membrane. Typical materials for the active separating layer are polyacrylonitrile, cellulose acetate, polysulfone or polyimide [11]. In addition to these polymeric membranes, inorganic membranes have been commercialized since the 1980s. Inorganic membranes, also termed ceramic membranes, are most often composed of alumina and titania. Like polymeric membranes, they possess an asymmetric structure.

The separation characteristics of an ultrafiltration membrane are usually expressed as the molecular weight cutoff (MWCO), i.e., the molecular weight of a solute of which 90% is retained in one filtration step. However, it is well known that the retention characteristics are determined not only by the mere molecular weight of the solute, but also by its solution conformation, chemical nature, etc., and by the solvent employed. Dextrans, certain proteins, and – on the lower molecular – weight end dyes are often used as test substrates, but frequently MWCOs are given in membrane suppliers' data sheets or in the literature without specification of the test solute. Moreover, there are no general standard conditions with respect to solvent, temperature, transmembrane pressure, concentration of the solute, flow rates, etc. Therefore, MWCOs are sometimes designated as nominal molecular weight cutoffs (NMWCOs) and they should be regarded rather as an order-of-magnitude information. Albeit the results cannot be transferred directly to the issue of ultrafiltration of polymers as a catalyst support because membrane pore sizes are not uniform and the interaction of the polymer with the membrane material is not trivial to quantify, it is nonetheless interesting to note that polymer

Figure 4 Structure of an ultrafiltration membrane.

translocation through nanometer-sized pores has also been considered on a fundamental level [12, 13].

Physico-chemical phenomena associated with membranes have contributed immensely to the understanding of the nature and behavior of colloids and dissolved molecules or ions. For example, Abbé Nollet had already observed the phenomenon later termed osmosis in the 18th century, when he found that water diffuses from a dilute to a more concentrated solution across a semipermeable membrane (a pig bladder in this case). By contrast, larger industrial applications have only emerged since the 1960s. A major enabling breakthrough was the development of suitable asymmetric membranes by Sourirajan and Loeb [14]. Reverse osmosis for seawater desalination was the first large application. In specific regard to the chemical industry, membrane techniques are employed primarily for the production of ultrapure feed water and for gas separation (nitrogen from air; hydrogen separation from refinery gas streams, and also hydrocarbons from waste gas streams) [15].

Major applications in ultrafiltration are the recovery of electropaint particles from rinsing water in electrocoating paint processes and the fractionation of cheese whey in the dairy industry. As in most other applications of ultrafiltration, aqueous systems are treated in these two examples. By contrast, the separation of polymer-bound catalysts will usually be performed in organic solvents, requiring solvent-stable membranes. In this context, an interesting application of membrane filtration which has already reached the commercial stage is the separation of organic solvents from larger-molecule hydrocarbons in refinery operations by reverse osmosis. In a refinery, vast amounts of residual oils from vacuum distillation are dissolved in organic solvents such as toluene and methyl ethyl ketone; cooling of the solutions results in the precipitation of wax components, which are isolated. Subsequently, the solvents are stripped by distillation. As an energy-saving alternative for the removal of a large part of the solvent, ExxonMobil and Grace have jointly developed a reverse osmosis process termed Max-DewaxTM (Figure 5) [15–17]. Polyimide

Figure 5 Simplified flow diagram of ExxonMobil's solvent dewaxing process employing reverse osmosis. (Adapted from [16], with permission.)

membranes with a molecular weight cutoff of 300 Da are employed in the form of spiral-wound modules (Figures 6 and 7). Operation conditions are around 3.5 MPa and -18 to 0 °C. A first commercial unit, processing 5800 m^3 of lube oil filtrate per day, was installed at ExxonMobil's refinery in Beaumont (Tx) in 1998. This example illustrates the viability of membrane filtration in an organic solvent on a large industrial scale.

Figure 6 Membrane filtration unit for solvent dewaxing.
(Photograph by courtesy of ExxonMobil Research and Engineering Company.)

Figure 7 Cross-section of a spiral-wound module. (Adapted from [16], with permission.)

Polymeric ultrafiltration membranes stable to organic solvents were developed by Linder, Perry, and co-workers. As a separating layer, cross-linked polyacrylonitriles or halomethylated poly(phenylene oxides), for example, are mentioned in patents [18–21]. These products, under the name SelRO[®], are now marketed by Koch industries [22, 23]. Flat sheet membranes as well as tubular and spiral modules are available. Two flat membranes, MPF-50 and MPF-60 with NMWCOs of 700 and 400 Da, respectively, are supplied. Both membranes are hydrophobic, with an asymmetric structure. The nature of the crucial separating layer is not disclosed, but from the patents it can be inferred that cross-linked polyacrylonitrile or polyethyleneimine, or bromomethylated phenylene oxide cross-linked with ammonia, may be involved. Another producer of solvent-stable polymeric membranes is the aforementioned Grace Davison; the products are marketed under the trade name Starmem[™] by Membrane Extraction Technology [24]. Again, flat membrane sheets as well as modules are available with NMWCOs ranging from 200 to 400 Da. According to the supplier, these are polyimide membranes. The operating conditions recommended for SelRO[®] and for Starmem[™] are roughly similar. Maximum temperatures are 40 to 60 °C and typical transmembrane pressures are 3 MPa. Flow rates are around 30 m² l⁻¹ h⁻¹ at this pressure. The membranes are stable toward solvents such as toluene, ethyl acetate, methyl ethyl ketone, hexane, or methylene chloride [22, 24]. It can be noted that polyaramide ultrafiltration membranes were also investigated intensively at the former Hoechst AG in the 1980s, and were made available for some time to academic research institutions [25].

For ultrafiltration as a unit operation for the separation of polymer-bound soluble catalysts in particular, the recovery process for a rhodium catalyst from the hydroformylation of dicyclopentadiene is an illustrative example (for another detailed example, see Section 7.5) [26, 27]. Toluene can be used as a solvent, with the polyaramide membrane employed. TPPTS, or TPPTS and also a sulfonated bidentate phosphine with large ammonium counterions, are used as ligands. For efficient recovery, molecular weights of the catalyst of more than 3000 g mol⁻¹ were required on the membrane used. Separation is performed in two steps [28]. A pilot plant was run successfully over an extended period of time three months.

Other examples of ultrafiltration as a separation operation on a laboratory scale employing continuously operated membrane reactors (vide infra) have been reported [1, 29, 30]. These examples will be discussed throughout Section 7.4. Continuous ultrafiltration of polymer-stabilized metal colloids, in addition to polymer-bound metal complexes, has also been studied [31].

Due to their high stability toward organic media, inorganic membranes [32] appear particularly suited for separations in organic solvents including the recovery of polymer-bound catalysts. To date they have found only limited attention for such purposes. The non-inorganic materials in modules, i.e., the seals, gaskets, and O-rings which hold the membrane elements in their housing, impose limitations. The brittleness of the ceramics requires relatively careful handling. Large pumping capacities are required to achieve the required flow rates in modules. Pore sizes of most commercial inorganic membranes are too large for efficient catalyst retention, although nanofiltration membranes are also available now [9]. There is also some

effort directed at the development of flat sheet inorganic membranes, which would be of particular interest for laboratory-scale research on catalyst recovery [33]. However, the pore sizes attainable in a defect-free fashion currently are still too large. While the aforementioned limitations may be a hurdle, particularly for academic laboratories not geared toward engineering, they pose no major limitations, and inorganic membranes certainly provide attractive future opportunities for soluble catalyst recovery (see also Section 7.4.1).

The recovery of homogeneous catalysts can be performed batchwise, subjecting the catalyst alternately to a catalytic reaction in a batch reactor and to a batch ultrafiltration (e.g., using an apparatus as depicted in Figure 3 for the filtration), or it can be carried out in a continuous fashion. Continuous filtration units comprise continuously operated membrane reactors, or loop reactors (Figure 8).

In many applications of a membrane filtration step, a completely selective retention of a given substrate is not in general mandatory, but rather an enrichment of the substrate is achieved (e.g., in the aforementioned Max-Dewax process). In other applications a complete retention is necessary. Even when defining “complete” as $\geq 99\%$, the latter requirement is much less demanding by comparison to the recovery and recycling of a polymer-bound soluble catalyst: in membrane applications in general the solution to be filtered is usually subjected to the filtration process only once. By contrast, a catalyst has to run through the “filtration step” many times (either in the form of a discrete filtration step, or by continuous filtration, such as in a continuously operated membrane reactor; cf. Figure 8). For a continuously operated membrane reactor of volume V_0 , the retention of the solute being considered, i.e., the polymer-bound catalyst, and the proportion remaining after the passing of $n = V_S/V_0$ reactor cell volumes of solvent (i.e., the substrate feed stream) through the reactor cell may be calculated from Eqs. (1) and (2).

Figure 8 Schematic representation of different reactor types for the continuous recovery of soluble polymer-bound catalyst.

- (a) Dead-end continuously operated membrane reactor;
- (b) cross-flow continuously operated membrane reactor;
- (c) loop reactor.

$$\text{Retention } R' = \frac{c_r - c_p}{c_r} = 1 - \frac{1}{(V_S/V_0)} \ln \frac{c_r(0)}{c_r(V_S)} \quad (1)$$

c_r, c_p = concentration of solute in retentate and permeate respectively at any given time; R' corresponds to retention per cell volume (for $R' > \text{ca. } 0.095$)
 V_0 = cell volume
 V_S = volume of solvent pumped through cell
 $c_r(0)$ = initial solute concentration
 $c_r(V_S)$ = solute concentration in retentate after passing of V_S

The portion of solute retained in the cell after passing of V_S is obtained from Eq. (2).

$$\frac{c_r(V_S)}{c_r(0)} = e^{-(1-R')V_S/V_0} \quad (2)$$

To retain 99% of the catalyst after $n = 100$ exchanged reactor volumes (i.e., a 1% catalyst loss from the reactor), a retention of $R' = 99.99\%$ per exchanged reactor cell volume is required (Figure 9). For commercial viability of continuously operated filtration, a minimum retention per exchanged reaction volume of $R' > 99.9\%$ (small-scale synthesis) to $R' > 99.999\%$ (bulk chemicals) can be estimated. It can be noted that noncontinuous filtration, e.g., to remove high-boiling side products from a catalyst from time to time, poses less stringent requirements on retention. In any case it is evident that appropriately designed catalysts in combination with suitable membranes and engineering of the filtration unit must be used.

Figure 9 Proportion of a soluble catalyst remaining in the reactor vs. the number of exchanged reactor volumes in a continuously operated membrane reactor for different catalyst retentions ($R' = 99.99\%$, 99.9% , 99% , and 95%).

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