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Continuous homogeneous hydroformylation with bulky rhodium catalyst complexes retained by nano-filtration membranes

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ABSTRACT

By employing polymer bound bulky phosphite ligands (synthesized in house) in conjunction with polyimide membranes with appropriate molecular weight cutoff (MWCO), homogeneous Rh complexes were effectively retained in solution. Batch filtration of toluene-based solutions of various phosphorus ligands at constant pressure revealed that Rh complexed with polymer bound bidendate ligands (average molecular weight from 7000 to 10,000) were most effectively retained in solution with Rh leakage in the permeate being on the order of tens of ppb. Continuous filtration of toluene-based solutions containing dissolved polymer bound phosphite ligand at constant pressure and cell hold-up revealed that the Rh and P concentrations in the permeate were steady after several hours at less than 100 ppb. The higher initial concentrations of Rh and P in the permeate suggests the removal of perhaps unbound Rh and P from the initial mixture and also from the fraction of the polymers that are smaller than the MWCO of the membrane. Continuous 1-olefin hydroformylation with Rh complexed with polymer bound bidentate ligand (JanaPhos) was demonstrated at 50 °C in a stirred reactor fitted with a nanofiltration membrane. The catalyst complex was dissolved in a toluene-based reaction mixture and the feed solution (containing the substrate) and syngas were added continuously to maintain a constant flow rate and reactor pressure (3.0 MPa). At optimized conditions, the continuous run reached a steady state characterized by nearly 50% 1-olefin conversion, >98% aldehydes selectivity and a *n*/*i* ratio of 3.5, all of which remained constant even after 22 h. The Rh concentrations in the effluent were steady at approximately 20 ppb even after 22 h. The makeup Rh cost required to offset this loss during continuous processing ($0.004/lb aldehyde) exceeds the economic viability criterion ($0.013/lb aldehyde).

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1. Introduction

Hydroformylation involves converting olefins with syngas to produce aldehydes, which are the intermediates for the manufacture of detergents, surfactants and plasticizers. Hydroformylation is one of the largest homogeneous processes in the chemical industry with a worldwide annual production capacity of over 15 billion pounds [1–3]. The most commonly demonstrated catalysts are unmodified or modified rhodium and cobalt complexes. The catalyst recovery for higher olefin ($>C_4$) hydroformylation poses a major challenge, since the catalyst complexes decompose at the high distillation temperatures required for separating the products. This remains an especially difficult barrier for employing Rh catalysts because of the nearly quantitative Rh recovery required for economic viability. With Co, the catalyst recovery target for economic viability is not as stringent. However, the cobalt-catalyzed process requires rather harsh reaction temperatures and pressures to activate and maintain the catalyst complex. Further, the separation of the catalyst metal from the reaction mixture and reconstitution of the active complex require complex processing steps involving the use of large amounts of acid and alkali. We previously reported a novel process concept that addresses these issues in higher olefin hydroformylation by investigating triphenylphosphine/rhodium catalyzed 1-octene hydroformylation in CO_2-expanded liquids under mild conditions [4,5]. The preliminary quantitative economic analyses indicate that the CXL process has clear potential to be economically feasible if the recovery of the rhodium is at least 99.8% per pass [6]. This translates to a Rh concentration of 560 ppb (or a loss of 0.013 $lb nonanal) in the reactor effluent stream of a continuous process.

Various methods of heterogenization of homogeneous Rh catalyst complexes have been reported in the literature [7]. However, these approaches have to date not produced a satisfactory catalyst. Cole-Hamilton and coworkers [8–12] demonstrated a continuous

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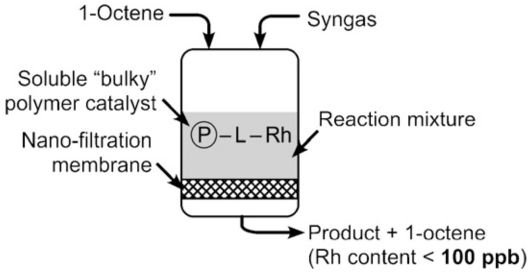

Fig. 1. Schematic of continuous homogeneous hydroformylation with simultaneous membrane filtration.

reactor system for performing homogeneous catalytic reactions in ionic liquid (IL)/*sc*CO_2 systems. The IL phase containing dissolved catalyst is retained in the reactor. The *sc*CO_2 is used to transport the soluble substrate into and products from the IL phase continuously. Constant activity for up to three days was demonstrated during continuous 1-octene hydroformylation with a Rh-based catalyst in [BMIm][PF_6]/*sc*CO_2 medium. Compared to the industrial cobalt-catalyzed processes, higher TOFs were observed; the selectivity to linear aldehyde (70%) is comparable to those attained in the industrial processes (70–80%). However, the air/moisture sensitivity of the ILs and the ligands and the leaching of the rhodium catalyst were cited as practical challenges to overcome. Cole-Hamilton and coworkers [11] have also reported a solventless homogeneous hydroformylation process using dense CO_2 to transport the reactants into and transfer the products out of the reactor leaving behind the insoluble Rh-based catalyst complex in the reactor solution. Abraham and coworkers [12] investigated 1-hexene hydroformylation over a rhodium–phosphine catalyst immobilized on a silica support and found that the rates in CO_2-expanded toluene and in supercritical CO_2 were comparable but faster than in normal toluene. However, the activity declined with time due to possible catalyst leaching.

Another approach to minimize Rh leaching to economically viable levels is to utilize bulky phosphite ligands to form soluble rhodium complexes that are amenable to filtration by size exclusion and can therefore be essentially retained in its active form by membrane filtration. Such membrane filtration techniques have been previously demonstrated to retain organometallic complexes in homogeneous solutions. Livingston's group applied nanofiltration in retaining transition metal catalysts, such as palladium complexes with ionic liquids from Suzuki reaction mixture [13], Ru-BINAP (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) with the ionic liquid from asymmetric hydrogenation reaction mixture [14], and the Jacobsen, Wilkinson and Pd-BINAP catalysts in organic solvents (ethyl acetate, tetrahydrofuran and dichloromethane, respectively) [15]. In some of those cases, the detectable catalyst retention was as high as 99.9% and high catalyst reactivity was maintained. Datta et al. [16] reported a nanofiltration technique for separating homogeneous catalysts for Heck, Sonogashira, and Suzuki coupling reactions of aryl halides and bromides using soluble phosphinated polymersupported palladium catalysts. Total reflection X-ray fluorescence (TXRF) and spectrophotometric analyses indicated >99.95% retention of the catalyst. The catalyst activity is almost unchanged, as shown by the nearly constant turnover frequencies and yields in the subsequent reactions up to 9 cycles. As shown elsewhere, this type of rhodium complexes may also be recycled by precipitation as solid particles (by adding methanol) followed by filtration and redissolution as a homogeneous catalyst [17].

Fig. 1 illustrates the envisioned scheme for continuous homogeneous hydroformylation with in situ retention of the bulky catalyst. In this scheme, the polymer bound rhodium complex, synthesized as described elsewhere [18], is dissolved in the hydroformylation reaction mixture to form a homogeneous solution. Pressurized gas (up to approximately 5 MPa consisting of syngas and an inert) is used to facilitate filtration of the reaction mixture across the nanofiltration membrane. When CO_2 is used as a pressurizing gas, a CO_2-expanded liquid (CXL) is created, due to the dissolution of CO_2 into the organic phase, while maintaining the catalyst in solution. The mixture of substrate and solvent is continuously fed into the reactor and the aldehyde products along with unreacted substrate, solvent and other products pass through the membrane, leaving the bulky polymer bound rhodium complex solubilized in the reaction mixture. By essentially retaining the catalyst complex in the reactor, the membrane separation process obviates post-reactor catalyst precipitation and regeneration steps that cause thermal decomposition of the rhodium complex and appreciable Rh loss. This article quantifies the retention of various Rh/ligand complexes with a nanofiltration membrane and also demonstrates the possibility of continuous homogeneous hydroformylation with minimal Rh loss with such nanofiltration techniques.

2. Experimental

2.1. STARMEM® membrane

The STARMEM® nano/ultra-filtration membrane was purchased from Grace-Davison Company (USA) [19]. The membrane is made of highly cross-linked asymmetric polyimide. The thickness of the membrane layer is less than 0.2 mm with an average pore size of <50 Å. The membrane has a diameter of 90 mm and an active surface area of 54 cm^2. The molecular weight cut-off (MWCO) of the membrane ranges from 200 to 400 Da, based on 90% retention of the solute. This membrane is compatible with most conventional organic solvents, such as alkanes, aldehydes, alcohols and aromatics. Its rated durability is for up to one year with a maximum operating temperature of 50 °C [20].

2.2. MET cell

The Membrane Extraction Technology (MET) cell shown in Fig. 2 was purchased from MET Ltd. in London, UK [21] and is made of 316 stainless steel. The thin membrane is placed at the bottom of the MET cell and supported by a porous sintered stainless steel disk. The maximum working volume of the cell is 270 mL. The two inlets (one for feed and the other for the pressurizing gas) enable continuous and air-free operation. The cell is equipped with a Teflon-coated magnetic stirrer bar fixed on a metal bracket soldered to the top lid. The maximum operating pressure is 6.9 MPa.

2.3. Membrane reactor setup

Fig. 3 shows the schematic of the membrane filtration setup. The cell body is wrapped with a heating tape and insulation, and placed on a magnetic stirrer and hot plate (Barnstead Cimarec Stirrer with a range of 60–1200 rpm). A thermocouple, interfaced with LabView® data acquisition system, monitors the solution temperature. The solvent or the substrate is pumped into the cell by a Primeline™ HPLC pump at a constant flowrate ranging from 0.01 to 20 mL/min. Both the feed reservoir and permeate receiver are blanketed with inert nitrogen gas. Besides nitrogen, there are a variety of gases that can serve as pressurizing gases. For performing homogeneous hydroformylation reactions with simultaneous filtration of the catalyst complex, either synthesis gas (CO/H_2 = 1:1 molar) by itself or its mixture with CO_2 will be employed as the pressurizing gas. Following filtration, the cell pressure is released gradually via a regulating valve to avoid membrane doming that results with a

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