

Continuous Homogeneous Hydroformylation with Nanofiltration for Retention of Polymer Supported Rh Catalyst Complexes

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Introduction

Industrial higher olefin ($> C_5$) hydroformylation processes require harsh temperatures and pressures (140 - 200 °C, 5 - 30 MPa) as well as tedious catalyst separation schemes involving hazardous reagents to recycle the cobalt catalyst [1]. The use of rhodium (Rh) as a catalyst would lower the operating temperature and pressure but requires almost quantitative recovery and recycle of the costly catalyst. In our previous work, higher olefin (1-octene as model substrate) hydroformylation with a modified rhodium catalyst complex was performed in CO₂-expanded liquid (CXL) media at mild pressures (tens of bars) and temperatures (< 100 °C) [2]. The batch experiments gave reasonable turnover frequency and high selectivity towards the linear C₉ aldehyde. For economic viability, analysis suggests a maximum Rh loss of 0.2% per pass during continuous operation [3]. This paper shows how this target is achieved by employing nanofiltration with specially designed soluble polymer supported phosphite ligands.

Experimental

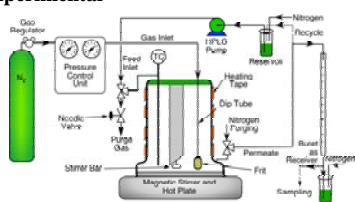


Figure 1 Membrane filtration setup configuration

The reaction was performed in a stirred stainless steel vessel (rated up to 75 °C and 70 bars) equipped with a STARMEM® nano/ultra filtration membrane [4] (Figure 1). Various phosphite ligands (Table 1) including bulky bidentate and polymer supported mono- or bidentate ligands were used to investigate the extent of Rh retention in the cell. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to quantify the Rh and phosphorous (P) concentrations at ppb levels.

Results and Discussions

Figure 2 gives the preliminary batch filtration results using different phosphite ligands. In these runs, the Rh and P concentrations in toluene (starting mixture) range from 70 to 300 ppm with a P/Rh ratio of 4 - 8. This solution was subjected to nanofiltration at room

temperature (~ 21 °C) using a constant pressure of nitrogen (10 bars). The Rh pass-through is estimated from the total Rh detected in the permeate relative to the total Rh in the initial solution. As shown in Figure 2, the polymer ligands (PBB10b and PBP10a) give very low Rh pass-through ($< 0.1\%$) and only tens of ppb of Rh are detected in the permeate stream. For the bidentate ligand, Rh concentrations in permeate are higher compared to the polymer ligands, which is attributed to the almost 10 fold smaller size of the non-polymer supported ligand and complex.

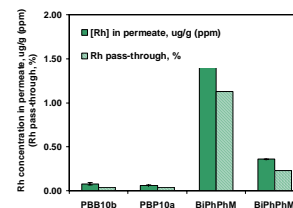


Figure 2 Rh concentrations and pass-through in permeate for the batch filtration runs

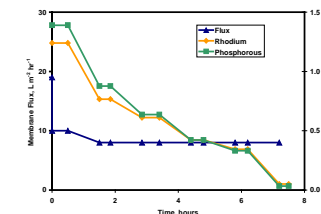


Figure 3 Membrane flux, Rh and P concentrations in permeate vs time

Figure 3 shows the temporal permeate flux along with the Rh and P concentrations in the permeate stream during continuous nanofiltration without reaction. In this run, polymer supported phosphite ligand (PBB10c) was dissolved in toluene. The Rh and P concentrations in solution range from 100 to 150 ppm with a P/Rh ratio of 4. The filtration conditions were the same as the batch runs. The flux remained constant throughout the run. The Rh and P concentrations in permeate continuously decreased with time leveling off at 50 ppb after 7 hours of filtration. Total Rh and P losses during this line-out period are each approximately 2%, implying that roughly 98% of the Rh and P are retained in the cell following the line-out period. Assuming that the Rh and P leaching is substantially complete during the line-out period, the targeted rhodium recovery rate 99.8% per pass is thus easily achieved beyond the line-out period.

These results along with continuous nanofiltration coupled with reaction at elevated temperature will be presented to demonstrate stable Rh catalyst activity and selectivity towards the linear aldehyde.

Significance

This work demonstrates a new hydroformylation process that integrates continuous reaction with nanofiltration using specially synthesized polymer-supported phosphite ligands with a narrow molecular weight distribution. The new process concept eliminates a separate catalyst recovery step post reaction and is generally applicable for other types of homogeneous catalysis reactions as well.

References

1. Frohling *et al.*, In: Cornils and Herrmann, eds. Weinheim, Germany: VCH; **1996**, 27
2. Jin *et al.*, *AIChE J.*, **2006**, 52, 2575
3. Fang *et al.*, *Ind. Eng. Chem. Res.*, **2007**, 46, 8687
4. Vandezande *et al.*, *Chem. Soc. Rev.*, **2008**, 37, 365