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Direct formation of propanol from a dilute ethylene feed via reductive-hydroformylation using homogeneous rhodium catalysts at low feed pressures

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ABSTRACT

This work details a system for the direct production of propanol from a dilute ethylene stream by reductive hydroformylation catalyzed by soluble rhodium complexes coordinated to tri-aryl or tri-alkyl phosphines.

Typically, in commercial production, normal alcohols are produced from primary olefins via a two step process consisting of hydroformylation of the olefins to aldehydes, followed by subsequent hydrogenation of the aldehydes to the corresponding alcohols. This work describes a method to produce propanol directly from dilute ethylene feeds.

In addition, the partial pressures of the syngas used in these experiments are significantly lower (approximately an order of magnitude) than reported for nearly all of the other rhodium catalyzed reductive-hydroformylation systems ($0.7-70 \text{ atm vs.} \sim 20-700 \text{ atm}$).

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1. Introduction

Industry is actively working to develop and deploy alternative sources of propylene production, as global propylene demand continues to grow at a pace exceeding ethylene (SRI consulting: 5.3% annual growth (polypropylene at 7.3%/a)). One alternate approach to propylene production is to utilize low cost waste streams containing ethylene [1] for the reductive hydroformylation of ethylene to propanol. For on-purpose propylene production, the product can either be propanol or propanal, which can subsequently be hydrogenated to propanol. Propanol is an easily transportable alcohol and can be dehydrated on site or easily shipped to another site for dehydration to the desired propylene gas. homogeneous rhodium catalysts make them promising candidates for dilute stream ethylene hydroformylation [4–7]. In this study, semi-batch experimentation explores the rate of propanol and propanal formation under a variety of gas feed conditions with an array of hydrocarbyl phosphine ligands capable of preferential production of the desired alcohol.

2. Experimental

All of the chemicals utilized in this study were purchased from commercial sources. All phosphine ligands were purchased from



Existing Multi-Step Process

While not as robust as their heterogeneous or supported counterparts [2,3], the high selectivity and catalyst stability of

Aldrich. The $Rh(acac)(CO)_2$ was purchased from Strem Chemical, and the solvents (tetraglyme and propanal) from Aldrich. All reagents were stored inside a nitrogen purged glove-box and used without further purification. The solvents were stored over 4Å molecular sieves.



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