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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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Entry	Ligand	Initial feed ratio	Ethylene pressure (atm)	Solvent	TOF	Ethane (mol%)
1	TOP	8:1:1	0.7	Butanol	232	0.1
2	TOP	8:1:1	0.7	Butanol/water ^a	258	0.1
3	THP	8:1:1	0.7	Butanol	206	0.07
4	TPP	8:1:1	0.7	Butanol	0 ^b	0.75
5	1,3-DCHPP	8:1:1	0.7	Butanol	5.15	1.5
6	THP	8:1:1	0.7	Texanol	103	0.1
7	THP	2:1:1	0.7	Butanol	232	1.2
8	THP	2:1:1	3.4	Butanol	258	0.2
9	TCHP	8:1:1	0.7	Butanol	0 ^c	0

Rate of propanol formation with varying phosphine ligands.

Conditions: 100 °C, 34 atm total pressure. Rhodium concentration was 400 ppm in all experiments.

^a 5 vol.% water was added to the n-butanol.

^b TOF of propionadehydel formation was 103.

^c TOF of propionaldehyde formation was 160.

These experiments were conducted in semi-batch mode in a 300 mL, high-pressure, stirred autoclave, from Parr Instrument Company (Model 4561). The reactor was equipped with baffles, a hollow shaft/gas-entrainment impeller and was stirred at 1300 rpm to insure thorough gas/liquid mixing during the reaction. The standard 1/8 hp variable speed stirrer motor was adapted with a larger pulley to permit stirring speeds in excess of 1000 rpm for optimal gas entrainment. The reactor had facilities for both gas and liquid sampling while in operation. In a typical experiment, the reactor was charged with the catalyst precursor dicarbonylacetylacetonato rhodium(I) (\sim 48 mg), the phosphine ligand (\sim 4 g), and solvent (~96 mL) inside a glove-box under nitrogen. The reactor was then sealed, removed from the glove-box, mounted to the heating and agitation system inside a fume hood, pressure tested with inert gas, and then heated to 100 °C. From a pre-mixed cylinder of hydrogen, carbon monoxide, and ethylene (either 2:1:1 or 8:1:1 mol ratio) the pressure was increased to the desired level (typically 7 atm), then 27 atm of helium was delivered to the reactor. The reactor pressure was maintained at 34 atm by introducing a constant stream of make-up feed gas $(2:1:1 H_2/CO/C_2H_4)$ to the reactor through a Brooks mass-flow controller. Analysis of the headspace of the reactor was performed before and after each run to quantify the amount of ethane formed. The liquid phase of the reactor was sampled throughout the run for analysis. Quantitative analysis of the liquid phase products of each reaction was carried-out on a Hewlett-Packard 6890 GC equipped with a methyl-silicone gum capillary column and a flame-ionization detector. Typically, only propanol, propanal, and the solvent were observed, but in a number of runs a small amount of pentanol was observed forming over the course of the run. The rate of formation of these products was calculated using the GC analysis of the liquid phase.

3. Results

Several rhodium catalysts were prepared in situ by adding an excess of phosphine ligand to the metal precursor as described above. An 8:1:1 ratio of hydrogen, carbon monoxide, and ethylene was used to favor selectivity to the alcohol over the aldehyde wherein turnover frequency (h^{-1}) is corresponding to only propanol unless otherwise stated (Table 1), and TOF is calculated as an average over the entire trial. From these results, it is observed that at very dilute ethylene feeds (0.7 atm), linear alkyl-containing phosphine ligands produce the highest rates of alcohol formation. The rates of alcohol production observed by the trioctylphosphine (TOP) and trihexylphosphine (THP) containing catalysts are comparable with TOFs of 232-258. Of note, however, is that triphenylphosphine (TPP), tricyclohexylphosphine (THCP), and 1,3-dicyclohexylphosphinopropane (DHCPP), all produce little or no alcohol, but are quite active towards the aldehyde, as indicated in Table 1 subtext. In entries 7 and 8, the feed ratio is

reduced to 2:1:1, and this change had little effect on the rate of alcohol formation, indicating that the 8:1:1 excess of hydrogen is not required. However, using the same catalyst and a 2:1:1 ratio of feed gas at an ethylene pressure of 3.4 atm severely reduces the selectivity to the alcohol, producing a TOF of 258, despite the increased feed concentration. Lastly, GC analysis of the headspace was performed to determine the amount of feed gas lost to ethane formation. It is observed that at an 8:1:1 feed ratio, the THP and TOP ligand catalysts have very low degrees of ethane formation, while phosphine ligands DHCPP and TPP are an order of magnitude greater. Reducing the feed ratio to 2:1:1 at dilute ethylene partial pressures diminishes this effect with ligand concentration and increases the ethane formation from 0.1 mol% to 1.2 mol%.

As described above, while at relatively dilute feed streams and with a 2:1:1 excess of hydrogen over ethylene and carbon monoxide, alkyl phosphine catalysts favor propanol formation. The rate and selectivities, shown in Fig. 1, indicate that an initial amount of propionaldehyde is formed before leveling off. Comparable rates are seen at lower ethylene partial pressures when an excess of hydrogen is used (8:1:1) in the feed, shown in Fig. 2. Two differences to note: the leveling-off effect seen in Fig. 1 is not seen in the case of the more dilute trials, and furthermore, small amounts of pentanol are also detected, reducing the selectivity in the dilute trials.

For comparison, under identical conditions using the in situ generated TPP bearing catalyst, the converse is observed. As shown in Fig. 3, propionaldehyde is strongly favored during the run, with only small amounts of propanol being formed. Comparing Figs. 2 and 3 at the same point of ethylene conversion show a THP selectivity to propanol of approximately 68%, while TPP has only a 8% selectivity towards alcohol. Once again, trace amounts of pentanol are also detected.



Fig. 1. Product formation with 4 wt. % Tri-n-hexylphosphine, 3.4 atm ethylene, 2:1:1. Triangles = propanol, diamonds = propionaldehyde.

Table 1



Fig. 2. Product formation with 4 wt. % Tri-n-hexylphosphine, 0.7 atm ethylene, 8:1:1. Triangles = propanol, diamonds = propionaldehyde, circles = pentanol.



Fig. 3. Product formation with 4 wt. % Triphenylphosphine, 0.7 atm ethylene, 8:1:1. Triangles = propanol, diamonds = propionaldehyde, circle = pentanol.

4. Discussion

From this study we find that the hydroformylation capability of these catalysts is highly ligand dependent, not just in activity, but in product selectivity. And while historically processes in industry and academia have focused more on converting ethylene to propanol utilizing triphenylphosphine to reach an aldehyde intermediate, [6,7] a direct method is readily available even at dilute feed streams. As shown in Figs. 2 and 3, a preference for propanol or propanal can be decided merely via the addition of the free ligand prior to reactor startup and in situ generation of the catalyst. While TPP and the other bulky, phosphine ligands heavily favor the aldehyde, alkyl phosphines more strongly favor the alcohol. It was previously proposed that this effect is highly correlated to the cone angle of the phosphine ligands, [8] wherein all three of the bulkiest ligands almost exclusively produce propanal. As demonstrated from Table 1, significant selectivity behaviors are affected by feed gas conditions. At a 2:1:1 excess of hydrogen over carbon monoxide and ethylene at 3.4 atm, ethane formation remains low for the linear alkyl phosphines. However as the feed gas becomes further diluted, this increases ethane formation by as much as a factor of ten. This is likely the result of less hydrogen being available to regenerate the rhodium catalyst, and to break up any

rhodium-rhodium dimers, resulting in deactivation. By increasing the excess of hydrogen to a ratio of 8:1:1 this dimer formation can be overcome. As previously mentioned, this impacted product selectivity, and as a result of the buildup of ethane, inhibited the amount of makeup feed gas to be introduced which is represented in a slight decrease in rate proportional to ethane formed.

Equally significant is the ability to perform this process under low ethylene pressures – far lower than what has been explored in any industrial process, thus demonstrating that ethylene otherwise used as fuel could potentially be converted directly to alcohol. This direct method provides a substantial economic incentive by eliminating the need for the aldehyde hydrogenation. And while it is expected that a more realistic gas stream other than syngas diluted in nitrogen will provide hurdles in the future, this work provides a proof of concept and 'base-case' scenario for evaluation of an industrially significant chemical process.

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