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Short Communication

Reactive separation of dilute ethylene by hydroformylation using slurried rhodium catalysts on phosphinated resins and silica

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ABSTRACT

A series of slurried rhodium catalysts on phosphinated resins and silica were tested for the reactive separation of dilute ethylene by hydroformylation to propanal. The amount of rhodium leaching was determined for most of the systems investigated. Leaching ranged from <2 to 11% for catalytic runs for resin supported systems, but was found to be much more significant for the phosphinated silica system studied, 19%. The level of rhodium leaching correlated well with the loss in rate of propanal formation between repeated experiments using recycled catalysts for the resin based systems, but the loss in rate was much more significant for the silica based system. This level of leaching is very high for a commercial process for basic chemical synthesis, for which leaching is typically at the ppb level. Rates of propanal formation for resin supported catalyst systems correlated well with the cone angle of the free phosphine, with rates as high as 0.35 mol/l/h. However, while smaller cone angles were found to be directly proportional to rate, supported systems were less active than homogeneous counterparts.

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1. Introduction

Global demand for propylene growth has been outpacing that for ethylene for more than a decade [1]. Historically, propylene has been produced as a by-product of ethylene production in steam crackers, and gasoline production in refinery FCC operations. There has traditionally been very little "on-purpose" propylene production. The recent addition of Middle-East ethane crackers is exacerbating this problem. Thus, there has been a recent trend toward development of alternative sources of propylene, without adversely affecting ethylene production.

To address this growing demand a number of on-purpose propylene technology offerings are being explored, including technologies such as metathesis, catalytic cracking of higher-olefin rich feeds, methanol-to-olefins/methanol-to-propylene, and propane dehydrogenation.

Refinery off-gas, particularly that produced by fluid catalytic cracker (FCC) units, typically contains fairly high quantities of olefin components which are not recovered economically by conventional cryogenic separations, and instead are burned as fuel. The concentration of these olefins can be quite substantial, often up to 20% in ethylene [2].



One technology being explored is the conversion of ethylene in lowvalue, dilute ethylene streams into n-propanol, a shippable intermediate, which can be subsequently converted to propylene via dehydration.

The first step can be accomplished either as a 1-step reductivehydroformylation of ethylene to propanol, or as a 2-step process of hydroformylation of ethylene to propanal, followed by a reduction of the propanal to propanol. Either of which can be essentially viewed as a reactive separation of ethylene from a dilute gas stream.

In this work we present results of an investigation of slurried rhodium catalysts ligated/supported by phosphine-functionalized polymers and a phosphinated silica for the hydroformylation of dilute ethylene. Each of the supported-phosphine/Rh complexes was generated *in situ* and tested for ethylene hydroformylation. The goals of this study were to establish the feasibility of using these supported catalysts for the aforementioned reaction, by the comparison of their reaction rates, lifetime, and selectivity to the non-supported counterparts. The major obstacle with the use of resin-supported hydroformylation catalysts, which has largely prevented their commercial

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application, [3] and in particular, their application in flow reactors, is the leaching of the active material from the support. Thus, an important point to be determined is the amount of catalyst that is leached from the support under reaction conditions.

The type of phosphinated supports used in this investigation are lightly cross-linked, macroporous, phosphine-functionalized poly(styrene-co-divinylbenzene), Merrifield-type resins, and a phosphinated silica gel. These resins are insoluble, but able to swell significantly in many organic solvent media. The phosphine loading levels, surface area, pore volume, mesh size, amount of cross-linking, and swelling volumes for the phosphinated supports are reported in Table 1. Rhodium hydroformylation catalysts supported on functionalized polymers have been studied since the early sixties [4]. These resins represent the most widely investigated class of catalyst supports used in studies of supported hydroformylation catalysts. They are commercially available, are inert toward reaction conditions, and offer ease of modification. Immobilization of a homogeneous catalyst on a support can increase the catalyst lifetime, or range of operation of the catalytic system. By binding the active component at particular sites and preventing aggregation to larger metal units the system activity may be maintained [5,6].

2. Experimental

All of the phosphinated resins and silica utilized in this study were purchased from commercial sources: triphenylphosphine, polymerbound (Aldrich), dicyclohexylphenylphosphine polymer-bound (Aldrich), di(n-butyl)phenylphosphine, polymer-bound (EMD Chemicals), benzyldiphenylphosphine, polymer-bound (Fluka), and 2-diphenylphosphinoethyl-functionalized silica gel (Aldrich). The (acac)Rh(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 4 Å molecular sieves.

These experiments were conducted in semi-batch mode in a 300 cm³, 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

Table 1	
Properties of the phosphine-modified supports.	

	P-loading (mmol/g)	Mesh	Cross link (% DVB)	Pore size (Å)	Surf. area ^b (m ² /g)	Swelling factor ^a
PS-Ph-PPh ₂	3.2	100-200	2	-	-	2.0
PS-Ph-P(n-Bu) ₂	0.66	100-200	1	-	-	3.3
PS-Ph-PCy ₂	1-2	50-100	1	-	-	2.9
PS-Bz-PPh ₂	2.5	200-400	2	-	-	1.2
Si-Et-PPh ₂	0.7	200-400	-	60	500	-

^a The swelling factor is the volume of the swollen resin divided by the volume of the equivalent amount of the dry resin. Determined in toluene after 3 h; no swelling in tetraglyme was observed after 3 h.

^b Measurement of the dry-state surface area of the resins was attempted by BET, but the results were not quantifiable due to the ultra-low surface areas, as expected with the gel-type morphology [7].

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) (~12 mg), the supported ligand (~100 mg), and solvent (100 mL) inside a glove-box under nitrogen. The reactor was then sealed, removed from the glovebox, mounted to heating/agitation system inside a fume hood, pressure tested with inert gas, and then heated to the desired temperature (typically 100 °C). From a 1:1:1 cylinder of ethylene, hydrogen, carbon monoxide the pressure was increased to the desired level (either 10 atm or 2 atm) and then nitrogen is added to the system to increase the total pressure to 34 atm. The 1:1:1 feed cylinder was connected to a Brooks mass-flow-controller operating as a flow-meter which maintained the pressure at 34 atm by introducing make-up feed gas to the reactor. Analysis of the headspace of the reactor was performed before and after each run to quantitate the amount of ethane formed. The liquid phase of the reactor was sampled at 0, 15, 30, 60, 90, and 120 min for analysis with 1 mL samples. 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, a flame-ionization detector, and quantitated using a calibration curve. Typically, only propanal and the tetraglyme solvent were observed in analyses. The rate of propanal formation was calculated using the GC analysis of the liquid phase, and/or the rate of feed consumption through the flow-meter.

The rhodium content of the solutions after the catalytic reactions was determined by flame atomic absorption spectroscopy. Swelling volume was determined in a graduated cylinder by recording the volume of a given quantity of dry resin and then measuring the expansion of the resin in an excess of toluene (or tetraglyme), after 3 hours at ambient temperature.

Rates are expressed in moles of aldehyde formed per mol of catalyst per liquid volume within the reactor.

3. Results

Each of the catalyst systems were evaluated at two sets of feed partial pressures. In the first case, 3.4 atm partial pressures of each ethylene, hydrogen, and carbon monoxide were charged to the reactor, which accounted for 10.2 atm of the total 34 atm pressure on the reactor. In the second, 0.7 atm each of ethylene, hydrogen, and carbon monoxide accounting for 2.0 atm of the total 34 atm on the reactor. The results of experiments at 3.4 atm and various process conditions are presented in Fig. 1 and Table 2.

All of the catalysts were found to exhibit stable rates of propanal formation over the course of each experiment (2-6 h). However, studies to test for deactivation over longer periods were precluded due to the semi-batch mode of operation. The rate was found to be independent of ligand-to-rhodium ratios over the range studied (P/Rh~2-6). Although an excess of the supported ligand should not



Fig. 1. Formation of propanal with time using rhodium with supported ligands: 34 atm of feed, with 3.4 atm of each CO, H_2 , and C_2H_4 . T = 100 °C, stirring rate = 1300 rpm.

Table 2					
Results at 3.4 atm	each	C ₂ H ₄ ,	H ₂ ,	and	CO. ^a

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	No.	Ligand	Rh (mmol)	P:Rh	Rate (mol/Lh)	% Ethane	T (°C)
	1	PS-Ph-PPh ₂	0.05	6	0.440 ± 0.1	4.393	100
	2	PS-Ph-PPh ₂	0.05	6	0.597	5.439	120 ^b
	3	PS-Ph-PPh ₂	0.05	6	0.481	5.175	140 ^b
	4	$PS-Ph-P(nBu)_2$	0.05	6	0.875 ± 0.2	0.220	100
	5	$PS-Ph-P(nBu)_2$	0.10	6	1.417	0.000	100
	6	PS-Ph-PCy ₂	0.05	6	0.251 ± 0.09	0.002	100
	7	PS-Ph-PCy ₂	0.06	3	0.185	0.687	100
	8	PS-Bz-PPh ₂	0.05	6	0.081	0.081	100
	9	Si-Et-PPh ₂	0.05	6	0.791	0.204	100

^a Total pressure was maintained at 34 atm; solvent = tetraglyme, 100 mL; T = 100 °C; stirring rate = 1300 rpm; reaction time = 2 h.

^b Experiments 2 and 3 were performed sequentially after the experiment at 100 °C.

be required, typically an excess of phosphine was used with the aim of suppression of metal leaching. Only the phosphinated silica catalyst system, Si–Et–PPh₂ exhibited an unstable performance. While the rate of propanal formation appeared to be stable over the period that the Si–Et–PPh₂ catalyst was studied, the rate of the second trial was significantly lower than if that condition had been run initially [8]. Formation of n-propanol was only observed using the Si–Et–PPh₂ system, and then only in trace amounts.

To insure that the system was not under any gas-liquid/liquid-solid mass transfer limitations, the effect of the rhodium pre-catalyst concentration on the rate of propanal formation was measured. The rate of propanal formation was found to be first order in rhodium; doubling the rhodium precursor concentration led to approximately double the observed rate, suggesting gas-liquid resistance is not affecting the rate as shown in Fig. 2.

In addition to varying the rhodium loading in the system, the affect of changing the agitation rate was tested. To do so, the rate of propanal formation was measured at two different agitation speeds as shown in Fig. 3. No change in the rate of propanal formation occurred when the agitation rate was adjusted from 1300 to 1500 rpm. Thus, gasliquid resistance and solid–liquid mass transfer are not affecting the rate. A rate of approximately 1000 rpm was necessary in previous tests for good mixing using the gas-entrainment impeller in-service in the system.

Reduction of the partial pressures of the feed to 0.7 atm each resulted in approximately a 3-fold decrease in the rate of propanal formation, which is in accordance with previous studies. Our results of dilute ethylene hydroformylation with 0.7 atm each of CO, H₂, C₂H₄, and 32 atm of nitrogen are presented in Fig. 4 and Table 3.

For comparison, $(acac)Rh(CO)_2$ run in the same reactor using 2% triphenylphosphine in tetraglyme, at 100 °C, 0.7 atm of each CO, H₂, C₂H₄, with 32 atm of nitrogen, an overall rate of propanal formation of 0.6 mol/Lh after 2 h was obtained, which is approximately three-



Fig. 3. Rate of propanal formation at two different agitation speeds using PS–Ph–PPh₂/Rh with 0.7 atm each CO, H₂, and C₂H₄. Blue diamonds are at 1300 rpm and red triangles are at 1500 rpm.

times the rate using the analogous supported system, PS–Ph–PPh₂/Rh. Approximately twice as much ethane was generated (0.29% using 2% PPh₃vs. 0.7% using PS–Ph–PPh₂) by the corresponding supported analog.

The rate was also examined in propanal solvent using the PS–Ph– PPh₂/Rh system and was found to be ~4 times slower (~0.1 mol/Lh at 3.4 atm each of the feeds).

Ethylene hydrogenation was accounted by quantification of the total ethane accumulated in the headspace of the reactor over the course of the run, Fig. 5. Hydrogenation was only significant for the PS–Ph–PPh₂ ligated system, the only sample where visual evidence of rhodium metal was observed (green solution, and grey material). It would be expected that if there were agglomerated metal in solution that it would be an excellent ethylene hydrogenation catalyst and thus the higher levels of ethane observed when using PS–Ph–PPh₃ is consistent.

It was observed that for the three ligand-modified resins wherein the phosphine was bound to the support through a phenyl linker (PS–Ph–PR₂, where R = Ph, Cy, n-Bu) that the observed rate of propanal formation was directly proportional to the cone angle of the free phosphine analog (PR₃), with the rate of propanal formation increasing with decreasing steric demand. The cone angle (θ) of a monodentate ligand is defined as the apex angle of a cylindrical cone (for phosphines, centered at 2.28 Å from the center of the phosphorous atom), which touches the outermost atoms of the model [9]. In the commonly accepted dissociative mechanism for hydroformylation, the rhodium complex formed with triphenylphosphine generates an active species such as (PPh₃)₃Rh(CO)H. If triphenylphosphine is substituted by a more sterically demanding phosphine, the increased steric hindrance around the rhodium center can inhibit ethylene association and may result in a decreased overall rate (Fig. 6).



Fig. 2. Rate of propanal formation using double the amount of catalyst typical (200 ppm Rh and 0.2% ligand), squares, PS–Ph–PPh₂/Rh with 3.4 atm each CO, H_2 , and C_2H_4 , triangles.



Fig. 4. Formation of propanal with time using rhodium with various supported ligands: 34 atm total, with 0.7 atm of each CO, H_2 , and C_2H_4 . T = 100 °C, stirring rate = 1300 rpm.

No.	Ligand	Ligand (mmol P)	Rh (mmol)	P:Rh	Rate (mol/Lh)	% Ethane
1	PS-Ph-PPh ₂	0.3	0.05	6	0.17 ± 0.04	0.71
2	$PS-Ph-P(nBu)_2$	0.3	0.05	6	0.23 ± 0.1	0.04
3	PS-Ph-PCy ₂	0.3	0.05	6	0.05 ± 0.004	0.00
4	PS-Ph-PCy ₂	0.2	0.06	3	0.05	0.19
5	PS-Bz-PPh ₂	0.3	0.05	6	0.03	0.00
6	PS-Bz-PPh ₂	0.1	0.05	2	0.02	0.03
7	Si-Et-PPh ₂	0.3	0.05	6	0.18	0.08

^a Total pressure was maintained at 34 atm. T = 100 °C, stirring rate = 1300 rpm, reaction time = 2 h, solvent = tetraglyme.

To determine the rhodium loss by leaching from the catalyst during the reaction, after the reaction was complete the liquids and gasses were removed from the reactor by venting and decanting, and then fresh solvent was added and the reaction was repeated using the used catalyst from the previous run. The difference in rate between the two runs was determined. The solvent from the first run was analyzed by atomic absorption spectroscopy to determine the amount of free rhodium present in the liquid phase. Significantly, no free rhodium was detected in the solution after heating (acac)Rh(CO)₂ with PS–Ph–P(n-Bu)₂ prior to initiating hydroformylation. For the PS–Ph–PPh₂ and PS–Ph–P(n-Bu)₂ ligated systems, the two most efficient systems reported in this study, these two values were found to correlate well with each other, see Table 4. Experiments using recycled PS–Bz–PPh₂/Rh and PS–Ph–PCy₂/Rh were not performed



Fig. 5. Mole % of ethane in the headspace of the reactor after the reaction using rhodium on various phosphinated supports.



Fig. 6. Relationship between the rate of propanal formation and the steric demand of the ligand.

Table 4	
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Rate loss	for recycled	catalyst and	rhodium	leaching.
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No.	Ligand	Rate loss (%) ^a	Rh _{soln} (ppm) ^b
1	PS-Ph-PPh ₂	9	9.9
2	$PS-Ph-P(n-Bu)_2$	5	5
3	PS-Ph-PCy ₂	-	< 2
4	PS-Bz-PPh ₂	-	11
5	Si-Et-PPh ₂	78	19
6	Blank ^c	-	< 2

^a Difference in rate before and after discharging reactor contents and reusing the catalyst in a fresh reaction; based on rates at 3.4 atm feed partial pressures.

^b Amount of rhodium in solution after the run by flame A.A.

 $^{\rm c}$ Solvent sample after heating (acac)Rh(CO)_2 with PS–Ph–P(nBu)_2 in tetraglyme prior to reaction.

since they were less active. However, this level of leaching (~5%) is very high for a commercial process for basic chemical synthesis, for which leaching is typically at the ppb level.

4. Conclusions

Rhodium ligated by phosphine-modified resin and silica supports have been investigated for the hydroformylation of ethylene in a dilute gas stream. Rates of propanal formation were determined to be directly proportional to catalyst concentration. While challenges will likely present themselves as one moves from a dilute ethylene stream in inert gas to a more complicated feed stream, these experiments begin to elucidate likely candidates moving forward and can provide some baseline economic analyses. Furthermore, using an array of several phosphine ligands, it was determined that the ligand cone angle has an indirect correlation with aldehyde formation, with a maximum rate of 0.85 mol/L/h. Ethane formation varied significantly from ligand to ligand. The amount of rhodium leaching was determined for most of the systems investigated and ranged from <2 to 11% for catalytic runs for resin supported systems. The level of rhodium leaching correlated well with the loss in rate of propanal formation between repeated experiments using recycled catalysts for the resin based systems, but the loss in rate was much more significant for the silica based system. As mentioned previously, the rates of supported systems are lower than the homogeneous analogues. However, should the metal leaching be reduced allowing for more complete catalyst recyclability, this would provide a cheap, easily recollected catalyst capable of hydroformylation of dilute streams.

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