Catalysis Communications 12 (2011) 1323–1327

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

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

William J. Tenn III, Russell C. Singley, Brandon R. Rodriguez *, Jennifer C. DellaMea

Hydrocarbons R&D, The Dow Chemical Company, 2301 N. Brazosport Blvd., Freeport, TX 77541, United States

ARTICLE INFO

Article history:
Received 23 March 2011
Received in revised form 27 April 2011
Accepted 4 May 2011
Available online 14 May 2011

Keywords:
Hydroformylation
Supported catalysts
Propanol
Propanal
Phosphine
Rhodium

ABSTRACT

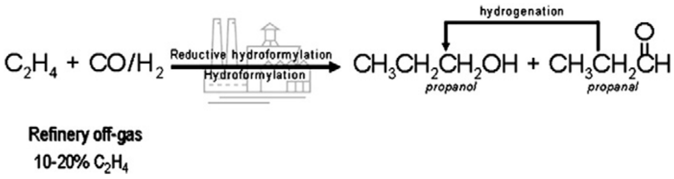
A series of slurried rhodium catalysts on phosphinated resins and silica were tested for the reactive separation of dilute ethylene by hydroformylation to propanal. The amount of rhodium leaching was determined for most of the systems investigated. Leaching ranged from <2 to 11% for catalytic runs for 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.

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 low-value, 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 reductive-hydroformylation 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

---

* Corresponding author. Tel.: +1 979 238 1389; fax: +1 979 238 0028.
E-mail address: barodriguez@dow.com (B.R. Rodriguez).

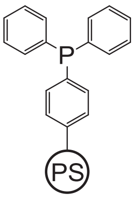
1566-7367/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2011.05.001

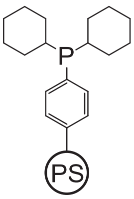
application, [3] and in particular, their application in flow reactors, is the leaching of the active material from the support. Thus, an important point to be determined is the amount of catalyst that is leached from the support under reaction conditions.

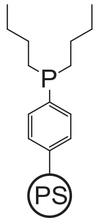
The type of phosphinated supports used in this investigation are lightly cross-linked, macroporous, phosphine-functionalized poly(styrene-co-divinylbenzene), Merrifield-type resins, and a phosphinated silica gel. These resins are insoluble, but able to swell significantly in many organic solvent media. 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].

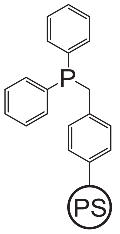
2. Experimental

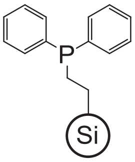
All of the phosphinated resins and silica utilized in this study were purchased from commercial sources: triphenylphosphine, polymer-bound (Aldrich), dicyclohexylphenylphosphine polymer-bound (Aldrich), di(n-butyl)phenylphosphine, polymer-bound (EMD Chemicals), benzyldiphenylphosphine, polymer-bound (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 cm^3, 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) (~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 glove-box, 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

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].

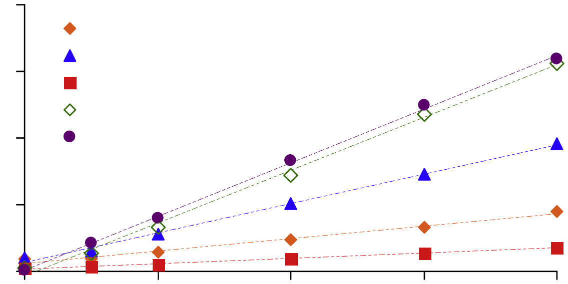


Fig. 1. Formation of propanal with time using rhodium with supported ligands: 34 atm of feed, with 3.4 atm of each CO, H$_2$, and C$_2$H$_4$. T = 100 °C, stirring rate = 1300 rpm.