



Polymer supported rhodium carbonyl complex catalyzed carbonylation of glycerol for the synthesis of carboxylic acids



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ABSTRACT

A new polymer anchored Rh(I) complex has been synthesized and characterized. The catalytic performance of the complex has been tested for the carbonylation of glycerol under carbon monoxide atmosphere to give butyric and isobutyric acids. The effects of temperature, CO pressure, reaction time and the catalyst amount are reported. This catalyst showed excellent activity and recyclability being easily recovered by filtration and reused more than five times without appreciable loss of its initial activity.

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1. Introduction

Transition-metal-catalyzed carbonylation reactions represents an important segment of the industrial processes that are currently used for large-volume synthesis of many industrially important compounds such as acetic acid, carbamates, ureas, heterocycles, esters and anhydrides [1–10].

Transition metal catalyzed glycerol carbonylation is an important process for the synthesis of industrially important chemicals. Glycerol can be converted into several important chemicals including acrolein by acid-catalysis [11], propylene glycol and 1,3-propanediol by hydrogenolysis and glyceric acid by oxidation [12–16]. A number of these chemicals are important intermediates of the petrochemical value chain or can become important platform chemicals for future routes to products of value. Among the more challenging conversions, the work of Deckwer and coworkers [17] who defunctionalized glycerol to 1,3-propanediol with the help of bacteria, *Clostridium butyricum* is worth mentioning. Vogel and coworkers [18] reported about catalytic dehydration of glycerol to acrolein in subspace and supercritical water. The

conversion of aqueous glycerol with a platinum catalyst to syngas under mild reaction conditions is another possibility for the potential industrial use of glycerol [19,20]. Butyric and iso-butyric acids are industrially important chemicals for manufacturing many valuable materials, such as plastics, lacquers, emulsifiers, disinfectants, pharmaceuticals, and esters [21,22]. Commercially available butyric and iso butyric acids are mostly produced by the oxidation of butyraldehyde and isobutyraldehyde, respectively [23].

Rhodium catalyzed glycerol carbonylation and catalytic conversion of glycerol to mono carboxylic acids such as butyric and iso-butyric acids is still rare. The first rhodium catalyzed carbonylation of glycerol were reported by Nakamura [24]. A rhodium complex $[\{\text{RhCl}(\text{CO})_2\}_2]$ was used in combination with HI as the co-catalyst at 180 °C and 35 bar CO pressure and glycerol was converted after 80 min to a mixture of 45 mol% butyric (BA) and 30 mol% isobutyric acid (IBA). The only other report in the literature on the carbonylation of glycerol is a recent high-throughput study by Schunk and co-workers, who used $[\{\text{RhCl}(\text{CO})_2\}_2]$ and CH_3I as the catalyst system and observed the formation of unsaturated acids such as vinyl acetic acid (VA) and crotonic acid (CA), in addition to the saturated acids BA and IBA [25].

Reported homogeneous rhodium catalyzed glycerol carbonylation suffer from several disadvantages [25,26]. Homogeneous

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rhodium catalysts may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse [27,28].

The development of novel, heterogeneous and recyclable catalyst for the carbonylation of glycerol is of much interest and it is also desirable to develop an efficient one-pot methodology for the production of butyric and iso-butyric acids from renewable resources due to increasing environmental concerns and the nature of limited fossil resources.

Thus we have synthesized polystyrene supported rhodium catalyst which is highly stable at high temperature. Herein we report the synthesis and characterization of a polymer anchored rhodium catalyst and illustrate its application for the carbonylation of glycerol using HI as a promoter.

2. Experimental

2.1. Materials

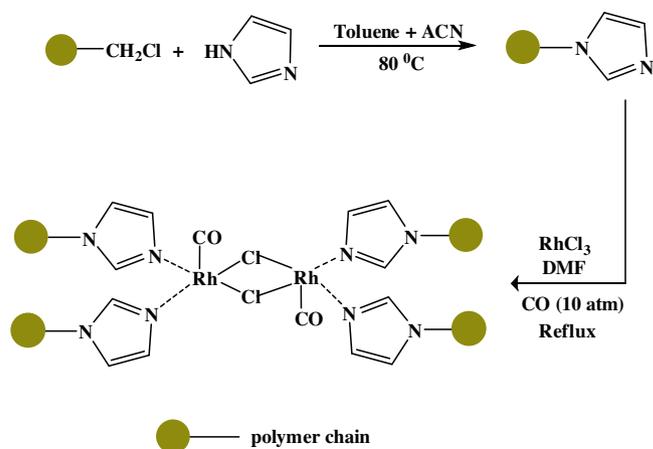
Analytical grade reagents and freshly distilled solvents were used throughout. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures. 5.5% crosslinked chloromethylated polystyrene and rhodium tri chloride were purchased from Aldrich Chemical Company; U.S.A. The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Perkin Elmer FT-IR 783 spectrophotometer using KBr pellets. UV–vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Rhodium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). Conversion was determined by GC.

2.2. Synthesis of metal complex

Chloromethylated polystyrene (3 g) was stirred with a 1:1 mixture of acetonitrile and toluene for 30 min. Then imidazole (1.2 g) was added to the above mixture of the polymer, and it was heated for 24 h at 80 °C. The white polymer-anchored ligand was filtered out, washed thoroughly with methanol and dried under vacuum. A 50 mL high-pressure reactor was charged with 0.026 g of RhCl_3 in DMF (10 mL) and 0.5 g of polymer anchored imidazole was added and then reactor was then purged with CO for about 5 min and then pressurized with CO gas (30 bar) at 100 °C for 24 h. A pale green colored complex was formed. It was filtered, washed first with ethanol and then with methanol (Scheme 1).

2.3. General procedure of glycerol carbonylation

A 50 mL high-pressure reactor was charged with AcOH (6.7 mL), glycerol (27 mmol), H_2O (1.5 mL), HI (57 wt%, 13 mmol) and polymer anchored rhodium catalyst (25 μmol) were taken into reactor. The reactor was then purged with CO for about 5 min and then pressurized with CO gas (30 bar). The carbonylation reactions were carried out at 180 °C for 5 h. The products were collected and analyzed by GC and NMR.



Scheme 1. Synthesis of the polymer anchored Rh(I) catalyst.

Table 1

Chemical composition of polymer anchored ligand and rhodium catalyst.

Compound	Color	C%	H%	Cl %	N%	Metal%
PS-IMD	White	76.32	6.36	2.15	9.39	–
PS-IMD-Rh	Green	68.62	5.61	3.60	14.71	5.61

3. Results and discussion

3.1. Characterization of the PS-IMD-Rh catalyst

Due to insolubilities of the polymer anchored rhodium catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM, TGA, IR and UV–vis spectroscopic data. Table 1 provides the data of elemental analysis of polymer anchored ligand (PS-IMD) and the polymer anchored rhodium catalyst (PS-IMD-Rh). Rhodium content in the catalyst determined by AAS suggests 5.61 wt% Rh in the catalyst.

The attachment of metal onto the support was confirmed by comparison of the FT-IR spectra (Fig. 1) of the polymer before and after loading with metal. The IR spectrum of pure chloromethylated polystyrene has an absorption band at 1261 cm^{-1} due to the C–Cl group, which was weak in the ligand and in the catalyst. IR spectra show a stretching vibration for $-\text{CH}_2$ at 2918 cm^{-1} for the polymer bound ligand and its complex. The stretching vibration of C=N bond appeared at 1613 cm^{-1} for the polymer anchored imidazole ligand which is shifted to 1618 cm^{-1} in the metal complex, indicating the coordination of azomethine nitrogen to the metal. Another band at 1319 cm^{-1} (in ligand) for C–N stretching is shifted to lower region in the metal complex. A new intense peak at around 1984–2080 cm^{-1} due to the CO is observed in the metal complex confirming the metal carbonyl coordination [29].

The electronic spectrum (Fig. 2) of the polymer anchored metal complex was recorded in diffuse reflectance spectrum mode as $\text{MgCO}_3/\text{BaSO}_4$ disks. The polymer anchored rhodium(I) complex is in the +1 oxidation state. The electronic spectra of the rhodium complex showed bands in the region 620–230 nm. The bands around 600–620 nm range have been assigned to the spin allowed d–d transition of five coordinated rhodium(I) complex [30]. The other high intensity bands around 309–370 nm have been assigned to charge transfer transitions (MLCT) arising from the excitation of electrons from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligands. The bands below 300 nm were characterized by intra-ligand charge transfer [30].

Field emission-scanning electron micrographs of single bead of polymer anchored ligand (PS-IMD) and its complex PS-IMD-Rh

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