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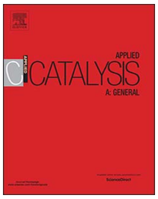

Highly efficient porous organic copolymer supported Rh catalysts for heterogeneous hydroformylation of butenes

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ABSTRACT

Porous organic copolymer (denoted as CPOL-BP&P) was afforded through the copolymerization of vinyl biphephos and *tris*(4-vinylphenyl)phosphine monomers under solvothermal conditions, and followed with impregnation method provided a highly efficient Rh/CPOL-BP&P catalyst with high activity (TOF = 11,200 h^{-1}) and regioselectivity (the ratio of linear to branched aldehydes, l:b = 62.2) for heterogeneous hydroformylation of 1-butene. High regioselectivity was also obtained in the hydroformylation of butene mixture (2-butene: l:b = 55.8, isomeric mixture of butenes: l:b = 56.0). The Rh/CPOL-BP&P catalysts were thoroughly characterized by means of nitrogen sorption isotherms, *in situ* FT-IR, XPS, solid-state ^{31}P MAS NMR, HAADF-STEM, SEM and TEM. The formation of unique coordination bonds with Rh species in the polymer skeleton was determined. Heterogeneous hydroformylation of butenes was effectively realized due to a synergetic effect between PPh_3 moiety and biphephos moiety.

1. Introduction

Olefin hydroformylation is a very prominent catalytic approach to aldehydes and alcohols in chemical industry [1–3]. As a 100% atom-economic reaction, nowadays, the production capacity is beyond 12 million tons annually [4,5]. On account of the wide availability of linear aldehydes and alcohols in production of detergents, surfactants and plasticizers, which is attributed to the better physical performance than branch analogues, the linear aldehydes and alcohols become preferred in industry community. Therefore, besides activity, stability and chemoselectivity of the catalysts, the regioselectivity expressed by the linear/branched ratio is also a key parameter to evaluate the reaction effect [6]. With regard to industrial hydroformylation, it is very attractive to selectively produce the linear butyraldehyde whose global consumption occupies more than 50% of all aldehydes by weight [7]. Linear butyraldehyde is a raw material to produce the standard plasticizer *bis*(2-ethylhexyl) phthalate (DEHP) which is mainly applied in the manufacture of polyvinyl chloride (PVC). However, DEHP has suffered from the potential harm of leakage which leads to pollution and toxicity. To overcome this inherent shortcoming, a much cheaper and more easily available butene mixture has been chosen as a new starting material for new plasticizers, with lower risk of leakage and less toxicity [8]. Nevertheless, the regioselectivity issue remains to be a big problem when butene mixture is used as the substrate of hydroformylation reaction (Scheme 1).

When it comes to the catalysts, the ligand-modified Rh catalysts have been successfully employed in industrial hydroformylation, which provided good catalytic activity and selectivity [9]. However, the separation and recovery as well as recycling of conventional homogeneous catalysts have not been satisfactorily resolved [10]. Many research efforts have been devoted to combining the advantage of catalyst recovery obtained with heterogeneous systems and the much more desirable activity and selectivity associated with homogeneous catalysts [11]. The attractive approaches can be mainly divided into two categories, *viz.* biphasic catalysis and immobilization [10,12]. As for biphasic catalysis, aqueous biphasic [13], fluorous biphasic [14] and the use of ionic liquids [[14],15] and supercritical fluids [16] have been explored to resolve the separation problems. However, these approaches have the shortcoming that some of the reaction media must be removed from the bulk before catalyst separation process, otherwise, the loss of catalyst would be increased. The supports for the immobilization method could be soluble or insoluble in various solvents [17]. Although the separation problem could be easily circumvented, the traditional heterogenisation technologies often cause a dramatic

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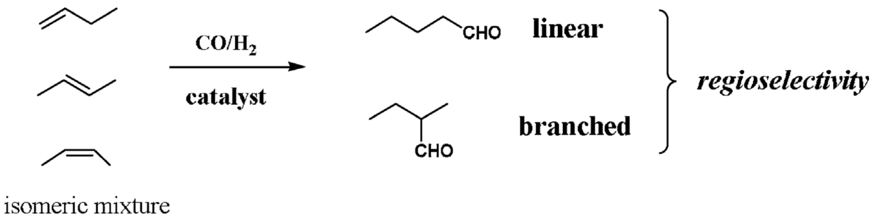

Scheme 1. Hydroformylation of isomeric mixture of butenes to linear and branched pentanals.

drop of catalytic activity and selectivity due to the limitation of mass transfer and the lower concentration of organic ligands around the metal centre [11].

Recently, porous organic polymers (POPs) has emerged as a powerful alternative support material in heterogeneous catalysis and drawn great attention of scientists owing to their excellent properties such as hierarchical porosity, high surface area, large pore volume, low skeleton density and the capability to tune compositions and properties at molecular level [11,18–20]. The POL-PPh_3 and CPOL-BP&P polymer have been synthesized in our laboratory [21,22], and CPOL-BP&P supported Rh catalysts displayed excellent activity and selectivity in the hydroformylation of propene and higher olefins. However, the role of two different types of P species in the Rh/CPOL-BP&P catalysts in hydroformylation reaction is ambiguous. Hence, much more works are required to study how the PPh_3 and biphephos moieties influence the catalytic performance.

Herein, the heterogeneous porous organic copolymer supported Rh catalyst has been extended to the hydroformylation of C4 alkenes. At the same time, the most attractive C4 feedstock like raffinate II contained 1-butene (40%), 2-butene (30%), and saturated C4 (30%) are extremely worthy to be studied. Therefore, in addition to 1-butene as a main research substrate, the hydroformylation of a mixture of 1-butene and 2-butene has also been investigated in this work. Moreover, in order to explore the role of two different types of P species in the framework of Rh/CPOL-BP&P, as a control catalyst, a similar analogue of Rh/CPOL-BP&Ph was obtained by the copolymerization of vinyl biphephos and tri(4-vinylphenyl)benzene. It was found that both of biphephos ligands with the acquired π-acceptor properties and the adequate available PPh_3 ligands in Rh/CPOL-BP&P catalyst, cooperatively contributed to the outstanding activity and regioselectivity of Rh/CPOL-BP&P catalysts in the hydroformylation of 1-butene. The characterizations of the *in situ* FT-IR, Nitrogen sorption isotherms, XPS, solid-state ^{31}P MAS NMR, HAADF-STEM, SEM, TEM techniques also provided very beneficial evidences to help us understand the synergetic effect between the vinyl-PPh_3 and vinyl-biphephos moieties.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone under argon. Azobisisobutyronitrile (AIBN, AR) was purchased and used without further purification. 1-butene (> 99.9%), 2-butene (*trans* and *cis*-2-butene, 1:1), their mixture (1-butene: 60%, *trans*-2-butene: 20% and *cis*-2-butene: 20%), Syngas (H_2/CO = 1:1, > 99.9%) were provided by Zhonghao Guangming Chemical Industry Corporation. $Rh(acac)(CO)_2$ was obtained from Aladdin Company. The 1,3,5-tri(4-vinylphenyl)benzene was synthesized according to published procedures [23]. *Tris*(4-vinylphenyl)phosphine and vinyl-functionalized biphephos ligands were synthesized according to our methods reported previously [18,24]. The monomers of A–C for polymerization are listed (Scheme 2).

2.2. Methods

2.2.1. Preparations of the catalysts

POL-PPh_3, CPOL-BP&P (Scheme 3) and polymers with different mass ratio of biphephos/PPh_3 (CPOL-0.5BP&10P, CPOL-2BP&10P and CPOL-3BP&10P) were synthesized according to literatures [21,22].

2.2.1.1. Preparation of CPOL-BP&Ph. As a typical run, in a glove box, in a THF (10 mL) solution of 1,3,5-tri(4-vinylphenyl)benzene (1.0 g) and vinyl biphephos (0.1 g), AIBN (25 mg) was added. After being stirred for 10 min at room temperature, the mixture was transferred into an autoclave and maintained at 100 °C in a muffle furnace for the solvothermal polymerization process without stirring for 24 h. After the reaction, a grey polymer was dried for 5 h under vacuum at 65 °C and obtained in almost quantitative yield.

2.2.1.2. Preparation of POL-PhPh_3. As a typical run, in a glove box, in a THF (10 mL) solution of 1,3,5-tri(4-vinylphenyl)benzene (1.0 g), AIBN (25 mg) was added. After being stirred for 10 min at room temperature, the mixture was transferred into an autoclave and maintained at 100 °C in a muffle furnace for the solvothermal polymerization process without stirring for 24 h. After the reaction, the title grey polymer was dried for 5 h under vacuum at 65 °C and obtained in almost quantitative yield.

2.2.1.3. Preparation of 0.125 wt% Rh/POPs. As a typical run, in a THF (20 mL) solution of $Rh(acac)(CO)_2$ (3.1 mg), 1.0 g of CPOL-BP&P was added. After stirring for 24 h under argon at room temperature, the resulting product was filtered, washed several times with excess of THF and dried for 5 h at 65 °C under vacuum. The white solid denoted as Rh/CPOL-BP&P was obtained. Same procedure was followed to synthesize other Rh/CPOL-BP&Ph, Rh/POL-PPh_3 and Rh/POL-PhPh_3 catalysts by impregnation of metal precursor $Rh(acac)(CO)_2$ onto the polymers in THF solvent. The exact Rh contents of the polymer catalysts were measured with inductively coupled plasma optical emission spectrometry (ICP-OES) method.

2.2.2. Hydroformylation of C4 olefins

The continuous flow fixed-bed reactor applied for C4 alkenes hydroformylation is depicted in Scheme 4. The C4 olefins were taken out of a cylinder with a liquid-phase tube and fed into the reactor via a pump. Furthermore, a precision electronic balance was used for measuring the mass changes of substrates. Syngas flows (CO/H_2 = 1:1) was adjusted by a mass-flow controllers before a filter was filled and after a one-way valve was equipped. After the back pressure, which was equipped to maintain the desired reaction pressure and outlet gas flow, the gas stream was online monitoring by an Agilent 3000A Micro gas chromatograph. The liquid phase products were obtained by a condenser and absorption tank and analyzed by an Agilent 6890A gas chromatography equipped with a FID.

2.2.3. Characterizations of catalysts

Nitrogen sorption isotherms were carried out with Quantachrome Autosorb-1 system at the temperature of liquid nitrogen. The samples were outgassed for 12 h at 120 °C prior to the measurements. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. The pore size distribution