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Enhancement of hydroformylation performance *via* increasing the phosphine ligand concentration in porous organic polymer catalysts

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ABSTRACT

The development of highly efficient and stable Rh-based heterogeneous catalysts for hydroformylation of heavier olefins is of both high fundamental and industrial interest, yet there still remains a tremendous challenge. In this contribution, a series of porous organic polymers bearing various concentrations of triphenylphosphine (PPh_3) moieties, a ligand of industrial choice, was synthesized and their performance in the hydroformylation of styrene, 1-ocetene, and 2-ocetene were investigated after metalation with Rh species. Both concentration of PPh_3 moieties and pore structure of the polymers were found to influence the catalytic performance. The polymer-based rhodium catalysts demonstrated an increase in catalytic activity, selectivity, and stability when the concentration of PPh_3 was increased and the porous polymer constructed by the functional PPh_3 monomer (POL-PPh_3) was found to be optimal among all the solid ligands tested. We anticipate these results will form the basis for a constructive perspective in the development of high performance heterogeneous Rh-based hydroformylation catalysts. Moreover, our observations indicate the considerable potential of porous organic polymers (POPs) as a new generation of heterogeneous catalytic platforms that may prove effective when targeting important but highly challenging reactions.

1. Introduction

Hydroformylation constitutes one of the most powerful and valuable tools for C−C bond formation and allows for the straightforward conversion of inexpensive chemical feedstocks, such as olefins and syngas, into broadly applicable aldehydes, which serve as major building blocks and versatile intermediates for numerous chemical products [1–5]. It has been the subject of extensive research in academia and industry because of increasing interest in developing an efficient transformation of the heavier olefins [6,7]. In view of the various metal catalysts involved in such transformations, rhodium-based catalysts typically work under mild conditions and afford a much higher selectivity in favor of the greater added value aldehyde product [8–12]. Nonetheless, all commercial plants running these reactions use cobalt catalysts, which require severe conditions and give poorer selectivities, because costs incurred in the recovery and recycling of the expensive Rh-based catalyst make this process prohibitive [13,14]. Solving the product separation problem in an effective and economically robust way while retaining the performance of the catalysts would represent a major step forward in hydroformylation.

Several elegant strategies have been proposed for the hydroformylation of heavier olefins with the aim of recycling the Rh catalysts. Examples include the use of fluorous biphase system catalysis in a non-aqueous environment and temperature-controlled multicomponent solvent system [15–17]. While reaction rate and selectivity is excellent, leaching of the catalytic components into the product phase remains a major drawback. To circumvent the concerns of catalytic components leaching and immiscibility of heavier olefins in the aqueous biphasic Rh-catalyzed hydroformylation, Pickering emulsions systems were developed [18,19]. Despite these progresses made in the homogeneous catalysis, anchoring active species to solid materials holds great promise for an essential and practical approach to facilitate separation of the catalyst from the product and thereby to improve the overall efficiency of the hydroformylation process. Materials such as inorganic oxides (often silica) or polymers have been extensively investigated [20–29]. For instance, Davis and coworkers reported the hydroformylation of higher olefins by supported aqueous-phase catalysts (SAPCs) formed by subtly adsorbing a thin aqueous layer containing a water-soluble catalyst onto a hydrophilic porous material [30]. The increased interfacial area and the solid nature of the support lead to the greatly improved activity together with the facilitated catalyst recovery. However, the SAPCs are often very sensitive to the content of water, and thereby its long-term stability is not adequate. It is known that covalent anchoring can be robust enough to withstand

the rather harsh conditions of the catalytic reaction, but these catalysts unfortunately suffer either from inferior selectivity and activity, or low recyclability, and hence, is currently not commercially feasible [31,32]. Therefore, there is still a need to develop high efficient and recyclable Rh-based hydroformylation catalysts.

Porous organic polymers (POPs) containing well-defined metal catalysts are emerging as amenable materials which combine the merits of homogeneous and traditional heterogeneous catalysts. Similar to molecular catalysts, POPs inherit the excellent chemical tunability afforded by the wide range of functionalized organic building blocks employed in their synthesis. Like solid catalyst supports, POPs have excellent thermal and chemical stability, thus enabling them to tolerate the harsh reaction conditions (*e.g.* high temperature and high pressure) usually employed in heterogeneous catalytic transformations [33–43]. Recently, we have reported the synthesis, characterization, and catalytic efficiency of a porous organic polymer constructed by PPh_3 moieties (POL-PPh_3), featuring high surface area and very high density of phosphine species with excellent spatial continuity. After metalation with Rh species, the resultant catalysts exhibit comparable catalytic performance in relation to the homogenous counterparts as well as excellent recyclability in hydroformylation of olefins, thus possessing great potential for practical applications [44,45]. By taking advantage of the tunability of polymer synthesis, in this work, a series of porous organic polymers bearing various amounts of PPh_3 moieties was synthesized from copolymerization of tris(4-vinylphenyl)phosphine with divinylbenzene. We then systematically investigated the influence of metal concentration and ligand excess on activity and selectivity as well as the stability of the catalysts. In view of these results, we propose an explanation for the leaching and low activity phenomena previously observed with heterogeneous hydroformylation catalysts synthesized by anchoring phosphine ligands on the conventional solid materials. Moreover, the influence of the porous structure on the catalytic performance was investigated using nonporous polymerized functionalized triphenylphosphine as a control sample.

2. Materials and methods

2.1. Materials

Solvents were purified according to standard laboratory methods. THF was distilled over $LiAlH_4$, and 4-bromostyrene was distilled over CaH_2. Other commercially available reagents were purchased in high purity and used without further purification.

2.2. Catalyst preparation

2.2.1. Synthesis of POL-PPh_3

As a typical run, 1.0 g of tris(4-vinylphenyl)phosphine was dissolved in 10 mL of tetrahydrofuran (THF), followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave (20 mL) and maintained at 100 °C for 24 h. The title polymer was obtained in nearly quantitative yield after being washed with CH_2Cl_2 and dried under vacuum. Tris(4-vinylphenyl)phosphine was synthesized from the treatment of PCl_3 (33 mmol in 30 mL of THF) and (4-vinylphenyl)magnesium bromide solution (100 mmol). The reaction was quenched by the addition of 50 mL of saturated NH_4Cl aqueous solution. The organic phase was extracted with excess ether, which was dried over $MgSO_4$. After filtering and purifying by silica gel chromatography (5% EtOAc/petroleum ether), tris(4-vinylphenyl) phosphine was obtained as white solid. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ 7.48 (d, 6H, $J = 7.6$ Hz), 7.22 (t, 6H, $J = 7.6$ Hz), 6.69–6.76 (m, 3H), 5.85 (d, 2H, $J = 18$ Hz), 5.30 (d, 2H, $J = 10.8$ Hz) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 115.76, 126.79, 126.86, 133.76, 133.95, 136.41, 136.55, 138.08 ppm ^{31}P NMR (162 MHz): δ −7.94 (s, 1P) ppm.

2.2.2. Synthesis of nonporous polymerized PPh_3 (poly-PPh_3)

As a typical run, 1.0 g of tris(4-vinylphenyl)phosphine was dissolved in 10 mL of ethyl acetate, followed by the addition of 25 mg of AIBN. The mixture was transferred into an autoclave (20 mL) and maintained at 100 °C for 24 h. The title polymer was obtained in 68% yield after being washed with CH_2Cl_2 and dried under vacuum. Note: The solvent used in the polymerization media plays a critical role in the formation of the nanoporous structure of the resultant polymer. To obtain a highly porous polymer, the formation of sufficiently extensive interconnected networks is necessary. It is well documented that in the initial stages of polymerization, the growth of polymer chains is favored by adding a new monomer unit, followed by the formation of crosslinks by mutual interconnection of polymer chains. As a consequence, the polymer synthesized using a porogenic solvent like THF, which is known to be one of the best compatible solvents with styrenic polymers, could facilitate the growth of polymer chains into an extended configuration, thereby facilitating the formation of a highly crosslinked polymer with a nanoporous structure. In contrast, using ethyl acetate, which is incompatible with styrenic polymers, the polymer chains are forced to aggregate into tighter polymer coils even at a very low polymerization degree and phase separation occurs, thus impeding the formation of an extensive network and resulting in the nonporous structure.

Synthesis of porous polymers with different PPh_3 moiety concentrations (PDVB-$m$$PPh_3$, m stands for the mole amount of PPh_3 moieties in per gram of polymer). A series of porous polymers with different PPh_3 moiety concentrations was prepared from copolymerization of divinylbenzene and tris(4-vinylphenyl)phosphine at different ratios. As a typical run, 0.068 g of tris(4-vinylphenyl)phosphine and 0.932 g of divinylbenzene were dissolved in 10 mL of THF, followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave and maintained at 100 °C for 24 h. After evaporation of the solvent, a white solid product with the PPh_3 moiety concentration in the polymer at 0.2 mmol/g was obtained in nearly quantitative yield, which was denoted as PDVB-*0.2*PPh_3.

2.2.3. Synthesis of xRh/POL-PPh_3 (x stands for the Rh weight percent in the polymer)

As a typical run, 0.1 g of POL-PPh_3 was swollen in 40 mL of toluene, followed by the addition of $Rh(CO)_2$(acac) (5.2 mg) or RhH(CO)$(PPh_3)_3$. After being stirred at room temperature under N_2 atmosphere for 24 h, the mixture was filtered, washed with excess toluene, and dried at 50 °C under vacuum. The light yellow solid obtained was denoted as 2.0 wt% Rh/POL-PPh_3.

2.2.4. Synthesis of 2.0 wt% Rh/poly-PPh_3

As a typical run, 0.1 g of poly-PPh_3 was stirred in 40 mL of toluene, followed by the addition of 5.2 mg of $Rh(CO)_2$(acac). After being stirred at room temperature under N_2 atmosphere for 24 h, the mixture was filtered, washed with excess toluene, and dried at 50 °C under vacuum. The light yellow solid obtained was denoted as 2.0 wt% Rh/poly-PPh_3.

2.2.5. Synthesis of 2.0 wt% Rh/PDVB-mPPh_3

As a typical run, 0.1 g of PDVB-*0.2*PPh_3 was swollen in 40 mL of toluene, followed by the addition of 5.2 mg of $Rh(CO)_2$(acac). After being stirred at room temperature under N_2 atmosphere for 24 h, the mixture was filtered, washed with excess toluene, and dried at 50 °C under vacuum. The light yellow solid obtained was denoted as 2.0 wt% Rh/PDVB-*0.2*PPh_3.

2.3. Catalytic tests

2.3.1. Hydroformylation of styrene

Rh catalyst (2.5 μmol), styrene (0.52 g), and toluene (10.0 g) were added to a stainless steel autoclave (100 mL) with a magnetic stir bar. After the autoclave was sealed and purged with syngas ($CO/H_2 = 1:1$)