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Highly active polymer–alumina dually supported palladium catalysts for the carbonylation of allyl halides under atmospheric pressure

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Polymer–alumina dually supported palladium catalysts (PVP–Pd/Al_2O_3, PVP = poly(N-vinyl-2-pyrrolidone); PPPO–Pd/Al_2O_3, PPPO = phosphinated poly(phenylene oxide)) were used to catalyze the carbonylation of allyl halides to form butenoic acid under the mild conditions of 40°C and 0.1 MPa. These catalysts exhibit high activity and stability towards the carbonylation of allyl halides. The maximum turnovers (mol CO/mol Pd) of PPPO–Pd/Al_2O_3 are up to 8.2×10^5 and 4.6×10^5 for the carbonylation of allyl bromide and allyl chloride respectively in an aqueous NaOH/benzene medium.

Keywords: alumina; supported palladium catalysts; carbonylation; allyl halides

1. Introduction

Carbonylation of allyl halides catalyzed by transition metal complexes is an attractive method for the synthesis of butenoic acid. There have been a number of articles on using nickel or palladium complexes to catalyze this reaction [1–5]. Palladium catalysts are preferable to nickel catalysts with respect to catalytic efficiency, but a high carbon monoxide pressure is usually required for the palladium-catalyzed carbonylation. Nevertheless, Kiji et al. recently reported that the carbonylation of allyl chloride proceeded virtually with $PdCl_2L_2$ (L = $Ph_2P(m\text{-}C_6H_4SO_3Na)$ or PPh_3) and Na_2PdCl_4 in a two-phase system under atmospheric pressure [6,7].

The incorporation of transition metal compounds into the soluble polymers, such as polyvinylpyrrolidone (PVP), can afford homogeneous polymeric catalysts, which usually exhibit high activity in some catalytic reactions. This kind of catalysts have been considerabally studied in the recent two decades [8,9]. Recently, we found for the first time that the palladium catalysts supported on the soluble polymers PVP and modified poly(phenylene oxide) were very active for the carbonylation of allyl halides in an aqueous NaOH/benzene medium under atmospheric pressure [10,11]. However, although the separation of the soluble polymeric catalysts from the product can be performed by using ultrafiltration, precipitation and extraction techniques, it is more inconvenient and expensive than the separation of the insoluble polymeric catalysts from the reaction mixture used in practice. In order to avoid this disadvantage an alternative approach was followed in this study. Palladium dichloride was first supported on the soluble polymers such as polyvinylpyrrolidone (PVP) or phosphinated poly(phenylene oxide) (PPPO), and the resulting soluble polymer-anchored palladium catalysts (PVP–Pd, PPPO–Pd) were further supported on alumina. Thus the polymer–alumina dually supported palladium catalysts, PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3, were obtained. These catalysts were used to catalyze the carbonylation of allyl halides in an aqueous NaOH/benzene medium under atmospheric pressure. The results show that those catalysts are not only easy to be recovered but also very active and efficient for the carbonylation of allyl halides.

2. Experimental

2.1. Materials and analysis

$PdCl_2$ was purchased from Johnson Matthey Co. Poly(phenylene oxide) (PPO, $M_w = 14000$) and (γ-Al_2O_3 (100 mesh, surface area 180 m^2/g) were supplied by the Shanghai Institute of Synthesis Resin and Fushong Petroleum Chemical Factory respectively. Polyvinylpyrrolidone (PVP, $K = 29$–33) was a product of BASF. γ-Al_2O_3 was heated in an oven at 500°C for 5 h and then cooled to room temperature under anhydrous conditions before use. $LiPPh_2$ was prepared according to the literature method [12]. All organic substrates and solvents were analytical reagents and were dried by 4 Å molecular sieves before use. Carbon monoxide with a purity of 98% was commercially available and directly used.

The bromine and phosphorus contents were determined by elemental analysis. The palladium content was analyzed by ICP/ECHELLE, Leeman Labs Co.

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2.2. Preparation of catalysts

Preparation of PPPO supported palladium catalyst: The modified PPO which had been substituted with bromine at aromatic carbon (bromine content 40 wt%) was prepared according to ref. [13]. Ten grams of this polymer were reacted with $LiPPh_2$ (8.6 g) in 80 ml THF under nitrogen atmosphere and stirred for 2 h at room temperature. The resulting phosphinated PPO (PPPO, phosphorus content 0.20 wt%) was precipitated in 95% ethanol and dried in vacuum. A mixture of PPPO (4.0 g) and 12 ml water solution of $PdCl_2$ (0.12 g) was stirred in 60 ml ethanol–benzene (3 : 1) mixture at refluxing temperature for 5 h. After filtration, washing and drying in vacuum, the PPPO supported palladium catalyst (PPPO–Pd, palladium content 1.53 wt%) was obtained.

Preparation of PVP supported palladium catalyst: A mixture of 1.4 g PVP and 11 ml aqueous solution of $PdCl_2$ (0.11 g) was stirred in 180 ml ethanol for 24 h at room temperature. The water-containing ethanol solution of PVP supported palladium catalyst (PVP–Pd, palladium content 3.5 μmol/ml) was obtained and directly used to catalyze the carbonylation of allyl halides.

Preparation of the polymer–alumina dually supported palladium catalysts: A 30 ml chloroform solution of PPPO–Pd (2.0 g) prepared as mentioned above was injected through a self-sealing silicon rubber cap into a flask containing 4.0 g Al_2O_3 in vacuum, and stirred for 10 h at room temperature. After filtration, washing and drying in vacuum, the dually supported palladium catalyst PPPO–Pd/Al_2O_3 (Pd content 0.09 wt%) was obtained. By the same way, the dually supported palladium catalyst PVP–Pd/Al_2O_3 (Pd content 0.20 wt%) was prepared by adding 20 ml ethanol solution of PVP–Pd prepared as mentioned above into a flask containing 3.0 g Al_2O_3.

2.3. Catalytic carbonylation of allyl halides

A typical carbonylation procedure was conducted as followed: catalyst, sodium hydroxide and phase transfer agent (if it was used) were added into a 50 ml three-necked, jacketed bottle closed with self-sealing silicon rubber cap, connected to the vacuum, carbon monoxide lines and constant pressure gas burette. The temperature of the circulating water passing through the jacket was maintained by a thermostat. Agitation was provided by means of magnetic stirring. After the atmosphere in the bottle was replaced with carbon monoxide, solvent was added. The mixture was stirred vigorously and allyl halide was then added. After the reaction was stopped, the aqueous layer of the reaction solution was acidified with hydrochloric acid and the resulting product was analyzed by HPLC (Shimadzu, type LC-5A).

3. Results and discussion

The activities of PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 in the carbonylation of allyl halides were investigated in an aqueous NaOH/benzene medium under the mild conditions of 40°C and 0.1 MPa and compared with those of PVP–Pd and PPPO–Pd. As the data show in table 1, PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 are very active for the carbonylation of allyl halides, but their activities are lower than those of their corresponding soluble ones, PVP–Pd and PPPO–Pd, respectively. The lower activity of PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 may be due to the diffusion limitation of the reactants to the catalytically active centre. It was also found that, when the substrate was completely converted and another batch of substrate was added, the activity of all the catalysts was nearly the same as that in the first cycle. This indirectly indicates that the palladium active species are firmly retained by the polymer or polymer/alumina support. If there were some palladium active species leaching from the support, the activity of the catalyst should be decreased since the non-supported active palladium species very easily aggregate to the inactive metallic one.

Phase transfer catalysis is an important technique in organic chemistry and has considerably been applied to metal-catalyzed reactions [14]. Since in the above carbonylation, NaOH is dissolved in water and allyl halide is

Table 1
Carbonylation of allyl halides catalyzed by the supported palladium catalysts [a]

Catalyst (Pd, μmol)	Substrate	Maximum TOF [b] (mol CO/(mol Pd min))	Turnover [c] (mol CO/mol Pd)
PVP–Pd	allyl bromide	150.0	5950 (110)
(1.88)	allyl chloride	28.5	6150 (510)
PVP–Pd/Al_2O_3	allyl bromide	56.0	5700 (280)
(1.88)	allyl chloride	17.6	6140 (620)
PPPO–Pd	allyl bromide	51.4	6250 (280)
(1.68)	allyl chloride	19.0	6510 (910)
PPPO–Pd/Al_2O_3	allyl bromide	40.0	5800 (280)
(1.68)	allyl chloride	10.6	6540 (1360)

[a] Reaction conditions: substrate 1 ml, solvent: water + benzene 20 ml (1 : 1), NaOH 1 g, 40°C, 0.1 MPa.

[b] Turnover frequency defined as moles of CO uptake per mole Pd per min.

[c] Turnover corresponds to the reaction time in parentheses (in min).

mostly dissolved in benzene, and the polymer–alumina dually supported catalyst is hydrophilic, the use of phase transfer agent (PTA) should be in favour for the reaction. However, the experimental results show that the catalytic activities of PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 in the presence of PTA, e.g., $(CH_3)_4NCl$, $(n\text{-}Bu)_4NCl$ and $C_{12}H_{25}SO_3Na$, are lower than those without PTA. Especially, the maximum TOF of PPPO–Pd/Al_2O_3 in the presence of $(n\text{-}Bu)_4NCl$ is only 6.2 mol CO/mol Pd min. It seems that in this case, the reaction product itself, sodium butenate, is already good enough as a phase transfer agent. This is just contrary to the effect of additional PTA on the reaction rate with PPPO–Pd and PVP–Pd catalysts in the carbonylation of allyl halides in an aqueous NaOH/benzene medium [11].

It should be mentioned that both 3-butenoic acid and 2-butenioc acid were formed using all of the above catalytic systems for the carbonylation of allyl chloride and allyl bromide. According to the HPLC analysis of the product, the amount of 2-butenoic acid formed over PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 is nearly the same as that with PVP–Pd and PPPO–Pd respectively. The ratios of 3-butenoic acid to 2-butenoic acid for PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 are 4.0 and 1.7 respectively. As we have previously reported [11], the isomerization reaction forming 2-butenoic acid may be related with the property of the catalyst used in addition to the concentration of the base.

Table 2 gives the efficiency of the four catalysts in the carbonylation of allyl halides. It can be seen that, by prolonging the reaction time, the maximum turnovers (mol CO/mol Pd) of PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 are higher than those of PVP–Pd and PPPO–Pd. Especially, the maximum turnover of PPPO–Pd/Al_2O_3 can be up to 8.2×10^5 and 4.6×10^5 for the carbonylation of allyl bromide and allyl chloride respectively. To our knowledge, this catalyst is the most efficient one among all of the reported catalysts for the carbonylation of organic halides. Fig. 1 shows that after the carbonylation has proceeded for 50 h, PVP–Pd/Al_2O_3 is still active but PVP–Pd already loses its activity. In addition, when another batch of substrate was added in the reaction mixture at this time, the CO uptake was not observed. This indicates that the PVP–Pd catalyst becomes irreversibly deactivated. We have characterized the dually supported catalyst PVP–Pd/Al_2O_3 in detail [15,16], and found that in this catalyst PVP is coordinated to the Lewis acid center Al^{3+} of Al_2O_3 and the palladium is coordinated with the N and O atoms offered from PVP. Therefore, we suppose that the higher stability of PVP–Pd/Al_2O_3 and PPPO–Pd/Al_2O_3 may be related to the interaction between PVP (or PPPO) and Al_2O_3, which may favour the prevention of the aggregation of the active palladium species. Accordingly, the present polymer–alumina dually supported palladium catalysts are not only easy to be recovered but also very efficient for the carbonylation of allyl halides, which are the two essential requirements for any industrial process.

4. Conclusions

The present polymer–alumina dually supported palladium catalysts are very effective catalysts for the carbonylation of allyl halides under the mild conditions of 40°C and 0.1 MPa. They are not only very active but also easy to be recovered. The interaction between polymer (PVP or PPPO) and alumina in the polymer–alumina dually supported palladium catalysts may favour the prevention of the aggregation of the active palladium species so that the catalysts, PVP–Pd/Al_2O_3 and PPPO–

Table 2
Stability of the supported palladium catalysts in the carbonylation of allyl halides [a]

Catalyst (Pd, μ)	Substrate (mmol)	Maximum TO [b] (mol CO/mol Pd)
PVP–Pd (0.42)	allyl bromide (46.0)	7.7×10^4 (50)
PVP–Pd/Al_2O_3 (0.21)	allyl bromide (92.0)	2.8×10^5 (90)
PPPO–Pd (0.42)	allyl bromide (46)	4.1×10^5 (45)
PPPO–Pd/Al_2O_3 (0.09)	allyl bromide (92.0)	8.2×10^5 (160)
PPPO–Pd/Al_2O_3 (0.18)	allyl chloride (100.0)	4.6×10^5 (260)

[a] Reaction conditions: substrate/NaOH (mole ratio) = 1 : 4; solvent: water + benzene 80 ml (1 : 1). The others are the same as those in table 1.

[b] Turnover corresponds to the reaction time in parentheses (h), and after the carbonylation has proceeded for that time, the catalysts are no longer active for the carbonylation.

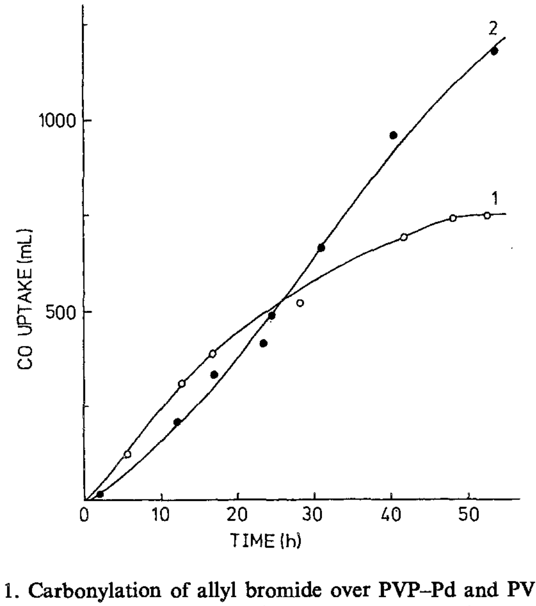

Fig. 1. Carbonylation of allyl bromide over PVP–Pd and PVP–Pd/Al_2O_3. (1) PVP–Pd, (2) PVP–Pd/Al_2O_3. Reaction conditions are the same as those in table 2.

Pd/Al_2O_3 are very stable during the carbonylation of allyl halides.

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