Polymer-supported palladium–nickel bimetallic catalyst for the regioselective hydroesterification of styrene

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Abstract

Polymer-supported $PVP–PdCl_2–4NiCl_2–PPh_3$ bimetallic system [PVP = poly(*N*-vinyl-2-pyrrolidone)] is an efficient catalyst for the hydroesterification of styrene with CO and methanol. This catalyst provides a very highly regiospecific hydroesterification to the branched acid ester with complete conversion at 80°C and CO pressure of 2.1 MPa. The high activity and selectivity of the catalyst are achieved by the synergic effect of Pd–Ni bimetallic system and the effect of polymer protection. In the presence of excess Hg or a base (NaOAc), all of the catalysts lose their activity entirely. The effect of mercury poison and the transmission electron micrograph measurement for the catalyst show that the catalytically active species are composed of particles of nanometric size in which Pd species are in the zero valent state. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In general, a homogeneous catalyst offers the potential advantage of high selectivity while a heterogeneous system is often less selective but more active [1]. Recently, homogeneous or polymer-supported bimetallic catalysts have showed enhanced activity, better selectivity in selective hydrogenations [2–5], hydrodehalogenations [6,7], carbonylations [8–10] and hydroformylations [11,12]. The enhanced activity and better selectivity are due to the cooperative or successive participation of two metals. It appears that a high efficiency in a homogeneous catalyst (or catalyst precursor) may be achieved by the cooperation of several components just like that in heterogeneous catalysis.

The transition metal complex catalyzed hydroesterification of olefins with CO and alcohol is of great interest for the synthesis of industrially valuable carboxylic esters such as linear fatty acid esters and branched 2-arylpropionic acid esters. The latter compounds include the most important classes of nonsteroidal antiinflammatory drugs such as ibuprofen and naproxen. The most investigated catalysts for hydroesterification are cobalt and palladium compounds. Recently, palladium complexes have received great attention because they are effective at relatively low pressures and selective for the
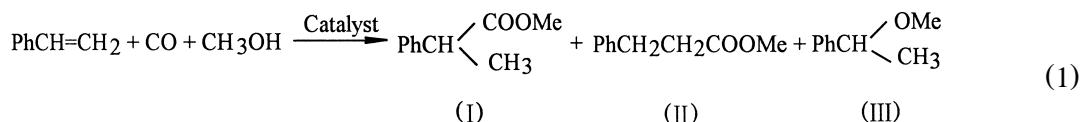
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generation of branched acid esters [13–24]. Example catalysts include the homogeneous bimetallic systems of Pd–Li [13,14], Pd–Sn,Ge [15,16] and Pd–Cu [17] developed by Alper et al. [25]. However, no report has been described in the literature using a polymer-supported bimetallic catalyst for this particular reaction. Here we wish to report an efficient polymer-supported $PVP-Pd-Ni-PPh_3$ bimetallic catalyst obtained in situ from $PVP-PdCl_2$, $NiCl_2$ and PPh_3 for the hydroesterification of styrene under rather mild reaction conditions.

2. Experimental

$PdCl_2$ was purchased from Johnson Matthey (Pd content 59.89%). Poly(N-vinyl-2-pyrrolidone) (PVP, $K = 27-33$) was a product of BASF. Carbon monoxide with a purity of 99.9% was commercially available and directly used. Solvents and metal chlorides were analytical grade and were used as received except styrene which was freshly distilled before use. $PVP-PdCl_2/MeOH$ ($N/Pd = 20$) containing a small amount of hydrochloric acid (0.2 mol HCl/l) was prepared via a literature procedure [4]. A 45 ml stainless steel autoclave was used as a batch reactor. In a typical run, 0.8 ml of $PVP-PdCl_2/MeOH$ (5×10^{-2} mol Pd/l), 0.16 mmol of MX_n ($MX_n = NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$), 10.6 mg (40 mmol) of PPh_3, 1 mmol of styrene and 10 ml of benzene were charged into the reactor. The gas phase in the reactor was flushed with carbon monoxide three times and pressurized to the desired pressure. The reactor was then placed in an oil bath maintained at constant temperature. The reaction mixture was magnetically stirred at ca. 300 rpm. After the reaction, the reactor was cooled to room temperature and slowly depressurized. The reaction mixture was analyzed by a GC (2 m DEGS column). The identification of GC peaks was accomplished with both authentic samples and employing GC-MS analysis. Transmission electron micrography was carried out using a JEM-1200 EX analytical electron microscope operated at 100 keV.

3. Results and discussion

$$PhCH{=}CH_2 + CO + CH_3OH \xrightarrow{\text{Catalyst}} PhCH{<}^{COOMe}_{CH_3} + PhCH_2CH_2COOMe + PhCH{<}^{OMe}_{CH_3} \quad (1)$$
$$(I) \qquad\qquad (II) \qquad\qquad (III)$$

The hydroesterification of styrene with CO and methanol is shown in Eq. (1). Two major products are formed. One is the branched methyl 2-phenylpropionate (I). The other is its linear isomer, methyl

Table 1
Hydroesterification of styrene using different catalysts[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			I	II	III
1	$PdCl_2$	0	–	–	–
2	$PdCl_2-5PPh_3$	42	82	18	0
3	$NiCl_2-5PPh_3$	0	–	–	–
4	$PdCl_2-4NiCl_2-5PPh_3$	76	95	4	1
5	$PVP-PdCl_2-4NiCl_2-5PPh_3$	99	95	4	1

[a]Reaction conditions: benzene 10 ml, MeOH 0.8 ml, Pd 0.04 mmol, $NiCl_2$ 0.16 mmol, styrene 1 mmol, $p(CO) = 2.1$ MPa (gauge pressure), 80°C, 10 h. PVP = poly(N-vinyl-2-pyrrolidone), I = $PhCH(CH_3)COOMe$, II = $PhCH_2CH_2COOMe$, III = $PhCH(CH_3)OMe$.

Table 2
Effect of PPh_3 in the $PVP-PdCl_2-4NiCl_2-nPPh_3$ catalyst system on the hydroesterification of styrene[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			I	II	III
6	$PVP-PdCl_2-4NiCl_2-0.5PPh_3$	1	97	3	0
7	$PVP-PdCl_2-4NiCl_2-PPh_3$	100	99	1	0
8	$PVP-PdCl_2-4NiCl_2-3PPh_3$	100	96	4	0
9	$PVP-PdCl_2-4NiCl_2-8PPh_3$	79	91	8	1
10	$PVP-PdCl_2-4NiCl_2-PPh_3$[b]	100	99	1	0
11	$PVP-PdCl_2-4NiCl_2-PPh_3$[c]	97	99	1	0

[a] Reaction conditions are the same as in Table 1.
[b] Styrene, 2 mmol; 20 h.
[c] Styrene, 4 mmol; 36 h.

3-phenylpropionate (II). The formation of ether (III) and other by-products is negligible. The results of styrene hydroesterifications catalyzed by various catalysts at 80°C and CO pressure of 2.1 MPa in benzene are summarized in Table 1. The conversion and the selectivity were calculated from GC chromatograms. Entry 1 shows that the $PdCl_2$ itself exhibits no catalytic activity under these reaction conditions. When excess PPh_3 is added to $PdCl_2$ (5:1), the conversion and the selectivity to the branched ester are 42% and 82%, respectively, in 10 h (entry 2). The $PdCl_2-4NiCl_2-5PPh_3$ catalyst gives 76% conversion and 95% selectivity, while $NiCl_2$, by itself, shows no catalytic activity (entries 3 and 4) under these conditions. These results indicate that $NiCl_2$ can markedly promote the catalytic behavior of $PdCl_2$. Apparently, the Pd–Ni bimetallic catalyst exhibits a remarkable synergic effect. In order to increase the activity further, we employed a polymer-supported $PVP-PdCl_2-4NiCl_2-5PPh_3$ catalyst. The conversion increases to 99% and the selectivity remains at 95% under the same reaction conditions (entry 5).

In order to determine the influence of PPh_3 on the reaction, the effect of the PPh_3/Pd mole ratio in the $PVP-PdCl_2-4NiCl_2-nPPh_3$ catalytic system was examined (Table 2). Entries 5–11 show that the best result with 100% conversion and 99% selectivity is obtained when the PPh_3/Pd mole ratio is 1. The effect of the $NiCl_2/Pd$ mole ratio in the $PVP-PdCl_2-nNiCl_2-PPh_3$ catalytic system is shown in Fig. 1. As the $NiCl_2/Pd$ mole ratio is raised from 1 to 6, the changes in conversion and selectivity are small. The best catalyst is $PVP-PdCl_2-4NiCl_2-PPh_3$. However, when $FeCl_3$ and $CoCl_2$ are used
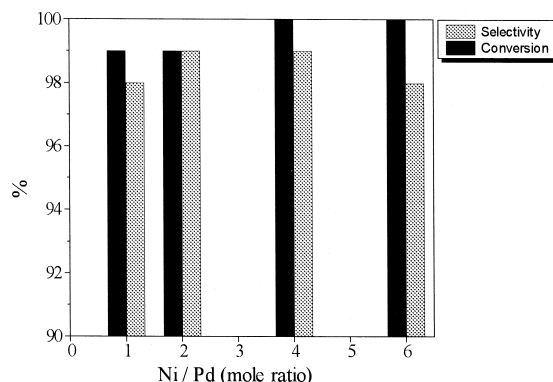

Fig. 1. Effect of $NiCl_2$ in the $PVP-PdCl_2-nNiCl_2-PPh_3$ system on the conversion of styrene and the selectivity to methyl 2-phenylpropionate. Reaction conditions are the same as in Table 1.

Table 3
Hydroesterification of styrene using other catalysts[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			I	II	III
12	$PVP-PdCl_2-4CoCl_2-PPh_3$	∼ 0	–	–	–
13	$PVP-PdCl_2-4CoCl_2-5PPh_3$	19	80	20	0
14	$PVP-PdCl_2-4FeCl_3-PPh_3$	∼ 0	–	–	–
15	$PVP-PdCl_2-4FeCl_3-5PPh_3$	62	82	18	0
16	$PVP-PdCl_2-4CuCl_2-PPh_3$	∼ 0	–	–	–
17	$PVP-PdCl_2-4CuCl_2-3PPh_3$	84	99	1	0
18	$PVP-PdCl_2-4CuCl_2-5PPh_3$	99	98	2	0
19	$PVP-PdCl_2-4CuCl_2-8PPh_3$	99	96	4	0

[a]Reaction conditions are the same as in Table 1.

instead of $NiCl_2$, the conversion and the selectivity are much lower (compare entries 12–15 in Table 3 and entries 5 and 7 in Tables 1 and 2).

It is noteworthy that when $CuCl_2$ is used as the second metal component, only at high PPh_3/Pd mole ratio does the polymer-supported $PVP-PdCl_2-CuCl_2-PPh_3$ catalytic system give high conversions. Otherwise, this system exhibits low or even no activity. The selectivity does not change appreciably with the amount of PPh_3 added (entries 17–19). The conversion and selectivity induced by the $PVP-PdCl_2-4CuCl_2-5PPh_3$ catalyst are 99% and 98%, respectively, at 80°C and CO at a pressure of 2.1 MPa in 10 h. This rate is slightly slower with slightly lower selectivity than that observed for the $PVP-PdCl_2-4NiCl_2-PPh_3$ catalyst.

The effect of temperature on the reaction is rather peculiar (Table 4). The $PVP-PdCl_2-4NiCl_2-PPh_3$ catalyst exhibits very low and no activity at 40°C and 20°C, respectively. As the temperature is raised from 60°C to 80°C, both the rate and selectivity increase. However, when the temperature is further raised to 100°C, the conversion and the selectivity decrease. The most suitable reaction temperature is 80°C. A similar effect was also observed for the $PdCl_2-CuCl_2-PPh_3$ catalytic system in the hydroesterification of styrene [26].

It has been reported that mercury can be used as a selective poison for the heterogeneous metallic (colloidal) catalysts, while the homogeneous catalysts (molecular compounds) are unaffected [27–30]. We found that in the presence of excess Hg or a base (NaOAc), all of the catalysts lost their activity entirely. The former suggested that colloidal Pd(0) particles were formed. Transmission electron micrograph (TEM) was taken for the $PVP-PdCl_2-4NiCl_2-PPh_3$ catalyst (Fig. 2). The TEM showed that the particles of nanometric size (3–20 nm) were formed. This result, together with the effect of

Table 4
Effect of temperature on styrene hydroesterification catalyzed by $PVP-PdCl_2-4NiCl_2-PPh_3$[a]

Entry	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)		
				I	II	III
20	20	46	∼ 0	–	–	–
21	40	14	3	–	–	–
22	60	12	63	98	2	0
23	80	10	100	99	1	0
24	100	10	59	95	5	0

[a]Reaction conditions are the same as in Table 1, except that the reaction time and temperature vary.
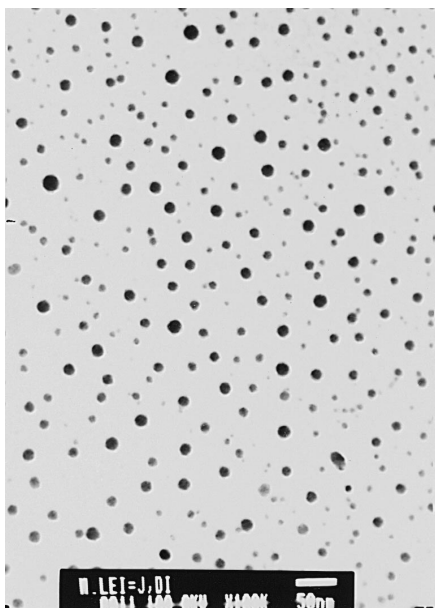
Fig. 2. Transmission electron micrograph of the PVP–PdCl$_2$–4NiCl$_2$–PPh$_3$ catalyst. The sample was taken 4 h after the hydroesterification had been started.

mercury poison on the catalyst, confirms that the catalytically active species are composed of particles of nanometric size in which Pd species are in the zero valent state for the PVP–PdCl$_2$–NiCl$_2$–PPh$_3$ catalytic system. Based on the above results, we suggest that the role of PPh$_3$ here is to stabilize the Pd(0) species as described in literature [21], while the role of PVP seems to protect the Pd(0) nanoparticles from the particle growth and also to serve as a ligand. The role of NiCl$_2$ and the effect of NaOAc are still not fully understood.

4. Conclusions

The PVP–PdCl$_2$–4NiCl$_2$–PPh$_3$ catalyst gives a 100% conversion and 99% selectivity to the branched ester in styrene hydroesterifications at 80°C and a CO pressure of 2.1 MPa in 10 h. A strong synergic effect of PdCl$_2$–NiCl$_2$ and the effect of polymer protection give rise to a remarkable increase in the selectivity and activity for the reaction. The results of the transmission electron micrograph measurement and mercury poisoning of the catalyst indicate that the catalytically active species are composed of particles of nanometric size in which Pd species are in the zero valent state.

Acknowledgements

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