

A remarkable synergic effect of water-soluble bimetallic catalyst in the hydrogenation of aromatic nitrocompounds

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Abstract

Hydrogenation of nitrobenzene can be catalyzed by the water-soluble catalyst $\text{PdCl}_2(\text{TPPTS})_2$ (TPPTS = tris(*m*-sulfonatophenyl)phosphine trisodium salt) under normal pressure at 65°C in H_2O /toluene biphasic solvent system. The water-soluble bimetallic catalyst $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$ exhibits higher catalytic activity and selectivity for the hydrogenation of aromatic nitrocompounds, compared with $\text{PdCl}_2(\text{TPPTS})_2$ or H_2PtCl_6 alone. The transmission electron micrographs demonstrate that the monometallic catalyst is composed of ultrafine palladium particles of almost uniform size while the particles of bimetallic catalyst are more widely distributed in size than those of the monometallic ones. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water-soluble bimetallic catalysts; Synergic effect; Hydrogenation; Aromatic nitrocompounds

1. Introduction

The use of water-soluble transition metal complexes as catalysts for various catalytic reactions in aqueous organic biphasic solvent system has received much attentions in recent years [1]. Hydrogenation of unsaturated aldehydes, ketones or acids catalyzed by water-soluble sulfonated phosphine complexes of rhodium, ruthenium and iridium has been investigated intensively [2–5]. Although many heterogeneous, homogeneous and polymer-supported catalysts are known for the hydrogenation of

aromatic nitrocompounds [6–9], there is no report on the use of water-soluble palladium catalyst for this reaction.

In order to improve the catalytic properties of the monometallic catalyst, much attention has been focused on the bimetallic catalysts [10]. The previous report on homogeneous bimetallic catalysts were usually concerned with the catalytic behaviors of bimetallic clusters [10–14]. Toshima et al. [15–17] stabilized the colloidal dispersions of the palladium–platinum bimetallic catalyst by the soluble polymer. In contrast with the corresponding monometallic catalysts, the bimetallic catalysts show remarkable synergic effect and exhibit very high catalytic activity for the selective hydrogenation of olefins.

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Here we wish to report the use of water-soluble mono- and bimetallic catalyst, $\text{PdCl}_2(\text{TPPTS})_2$ and $\text{PdCl}_2(\text{TPPTS})_2\text{-MX}$, for the hydrogenation of aromatic nitrocompounds in $\text{H}_2\text{O}/\text{toluene}$ biphasic solvent system under normal pressure of hydrogen at 65°C . The results reveal that the catalytic activity of $\text{PdCl}_2(\text{TPPTS})_2$ for the hydrogenation of aromatic compounds can be greatly increased by the addition of a second transition metal component, H_2PtCl_6 .

2. Results and discussion

Table 1 shows that the hydrogenation of nitrobenzene can be catalyzed by the water-soluble catalyst $\text{PdCl}_2(\text{TPPTS})_2$ under normal pressure of hydrogen at 65°C in $\text{H}_2\text{O}/\text{toluene}$ two-phase solvent system. The selectivity for aniline is 100%. In order to increase the catalytic activity of $\text{PdCl}_2(\text{TPPTS})_2$, the catalytic behavior of bimetallic catalyst was investigated by adding a second transition metal compound. It can also be seen from Table 1 that among the transition metal compounds tested, H_2PtCl_6 leads to an acceleration of the reaction rate significantly,

although the catalytic activity of H_2PtCl_6 is rather low when it is used alone. Fig. 1 shows the dependence of the reaction rate on the metal compositions in the bimetallic catalysts. A striking feature of $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$ is that its activity is much higher than the corresponding monometallic catalysts when the palladium content in the bimetallic catalysts varies from 20 to 95 mol%. The synergic effect can also be observed even if the platinum content is only 2 mol%. In the case of the polymer-supported palladium–platinum bimetallic catalyst, only in a limited range of Pd/Pt ratio can the bimetallic catalyst exhibit much higher catalytic activity than the monometallic ones [15–17].

Table 2 summarizes the results of various substituted nitrobenzene catalyzed by $\text{PdCl}_2(\text{TPPTS})_2$ and $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$. In most cases, the synergic effects of the bimetallic catalysts are remarkable. For example, the maximum reaction rate is only 8.1 min^{-1} in the hydrogenation of *o*-nitroaniline catalyzed by $\text{PdCl}_2(\text{TPPTS})_2$ while the use of $0.5\text{PdCl}_2(\text{TPPTS})_2\text{-}0.5\text{H}_2\text{PtCl}_6$ obviously raises the maximum reaction rate to 39.2 min^{-1} . In the hydrogenation of *p*-nitrotoluene, the maximum reac-

Table 1
Catalytic behaviors of $\text{PdCl}_2(\text{TPPTS})_2$ and $\text{PdCl}_2(\text{TPPTS})_2\text{-MX}$ for the hydrogenation of nitrobenzene^a

Catalyst	Reaction rate (min^{-1}) ^b	Reaction time (min)	Aniline yield (%) ^c
$\text{PdCl}_2(\text{TPPTS})_2$	27.8	138	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-NiCl}_2$	20.6	220	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-LaCl}_3$	28.8	211	> 99
$\text{PdCl}_2(\text{TPPTS})_2\text{-FeCl}_3$	18.2	218	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-CoCl}_2$	25.3	218	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-CrCl}_3$	27.9	117	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-CuCl}_2$	0	126	0
$\text{PdCl}_2(\text{TPPTS})_2\text{-RuCl}_3$	22.2	178	100
$\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$	61.8	34	100
H_2PtCl_6	4.1	392	76
$\text{H}_2\text{PtCl}_6\text{-}2\text{TPPTS}$	1.7	120	9
$\text{PdCl}_2(\text{TPPTS})_2^{\text{d}}$	33.6	145	84
$\text{H}_2\text{PtCl}_6^{\text{d}}$	4.8	120	18
$\text{H}_2\text{PtCl}_6\text{-}2\text{TPPTS}^{\text{d}}$	~ 0	110	< 4

^aReaction conditions: 65°C ; 0.1 MPa; nitrobenzene, 5 mmol; catalyst, 0.01 mmol Pd or Pd + M, M/Pd = 1; water, 10 ml; toluene, 10 ml.

^bThe maximum reaction rate, mol H_2/mol (Pd or Pd + M) min, calculated from the amount of dihydrogen uptake.

^cBased on the data of HPLC analysis.

^d0.005 mmol catalyst was used.

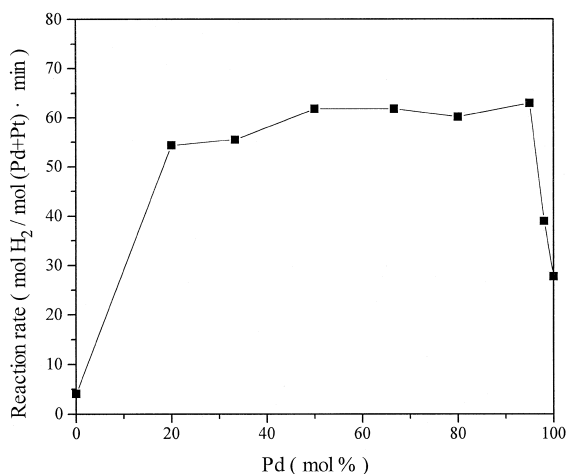


Fig. 1. The dependence of catalytic activity of the $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$ bimetallic catalyst on its metal composition in the hydrogenation of nitrobenzene. Reactions conditions: the same as Table 1.

tion rate is not increased significantly, but only 60 min is required to complete the reaction when $0.95\text{PdCl}_2(\text{TPPTS})_2\text{-}0.05\text{H}_2\text{PtCl}_6$ was used as catalyst while the monometallic catalyst $\text{PdCl}_2(\text{TPPTS})_2$ gives only 96% conversion in 212 min. In this case, the average catalytic activity is increased significantly.

Usually, the hydrogenation of halo-substituted aromatic nitrocompounds is accompanied by the hydrodehalogenation of these compounds. A number of methods, for example, the

addition of phosphoric acid or sulfouret to the catalytic system [18], and the use of polymer-supported palladium–ruthenium bimetallic catalyst [19], have been reported in order to increase the selectivity for halo-substituted aromatic amines. The data in Table 2 also show that using the present catalytic system, both the water-soluble mono- or bimetallic catalysts exhibit high selectivity for the chloroaniline in the hydrogenation of chloronitrobenzene.

Fig. 2 gives the kinetic curves of hydrogenation of *p*-nitrotoluene catalyzed by $\text{PdCl}_2(\text{TPPTS})_2$, H_2PtCl_6 and $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$. These curves show that the catalytic behavior of bimetallic catalyst $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$ is very different from that of the corresponding monometallic catalyst, $\text{PdCl}_2(\text{TPPTS})_2$ and H_2PtCl_6 . In the case of the bimetallic catalyst, the reaction rate is not influenced by the substrate concentration within a wide range while in the case of the monometallic catalyst, the reaction rate strongly depends on substrate concentration. Under constant hydrogen pressure, temperature and catalyst concentration, the reaction rate equation may be expressed as follows:

$$R = kC^n \quad (1)$$

where R , k , C and n are the reaction rate, rate constant, concentration of *p*-nitrotoluene and

Table 2
Hydrogenation of substituted nitrobenzene ($\text{RC}_6\text{H}_4\text{NO}_2$) using $\text{PdCl}_2(\text{TPPTS})_2$ and $\text{PdCl}_2(\text{TPPTS})_2\text{-H}_2\text{PtCl}_6$ catalysts^a

R	Reaction rate (min^{-1}) ^b			Conversion (%) ^c		
	Pd	0.50Pd + 0.50Pt	0.95Pd + 0.05Pt	Pd	0.50Pd + 0.50Pt	0.95Pd + 0.05Pt
H	27.8	61.8	63	100(138)	100(36)	100(71)
4-Me	41.4	88.7	52.6	96(212)	100(28)	100(60)
4-COOMe	33.5	67.4	45.4	100(85)	100(37)	100(60)
4-OMe	22.0	57.9	–	100(93)	100(44)	–
2-NH ₂	8.1	39.2	16.2	84(150)	100(126)	74(128)
4-Cl	15.5	49.0	33.2	98(270)	100(57)	97(155)
3-Cl	19.4	48.4	26.7	95(180)	100(77)	79(131)
2-Cl	14.6	69.4	32.2	70(120)	100(54)	86(120)

^aReaction conditions: 65°C; 0.1 MPa; catalyst, 0.01 mmol (Pd or Pd + Pt); substrate, 5 mmol; water, 10 ml; toluene, 10 ml.

^bThe maximum reaction rate, mol H₂/mol (Pd or Pd + Pt) min, calculated from the amount of dihydrogen uptake.

^cBased on the data of HPLC analysis. The value in the parentheses is the reaction time (in minutes) for the given conversion (%). The selectivity for the corresponding amine is 100% expected for the 2-, 3- or 4-chloronitrobenzene (a small amount of aniline is formed due to the dechlorination; the selectivity for the corresponding chloroaniline is 91–95%)

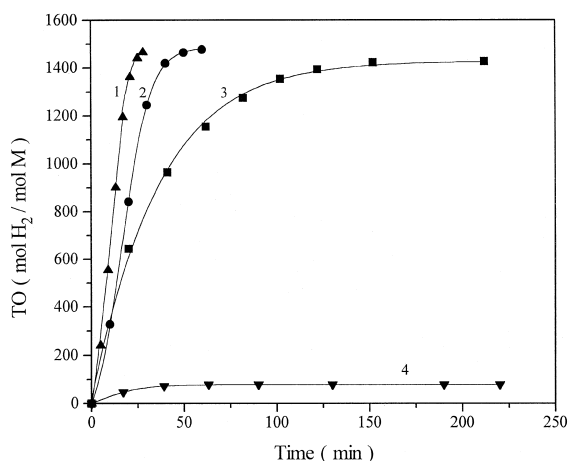


Fig. 2. Hydrogenation of *p*-nitrotoluene catalyzed by mono- and bimetallic catalysts. Reaction conditions: the same as Table 1. 1 = $0.50\text{PdCl}_2(\text{TPPTS})_2-0.50\text{H}_2\text{PtCl}_6$. 2 = $0.95\text{PdCl}_2(\text{TPPTS})_2-0.05\text{H}_2\text{PtCl}_6$. 3 = $\text{PdCl}_2(\text{TPPTS})_2$. 4 = H_2PtCl_6 .

reaction order, respectively. A plot of $\log R$ vs. $\log C$ results in a straight line, the slope of which gives the reaction order (Fig. 3). When $\text{PdCl}_2(\text{TPPTS})_2$ was used as the catalyst, the reaction order is 1.4, while the reaction order is almost zero when bimetallic catalyst was used. Linear relationship was obtained with a plot of $\log k$ vs. $1/T$ which was in agreement with the Arrhenius equation. The activation energies for the hydrogenation of *p*-nitrotoluene catalyzed by $\text{PdCl}_2(\text{TPPTS})_2$ and $0.50\text{PdCl}_2(\text{TPPTS})_2-0.50\text{H}_2\text{PtCl}_6$ are 66.4 and 44.7 kJ/mol, respectively. These results indicate that the active species have been changed greatly from monometallic catalyst to bimetallic catalyst.

For the hydrogenation of nitrobenzene with $\text{PdCl}_2(\text{TPPTS})_2$ catalyst, the addition of excess mercury completely inhibited the reaction, which indicates that the catalyst is reduced by hydrogen possibly forming Pd(0) particles [20]. Under hydrogen atmosphere at 65°C , the colour of $\text{PdCl}_2(\text{TPPTS})_2$ aqueous solution changes from yellow to red rapidly and the solution remains visibly clear. When H_2PtCl_6 was used as catalyst, platinum black was observed immediately. The solution of $\text{PdCl}_2(\text{TPPTS})_2-\text{H}_2\text{PtCl}_6$ reduced by hydrogen looks homogeneous. The

transmission electron micrographs of $\text{PdCl}_2(\text{TPPTS})_2$ and $0.50\text{PdCl}_2(\text{TPPTS})_2-0.50\text{H}_2\text{PtCl}_6$ aqueous solution reduced by hydrogen are shown in Fig. 4. These photographs clearly demonstrate that the monometallic catalyst is composed of ultrafine particles of almost uniform size (average diameter, 1–2 nm) while the particles of bimetallic catalyst is larger (average diameter, 2–3 nm) and more widely distributed in size than those of the monometallic ones. These experimental data reveal that there are some cooperative interactions between palladium and platinum. New catalytic species of bimetallic catalyst may be formed which are different from those of the $\text{PdCl}_2(\text{TPPTS})_2$ catalyst.

Toshima et al. [15–17] found that the particles of PVP-stabilized monometallic colloids of either Pd or Pt were very small, they had a tendency to agglomerate, whereas excellent uniformity of particle size was observed for PVP-stabilized bimetallic colloids. Other reports described the surfactant-stabilized colloids and their use as hydrogenation catalysts in biphasic media [21]. Larpent et al. [22] reported that the Rh colloidal mixtures were used as catalysts for

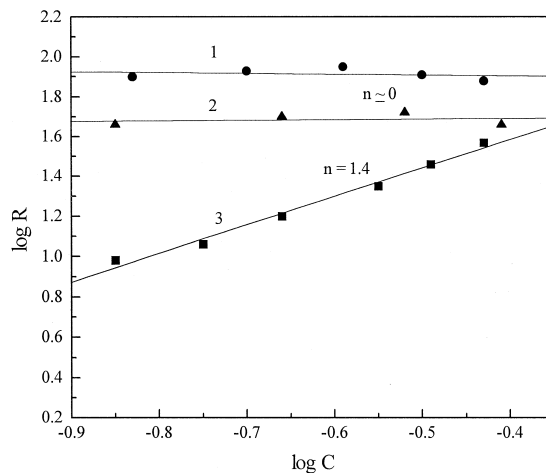


Fig. 3. Comparison of the order of reaction respect to substrate using mono- and bimetallic catalysts. Reaction conditions: the same as Table 1. 1 = $0.50\text{PdCl}_2(\text{TPPTS})_2-0.50\text{H}_2\text{PtCl}_6$. 2 = $0.95\text{PdCl}_2(\text{TPPTS})_2-0.05\text{H}_2\text{PtCl}_6$. 3 = $\text{PdCl}_2(\text{TPPTS})_2$.

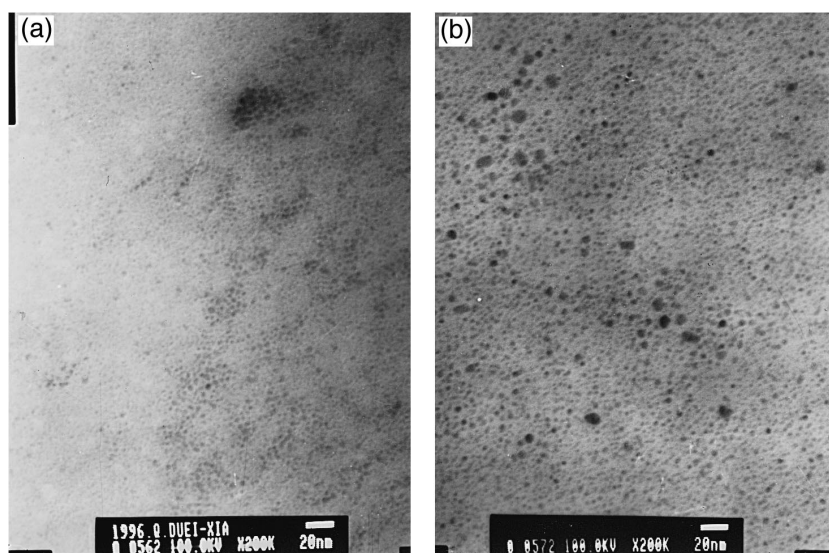


Fig. 4. Transmission of electron micrographs of (a) $\text{PdCl}_2(\text{TPPTS})_2$ (reduced by H_2) and (b) $0.50 \text{PdCl}_2(\text{TPPTS})_2-0.50\text{H}_2\text{PtCl}_6$ (reduced by H_2).

the hydrogenation of liquid alkenes in a biphasic system without solvent. Using water-soluble surfactant $\text{RC}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3$ to stabilize the colloid. The diameter of $[\text{Rh}]$ is around 2 nm. In the present catalytic system, the reduced Pd–Pt species may be stabilized by the coordination of TPPTS.

3. Experimental

3.1. Materials and apparatus

PdCl_2 was purchased from Johnson Matthey (Pd content 59.89%). Toluene and aromatic nitrocompounds were of analytical grade. Water was doubly distilled. TPPTS was synthesized according to the known procedures [23]. Elemental analyses were performed on a Plasma-Spec-I Analyzer. Thermogravimetry (TG) analyses were carried out on a Shimadzu DT-20B Thermal Analyzer under flowing nitrogen. The ^{31}P NMR was recorded on a Varian FT-80A spectrometer using 85% phosphoric acid as internal standard. XPS data was obtained with a VGE SCALAB mk-2 X-ray photoelectron spectrometer. Transmission electron microscopy (TEM) was recorded on a JEM-1200 EX. The

hydrogenation product was analyzed by HPLC (Shimadzu LC-5A, 4.6 mm i.d. \times 25 cm Zorbax ODS column; mobile phase, $\text{MeOH}/\text{H}_2\text{O} = 7/3$ (v/v)).

3.2. Preparation and characterization of $\text{PdCl}_2(\text{TPPTS})_2$

100 mg of PdCl_2 and 2 ml of 2 N HCl were added into a Schlenk flask and the mixture was stirred at 50°C until PdCl_2 was dissolved completely. After the flask was cooled to room temperature and flushed with argon, 0.80 g of TPPTS was added into the flask under stirring. The colour of the solution changed from dark red to bright yellow immediately. After 10 min stirring, 15 ml of absolute ethanol were added, a light yellow powder was precipitated and the mixture was stirred for 30 min. The filtered precipitate was washed three times with 30 ml warm ethanol (95%) and dried in vacuum.

The ^{31}P NMR determination shows that only one peak was observed, the chemical shift was 34.7 ppm, indicating that only the stable *trans*-complex was obtained and there was no sodium salt of tri(sulfonphenyl)-phosphine oxide. Palladium content: found, 7.8% (calculated, 8.0%).

The TG analysis of $\text{PdCl}_2(\text{TPPTS})_2$ revealed that the first stage weight loss was in the temperature region of 60° to 180°C and the second weight loss was observed at 380–465°C. The binding energy of Pd 3d_{5/2} and P 2p was 338.0 and 131.8 eV respectively. It is analogous to that of $\text{PdCl}_2(\text{PPh}_3)_2$ (Pd 3d_{5/2}, 338.1 ± 0.3 eV; P 2p, 131.7 ± 0.1 eV) [24].

3.3. Hydrogenation of aromatic nitrocompounds

A typical procedure was conducted as follows: catalyst and water were added into a 50-ml three-necked, jacketed bottle closed with self-sealing silicon rubber cap, connected to the vacuum, hydrogen lines and constant pressure gas burette. The temperature of the circulating water passing through the jacket was maintained by a thermostat. After the atmosphere was replaced with hydrogen and was stirred vigorously for 5 min, the substrate in toluene solution was added. After the reaction, the product in organic layer was analyzed by HPLC.

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