Hydrogenation of nitroaromatics by polymer-anchored bimetallic palladium–ruthenium and palladium–platinum catalysts under mild conditions

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Abstract

Polymer-anchored monometallic palladium catalyst PVP–PdCl$_2$ (PVP = poly(N-vinyl-2-pyrrolidone)) exhibits very high activity for the hydrogenation of p-chloronitrobenzene (CNB) to aniline (AN) in the presence of base at 65°C and atmospheric pressure. In this case, the substrate is rapidly hydrodechlorinated to nitrobenzene (NB) which is then reduced to AN. Using the polymer-anchored bimetallic palladium–ruthenium catalyst, PVP–PdCl$_2$–RuCl$_3$, and in the presence of 1.0 mol% of sodium acetate, a strong synergic effect gives rise to a remarkable increase of the selectivity for p-chloroaniline (CAN) and the maximum selectivity of CAN is up to 94%. For the hydrogenation of the non-halo-substituted nitroaromatics to the corresponding aromatic amines, the monometallic PVP–PdCl$_2$ catalyst only shows mild or poor activity, but the colloidal polymer-anchored bimetallic palladium–platinum catalyst, PVP–Pd-$1/4$Pt, exhibits very high activity and selectivity.

Keywords: Nitroaromatics hydrogenation; Palladium–ruthenium; Palladium–platinum; Polymers; Aniline

1. Introduction

Hydrogenation of halonitroaromatics to the corresponding haloanilines and non-halo-substituted nitroaromatics to the corresponding aromatic amines is an interesting subject in catalysis and industrial applications. This field has been extensively reviewed [1–4]. The recently preferred route to generate haloanilines from halonitroaromatics is the selective hydrogenation over heterogeneous catalysts, among which monometallic platinum catalysts and bimetallic platinum-based catalysts are particularly attractive [5–10]. Although heterogeneous and heterogenized palladium catalysts can also exhibit considerable activity for the selective reduction of halonitroaromatic compounds at relatively high dihydrogen pressures [5,11,12], platinum seems to be the best catalyst for minimizing dehalogenation combined with a fast rate of reduction of the nitro group. So far, in this respect only a few papers on homogeneous or heterogenized palladium catalysts have been reported because palladium catalysts are usually active for the hydrodehalogenation of the aromatic C–X bonds (X = halogen) [13–18]. The

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catalytic reduction of non-halo-substituted nitroaromatics has also attracted more and more attention due to the serious environmental contamination from the chemical processes [19–22].

In order to improve the catalytic properties of homogeneous catalysts, the strategy of preparing multi- or bimetallic catalysts analogous to that in heterogeneous catalysis gives great potential. Recently, homogeneous and polymer-anchored bimetallic catalysis has attracted much attention, since enhanced reaction rates, selectivities and new types of reactions are expected to arise from the cooperation or successive participation of two or more kinds of metal components [23–26]. The previous reports on polymer-anchored bimetallic catalysts were focused on the polymer-anchored colloidal sols of transition metals prepared in alcohol–water medium. In our recent study, we found that the polymer-anchored monometallic catalyst, PVP–PdCl$_2$, is effective for the hydrodehalogenation of some organic halides [17,18] and prompts the hydrogenation of nitrobenzene in the presence of base [27], and the polymer-anchored bimetallic palladium-based catalysts prepared by means of addition of a second transition metal component to the polymer-anchored monometallic catalyst, e.g., PVP–PdCl$_2$, can result in an obvious synergic effect on the reaction rates and the selectivities for the desired product in the carbonylation of allyl halides under atmospheric pressure [28,29]. It is known that the other type of polymer-anchored bimetallic catalyst, the colloidal sol of PVP-anchored Pd–Pt can effectively catalyze the selective hydrogenation of conjugate dienes to monoalkenes [25]. So, it is reasonably expected that these two types of polymer-anchored bimetallic palladium-based catalysts may be effective for the selective hydrogenation of halonitroaromatics to haloanilines and improve the hydrogenation of non-halo-substituted nitroaromatics to the corresponding amines under mild conditions.

In a short communication [30], we reported a remarkable synergic effect of the polymer-anchored bimetallic palladium–ruthenium catalysts prepared by virtue of our strategy to obtain the polymer-anchored bimetallic catalysts with high activity and/or selectivity in the selective hydrogenation of p-chloronitrobenzene (CNB). In this paper, we wish to present the detailed results on the catalytic behaviors of the polymer-anchored bimetallic palladium–ruthenium catalysts, PVP–PdCl$_2$–RuCl$_3$, in the hydrogenation of p-chloronitrobenzene and the hydrogenation of the non-halo-substituted nitroaromatics catalyzed by the other type of polymer-anchored bimetallic catalyst, e.g., the colloidal PVP–Pd–1/4Pt catalyst.

2. Experimental

2.1. Reactants

High purity dihydrogen ($> 99.9\%$) is used for the catalytic experiments. Absolute methanol is dried through 5A molecular sieves prior to use. PVP (BASF, purity $> 95\%$, $K = 27$–33), CNB (Aldrich, purity $> 99\%$), and other reagents are used without further purification. RuH$_2$(PPh$_3$)$_4$ is synthesized by means of the reported procedure [31].

2.2. Preparation of the polymer-anchored bimetallic catalysts PVP–PdCl$_2$–mMX

To a stirred mixture of 0.037 g of PdCl$_2$ and 0.5 ml of 5 mol · dm^{-3} hydrochloric acid, 100 ml of absolute methanol and 0.560 g of PVP are added successively. After the mixture is stirred at room temperature for 48 h, the polymer-anchored monometallic catalyst, PVP–PdCl$_2$ (2×10^{-3} mmol Pd/ml, N:Pd = 23), is obtained. To the monometallic catalyst, a second transition metal component, MX, e.g. FeCl$_3$ · 6H$_2$O, Co(OAc)$_2$ · 4H$_2$O, NiCl$_2$ · 6H$_2$O, RuCl$_3$ · 3H$_2$O, RhCl$_3$ · 3H$_2$O, or RuH$_2$(PPh$_3$)$_4$, is added and stirred at room temperature for 24 h, then the polymer-anchored bimetallic catalyst (PVP–PdCl$_2$–mMX, 2×10^{-3} mmol Pd/ml, M:Pd = m, N:Pd = 23) is prepared. PVP–MX is prepared by using a similar procedure.

2.3. Preparation of the colloidal polymer-anchored bimetallic catalyst PVP–Pd–1 / 4Pt

The colloidal sol of the polymer-anchored palladium–platinum is prepared by an alcohol-reduction method [25]. An ethanol/water (1/1, v/v) (50 ml) solution containing both Pd^{II} and Pt^{IV} ions is prepared by mixing 20 ml of palladium(II) chloride solution (0.033 mmol in 25 ml of ethanol), 5 ml of hexachloroplatinic(IV) acid solution (0.033 mmol in 25 ml of water), 5 ml of ethanol, and 20 ml of water, and is followed by adding PVP (0.160 g, 1.36 mmol as monomeric unit). Refluxing the solution at ca. 100°C for 3 h under argon gives the stable dark brown homogeneous solution of colloidal polymer-anchored palladium–platinum dispersion (PVP–Pd–1/4Pt, Pt:Pd = 1/4, N:(Pt + Pd) = 41).

2.4. Catalytic tests

Hydrogenation of the nitroaromatics is carried out in a 65-ml three-necked, jacketed bottle closed with a self-sealing silicon rubber septum, connected to the vacuum line and a condenser which is connected to a constant pressure burette of dihydrogen. The temperature of the circulating water passing through the jacket is controlled by a thermostat and the reaction mixture is magnetically stirred at ca. 800 rpm. A typical run is as follows. Definite amount of base is put into the bottle and the atmosphere is replaced by hydrogen. Then, 15 ml of absolute methanol and the catalyst solution (2 ml, 4 × 10^{-3} mmol Pd) arc added successively. After the catalyst is reduced in situ under the reaction conditions for 30 min, the substrate (4 mmol of CNB in 5 ml of warm absolute methanol) is introduced into the reactor through the silicon rubber septum via a syringe. The reaction is monitored by hydrogen uptake and HPLC.

2.5. Analytical methods

Products are analyzed by HPLC (Shimadzu LC-5A, 4.6 mm i.d. × 25 cm Zorbax ODS col-umn; mobile phase, (v/v) MeOH:H_2O = 60:40) and GC (2 m DEGS column). Products are identified by comparison with authentic samples.

3. Results and discussion

Our aim is to investigate the synergic effect of two different types of soluble polymer-anchored bimetallic palladium-based catalysts on the selectivities and/or rates for the hydrogenation of nitroaromatics and verify our strategy to prepare the new type of polymer-anchored bimetallic catalysts, e.g., PVP–$PdCl_2$–mMX (M:Pd = m, MX = the second transition metal component), with high activity and/or selectivity.

3.1. Catalytic hydrogenation of CNB by PVP–$PdCl_2$

3.1.1. Hydrodechlorination and reduction of CNB

It can be seen from Table 1 that PVP–$PdCl_2$ exhibits very high activities in the presence of base both for the hydrodechlorination and reduction of CNB. The hydrogenation usually follows the pathways shown in Fig. 1. In the presence of a base, a rapid hydrodechlorination of the substrate initially generates nitrobenzene (NB) which is then reduced to aniline (AN). In the cases of using Na_2CO_3, NaOAc, or n-Bu_3N
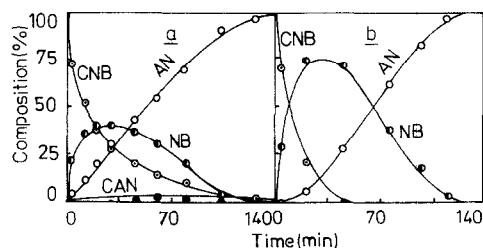

Fig. 1. Hydrogenation of p-chloronitrobenzene (CNB) catalyzed by PVP–$PdCl_2$. The reaction conditions are shown in Table 1. Base/CNB = 1.0: (a) NaOAc; (b) Na_2CO_3. AN = aniline, CAN = p-chloroaniline, NB = nitrobenzene.

Table 1

Hydrodechlorination and reduction of p-chloronitrobenzene (CNB) by PVP–PdCl$_2$ [a]

Base	Base/CNB (molar ratio)	TOF$_{max}$ [b] (min^{-1})	Conversion [c] of CNB (%)	Selectivity (%) [d]		
				AN	CAN	NB
–	–	2.0	1.4 (56)	–	–	–
NaOH	2.0	58.3	100 (102)	97.6	2.2	0
NaOH	1.0	72.6	100 (75)	97.2	0	0
NaOH	0.02	31.8	89.1 (210)	89.5	9.9	0.5
NaOAc	2.0	57.2	100 (160)	99.5	0.4	0
NaOAc	1.0	80.2	100 (140)	97.7	2.2	0
NaOAc	0.02	42.5	90.4 (240)	75.7	21.7	0.2
NaOAc	0.01	25.2	92.5 (290)	76.3	18.5	3.7
Ca$_3$(PO$_4$)$_2$ [e]	0.02	7.9	38.4 (240)	0	81.8	15.5
MgO	0.02	12.0	26.8 (240)	58.2	30.8	10.9
n-Bu$_3$N	1.0	94.4	99.2 (200)	99.2	0.2	0
n-Bu$_3$N	0.02	20.0	95.4 (330)	79.1	14.4	0.1
Pyridine	0.02	4.1	31.0 (240)	36.0	26.2	15.2
Bipyridine	0.02	ca. 0	ca. 0 (240)	–	–	–
EDTA	0.02	ca. 0	ca. 0 (240)	–	–	–

[a] Reaction conditions: 0.1 MPa, 65°C; methanol, 22 ml; 4×10^{-3} mmol Pd; CNB, 4 mmol.
[b] The maximum turnover frequency (TOF, the mol of H$_2$ uptake per mol Pd per min).
[c] The conversion based on the GLC analysis at the time indicated in parentheses (in min).
[d] AN = aniline, CAN = p-chloroaniline, NB = nitrobenzene.
[e] Catalyst, 8×10^{-3} mmol Pd.

as base, the intermediate products in the reaction course are very simple (Fig. 1), but in other cases a small amount of other intermediate products are detected by HPLC.

3.1.2. Effect of bases

The presence of base is essential for the hydrodechlorination of p-chloronitrobenzene (CNB) and p-chloroaniline (CAN) and the re-

Table 2

Hydrodechlorination and reduction of p-chloronitrobenzene (CNB) by PVP–PdCl$_2$–mMX [a]

Catalyst	Base [b] (Base/CNB)	TOF$_{max}$ (min^{-1})	Conversion of CNB (%)	Selectivity (%)		
				AN	CAN	NB
PVP–PdCl$_2$	NaOAc (0.02)	42.5	90.4 (240)	75.7	21.7	0.2
PVP–PdCl$_2$–FeCl$_3$	NaOAc (0.02)	11.2	82.8 (430)	69.8	24.3	1.6
PVP–PdCl$_2$–Co(OAc)$_2$	NaOAc (0.02)	30.5	99.2 (350)	88.0	11.3	0
PVP–PdCl$_2$–NiCl$_2$	NaOAc (0.02)	0	–	–	–	–
PVP–PdCl$_2$–RuCl$_3$	–	1.6	5.5 (137)	10.2	89.8	0
PVP–PdCl$_2$–RuCl$_3$	NaOAc (0.01)	7.7	98.6 (520)	5.5	94.1	0.3
PVP–PdCl$_2$–RuCl$_3$	NaOAc (0.02)	10.1	98.0 (480)	36.6	62.8	0
PVP–RuCl$_3$	NaOAc (0.01)	0	–	–	–	–
PVP–PdCl$_2$–RuH$_2$(PPh$_3$)$_4$	NaOAc (0.01)	4.2	83.5 (650)	32.2	66.5	1.2
PVP–PdCl$_2$–RhCl$_3$	Na2CO$_3$ (0.02)	20.8	99.5 (400)	84.4	15.3	0
PVP–PdCl$_2$–RhCl$_3$	Na$_2$CO$_3$ (0.01)	6.6	88.5 (500)	27.4	70.2	2.2
PVP–Pd–1/4Pt [c]	–	123.0	100 (114)	78.6	21.4	0
PVP–Pd–1/4Pt [c]	NaOAc (1.0)	111.6	100 (60)	91.8	8.2	0
PVP–Pd–1/4Pt [c]	NaOAc (0.01)	149.6	100 (101)	81.5	18.5	0

[a] Reaction conditions: 0.1 MPa, 65°C; 4×10^{-3} mmol Pd (M:Pd = m). CNB, 4 mmol.
[b] The value in parentheses is the mole ratio of a base to CNB.
[c] Catalyst, 4×10^{-3} mmol (Pd + Pt), Pt:Pd = 1/4. Other demonstrations are the same as those in Table 1.

duction of the nitro group of CNB and also important for the hydrogenation of nitrobenzene (NB). In the absence of base, the hydrodechlorination of CNB and CAN and the reduction of the nitro group of CNB are difficult to occur and the hydrogenation of NB only proceeds at a moderate rate (Fig. 2). The amount of base shows great influence on the rate and selectivity for the hydrogenation of CNB. Comparing with the case of using an equimolar ratio of base, decreasing the amount of base leads to a decrease of the hydrogenation rate and some increase of the selectivity for CAN, but the major product is still AN. Excess base also reduces the hydrogenation rate. $Ca_3(PO_4)_2$ dramatically inhibits the hydrodechlorination of the substrate and the reduction of the intermediate product, NB, to AN, but the reaction rate is low (Table 1). Polydentate organic bases, e.g., bipyridine, 8-hydroxyquinoline, and EDTA, etc. nearly deactivate the monometallic catalyst, but monodentate tri-n-butylamine and pyridine prompt the reaction, which is attributed to the strong coordinating ability of the polydentate base ligands that inhibit the formation of the coordinatively unsaturated active palladium centers. The role of a base may be understood as follows: (a) A base prompts the catalyst, $PVP–PdCl_2$, to be reduced in situ to the catalytically active species,
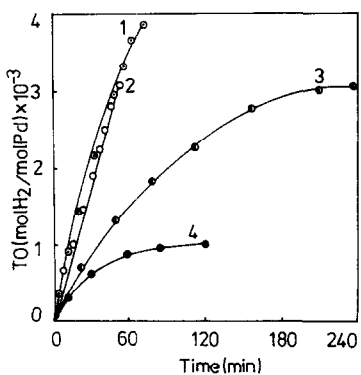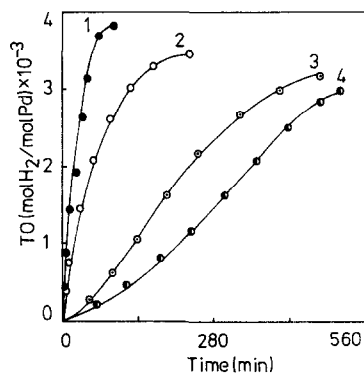

Fig. 3. Effect of base amount on the hydrogenation of p-chloronitrobenzene (CNB) catalyzed by $PVP–PdCl_2–RuCl_3$. The reaction conditions as shown in Tables 1 and 2. Base/CNB: 1, NaOAc (1.0); 2, without $RuCl_3$, NaOAc (0.02); 3, NaOAc (0.02); 4, NaOAc (0.01).

e.g., the coordinatively unsaturated polymer-complex, 'PVP–Pd'. (b) The base neutralizes hydrochloride released from the catalyst and produced in the reaction course, which in turn favors the hydrogenation of CNB. (c) The base intervenes in the catalytic cycle as a ligand to the active palladium center.

Under the same conditions, the homogeneous catalysts, $PdCl_2$ and $Pd(PPh_3)_2Cl_2$, can exhibit considerable initial activities for the hydrogenation of CNB, but they are easily deactivated in the reaction course and the major product is nitrobenzene.

3.2. Catalytic hydrogenation of CNB by PVP–PdCl_2–mMX

3.2.1. Effect of the second transition metal components

Multi- or bimetallic catalysis provides an approach to improve the catalytic properties of a monometallic catalyst. In our study, the soluble polymer-anchored bimetallic catalyst, $PVP–PdCl_2–mMX$, can be conveniently prepared by means of addition of a second transition metal component to the polymer-anchored monometallic catalyst, $PVP–PdCl_2$. The addition of a second transition metal component usually results in a decrease of the hydrogena-

Fig. 2. Hydrogenation of p-chloronitrobenzene (CNB), nitrobenzene (NB) and p-chloroaniline (CAN) catalyzed by $PVP–PdCl_2$ 0.1 MPa, 65°C; methanol, 22 ml; 4×10^{-3} mmol Pd; substrate, 4 mmol. 1 (CNB), 2 (NB), 4 (CAN): NaOH, 4 mmol; 3 (NB): no base.

tion rate of CNB (Table 2 and Fig. 3). In the cases of using 2.0 mol% of base and $FeCl_3$, $Co(OAc)_2$ or $RhCl_3$ as the second component, the selectivities for the desired product, CAN, are not obviously affected in comparison with the case of using the monometallic $PVP–PdCl_2$ catalyst, i.e., the major product is AN. The addition of $RuCl_3$ leads to an obvious increase of the selectivity for CAN (Table 2 and Fig. 4). Beyond our expectation, the addition of $NiCl_2$ makes the catalyst entirely deactivated. If a lower molar ratio (1.0 mol%) of base is used, the addition of $RhCl_3$ or $RuCl_3$ dramatically increases the selectivity of CAN. A base gives similar influences on the hydrogenation of CNB catalyzed by the polymer-anchored bimetallic palladium-based catalysts to that by the polymer-anchored monometallic catalyst, PVP–$PdCl_2$. For the hydrogenation of CNB catalyzed by the colloidal polymer-anchored bimetallic catalyst, PVP–Pd–1/4Pt, the addition of platinum can not obviously influence the selectivity of CAN, which is different from the cases of using the heterogenized platinum catalysts and bimetallic platinum-based catalysts. It is known that heterogenized platinum-based catalysts usually improve the selectivities of haloanilines in the selective hydrogenation of halonitroaromatics [5–12].

3.2.2. PVP–PdCl₂–mRuCl₃ catalysts

A synergic effect of the catalyst, PVP–$PdCl_2$–$m$$RuCl_3$, gives rise to a remarkable increase of the selectivity for CAN (Table 2 and
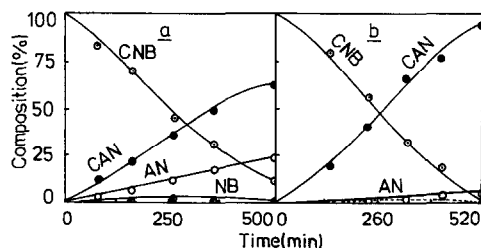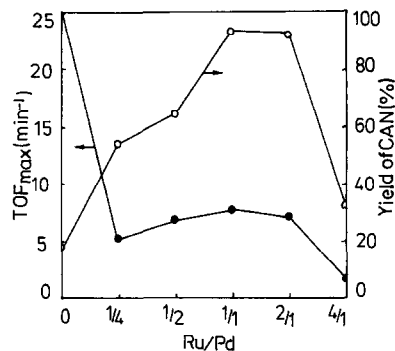

Fig. 5. Plot of the maximum catalyst activities and yields of p-chloroaniline (CAN) vs. Ru/Pd molar ratios in the hydrogenation of CNB by PVP-PdCl₂-mRuCl₃. The reaction conditions as shown in Tables 1 and 2.

Fig. 5). The optimum catalyst efficiency is achieved by the bimetallic catalysts PVP–$PdCl_2$–$RuCl_3$ with a Ru/Pd molar ratio of 1:1 or 2:1 in the presence of 1.0 mol% of sodium acetate (Fig. 5), in which case, the selectivities for CAN are more than 94%. The analyses of the intermediate products indicate that the hydrogenation of CNB follows the pathways shown in Fig. 4. In heterogeneous catalysis, monometallic ruthenium catalysts are highly selective but exhibit poor activity for haloaromatic amine formation [7] and the bimetallic ruthenium-based catalysts can show considerable activity for the selective hydrogenation of CNB [32]. In our case, although PVP–$RuCl_3$ itself is not active both for the hydrodechlorination and reduction of CNB, ruthenium species formed in situ plays an important role in the catalytic cycle. It seems plausible to explain that such ruthenium species acts as a ligand to the catalytically active palladium centers and thus inhibits the oxidative addition of the C–Cl bond of CNB to the active palladium centers. In addition, the interaction of ruthenium species and palladium species may reduce the coordination of dihydrogen to the active palladium species, which dramatically decreases the hydrodechlorination rate of CNB and in turn obviously increases the selectivity of CAN. Using $RuH_2(PPh_3)_4$ as the ruthenium species, the selectivity for CAN is also obviously increased,

Fig. 4. Hydrogenation of p-chloronitrobenzene (CNB) catalyzed by PVP–$PdCl_2$–MX. The reaction conditions are listed in Table 2. (a) MX = $RhCl_3$, Na_2CO_3/CNB = 0.01; (b) MX = $RuCl_3$, NaOAc/CNB = 0.01; dashed line, NB (< 2%).

Table 3
Hydrogenation of non-halo-substituted nitroaromatics by PVP–PdCl$_2$

Substrate	TOF$_{max}$ (min^{-1})	Reaction time (min)	Conversion (%)	Selectivity of the amine (%)
Nitrobenzene	205	30	100	aniline (100)
Nitrobenzene [a]	178	35	100	aniline (100)
Nitrobenzene [b]	23	240	100	aniline (100)
p-Nitrotoluene	45	120	98.0	p-toluidine (100)
m-Dinitrobenzene [c]	267	64	100	m-phenylenediamine (100)
2,4-Dinitrotoluene [c]	87	120	78.2	–
o-Nitroaniline	35	120	69.3	o-phenylenediamine (100)
m-Nitroaniline	41	120	66.4	m-phenylenediamine (100)
p-Nitroaniline	10	120	22.3	p-phenylenediamine (100)
o-Nitrophenol	83	120	100	o-hydroxylaniline (100)
p-Nitrophenol	24	120	67.9	p-hydroxylaniline (100)
o-Nitrobenzoic acid	32	120	80.9	o-aminobenzoic acid (100)
m-Nitrobenzoic acid	82	70	99.5	m-aminobenzoic acid (100)
p-Nitrobenzoic acid	0	64	0	–

Reaction conditions: 0.1 MPa, 65°C; NaOAc, 0.08 mmol; ethanol, 22 ml; 4 × 10^{-3} mmol Pd; substrate, 4 mmol.
[a] NaOAc, 0.04 mmol.
[b] No base.
[c] Substrate, 2 mmol.

but the effect is not so remarkable as that of using RuCl$_3$ as the second transition metal component. This result reveals that the ruthenium species derived from the catalyst, PVP–PdCl$_2$–RuCl$_3$, should be present in the low-valent state under the reductive atmosphere.

3.3. Hydrogenation of non-halo-substituted nitroaromatics by PVP–PdCl$_2$

With respect to the catalyst activity and the selectivity for the desired product, aniline, the presence of 1.0–2.0 mol% of anhydrous sodium acetate seems most favorable for the hydrogenation of nitrobenzene to aniline. Under the same conditions, a base also improves the hydrogenation of the non-halo-substituted nitroaromatics to the corresponding aromatic amines by PVP–PdCl$_2$ (Table 3). As compared with the case of nitrobenzene, the monometallic PVP–PdCl$_2$ catalyst only shows mild or poor activity in the hydrogenation of these substituted nitroaromatics. For example, in the hydrogenation of p-nitroaniline, the maximum turnover frequency

Table 4
Hydrogenation of nitrobenzene (NB) by PVP–Pd-1/4Pt

Catalyst	TOF$_{max}$ (min^{-1})	Reaction time (min)	Conversion (%)	Selectivity of aniline (%)
PVP–Pd	104	45	100	100
PVP–Pt	100	48	100	> 99
PVP–Pd-1/10Pt	125	42	100	100
PVP–Pd–Pt	160	26	100	100
PVP–Pd-1/4Pt	190	20	100	100
PVP–Pd-1/4Pt [a]	114	39	100	100
PVP–Pd-1/4Pt [b]	250	14	100	> 99

Reaction conditions: 0.1 MPa, 65°C; solvent, ethanol (19 ml) + water (3 ml); catalyst, 4 × 10^{-3} mmol (Pd + Pt), Pt:Pd = m; NaOAc, 0.04 mmol; substrate, 4 mmol.
[a] No base.
[b] NaOAc, 4 mmol.

Table 5
Hydrogenation of non-halo-substituted nitroaromatics by PVP–Pd–1/4Pt [a]

Substrate	TOF_{max} (min^{-1})	Reaction time (min)	Conversion (%)	Selectivity of the amine (%)
Nitrobenzene	190	20	100	aniline (100)
p-Nitrotoluene	167	22	100	p-toluidine (100)
m-Dinitrobenzene [b]	156	24	100	m-phenylenediamine (100)
2,4-Dinitrotoluene [b]	108	37	99	2,4-diaminotoluene (100)
o-Nitroaniline	140	35	94.1	o-phenylenediainine (100)
m-Nitroaniline	106	80	98.6	m-phenylenediamine (100)
p-Nitroaniline	65	165	100	p-phenylenediamine (100)
o-Nitrophenol	205	16	99.5	o-hydroxylaniline (100)
p-Nitrophenol	117	80	99.7	p-hydroxylaniline (100)
o-Nitrobenzoic acid	124	50	99.9	o-aminobenzoic acid (100)
m-Nitrobenzoic acid	216	43	99.7	m-aminobenzoic acid (100)
p-Nitrobenzoic acid	64	150	99.5	p-aminobenzoic acid (100)

[a] The reaction conditions are the same as those in Table 4.
[b] Substrate, 2 mmol.

(TOF_{max}) of the monometallic catalyst is 10 min^{-1} and 2 h later the conversion of the substrate is only up to 22.3%. In particular, the catalyst exhibits no activity for the hydrogenation of p-nitrobenzoic acid to p-aminobenzoic acid. It seems that the substituents inhibit the hydrogenation to some extent.

3.4. Hydrogenation of non-halo-substituted nitroaromatics by PVP–PdCl$_2$–1/4Pt

In the stable colloidal sol, the catalyst PVP–PdCl$_2$–1/4Pt is present in the form of the bimetallic clusters. The synergic effect of this catalyst in the selective hydrogenation of 1,3-cyclooctadiene may result from the interaction of Pd and Pt atoms [26]. It is of interest that the presence of base is also favorable for the effective hydrogenation of nitrobenzene to aniline catalyzed by PVP–Pd–1/4Pt (Table 4). It can be seen from Tables 3–5 that the synergic effect of this bimetallic catalyst obviously improves the catalyst activity of the monometallic PVP–PdCl$_2$ or PVP–Pd catalyst for the hydrogenation of the substituted nitroaromatics. Using this bimetallic catalyst and in the presence of a small amount of base, the hydrogenation can be effectively carried out under mild conditions. For the unreactive substrates, e.g., p-nitroaniline and p-nitrobenzoic acid, they can also be easily hydrogenated to the amines. In all the cases, the corresponding aromatic amines are generated in high yields (94–100%).

4. Conclusions

It appears that the approach to prepare the soluble polymer-anchored bimetallic catalysts with high activity and/or selectivity, i.e., PVP–PdCl$_2$–mMX, is practicable. The polymer-anchored bimetallic catalyst, PVP–PdCl$_2$–RuCl$_3$, can result in a remarkable synergic effect on the selectivity of p-chloroaniline in the selective hydrogenation of p-chloronitrobenzene. The colloidal polymer-anchored bimetallic catalyst, PVP–Pd–1/4Pt, can catalyze the hydrogenation of non-halo-substituted nitroaromatics to the corresponding aromatic amines in high yields under mild conditions. The interaction of two kinds of metal atoms and the intervention of a suitable amount of base in the catalytic cycle may account for the synergic effect of these two different types of polymer-anchored bimetallic catalysts.

Acknowledgements

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