

# A Remarkable Synergic Effect of Polymer-anchored Bimetallic Palladium–Ruthenium Catalysts in the Selective Hydrogenation of *p*-Chloronitrobenzene

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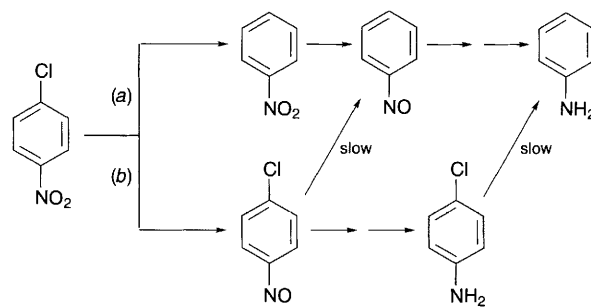
A synergic effect of the polymer-anchored bimetallic palladium–ruthenium catalysts can lead to a remarkable increase in the selectivity for *p*-chloroaniline in the selective hydrogenation of *p*-chloronitrobenzene under atmospheric pressure and in the presence of a small amount of base.

Homogeneous and polymer-protected multimetallic catalysis has attracted much attention in recent years, since enhanced reaction rates, selectivities and new types of reactions are expected to arise from cooperative or successive participation of two or more kinds of metal atoms.<sup>1–3</sup> The previous reports on polymer-protected bi- or multi-metallic catalysts are usually focused on the catalytic behaviours of colloidal sols of transition metals.<sup>2,3</sup> In this paper, we report a remarkable synergic effect of polymer-anchored palladium–ruthenium catalysts on the selectivity of the hydrogenation of *p*-chloronitrobenzene in methanol under atmospheric pressure. The results reveal that the selectivity for the desired product, *p*-chloroaniline, can be increased with the addition of a second transition metal component RuCl<sub>3</sub> to the monometallic catalyst PVP–PdCl<sub>2</sub> [PVP = poly(*N*-vinyl-2-pyrrolidone)].<sup>†</sup>

In heterogeneous or homogeneous catalysis, palladium catalysts are usually active for the hydrodehalogenation of organic halides<sup>4</sup> in the presence of a base. At a relatively high dihydrogen pressure and/or by means of platinum catalysts,<sup>5,6</sup> the selectivities for the desired products, halo-substituted aromatic amines, in the hydrogenation of halo-substituted aromatic nitro compounds can be increased. It is known that only in the presence of a base, can the monometallic catalyst PVP–PdCl<sub>2</sub> exhibit very high activity both in the hydrogenation of nitrobenzene,<sup>7</sup> and in the hydrodechlorination of aromatic chlorides.<sup>4c</sup> Otherwise, the hydrogenation rate of nitrobenzene is moderate and the hydrodechlorination of aromatic chlorides can proceed only at a very low rate. It can be seen from Table 1 that PVP–PdCl<sub>2</sub> can show very high catalytic activity for the hydrodechlorination and reduction of *p*-chloronitrobenzene. With an equimolar amount of base to the substrate, the reaction proceeds *via* path (a) as shown in Scheme 1, *i.e.* the substrate can be rapidly hydrodechlorinated to nitrobenzene, and the latter is then reduced to aniline. Decreasing the amount of base

added can reduce the rate of hydrodechlorination, but the main product is still aniline.

By means of the addition of a second transition metal component to the catalyst, we found that NiCl<sub>2</sub> deactivated the catalyst, FeCl<sub>3</sub> and Co(OAc)<sub>2</sub> did not exhibit a very obvious influence on the selectivity of *p*-chloroaniline, but RhCl<sub>3</sub> and RuCl<sub>3</sub> can remarkably increase this selectivity despite a decrease in the catalyst activity. The maximum selectivities can be achieved by using the bimetallic catalyst PVP–PdCl<sub>2</sub>–RuCl<sub>3</sub> with a Pd:Ru mole ratio of 1:1 or 1:2 and in the presence of 0.01% of sodium acetate. The analyses of the intermediates for the hydrogenation of *p*-chloronitrobenzene in this case show that the reaction proceeds *via* path (b). This remarkable synergic effect may result from the interaction of the two kinds of metal atoms. Although ruthenium species are not active both for the hydrodechlorination and reduction of the nitro group of the substrate, the presence of ruthenium species formed *in situ* may



**Scheme 1** Reagents: (a) Base/CNB = 0.01–1.0, [Pd] cat.; (b) Base/CNB = 0.01, [Pd–Ru] cat. A small amount (< 2%) of *p*-chloronitrosobenzene and trace of chlorobenzene, azo- and azoxy-dichlorobenzene can be detected by HPLC.

**Table 1** Hydrogenation and hydrodechlorination of *p*-chloronitrobenzene<sup>a</sup>

Catalyst	Base <sup>b</sup>	TOF <sub>max</sub> <sup>c</sup> /min <sup>-1</sup>	Conversion <sup>d</sup> of CNB (%)	Selectivity (%) <sup>e</sup>		
				AN	CAN	NB
PVP–PdCl <sub>2</sub> <sup>†</sup>	—	2.0	1.4 (56)	—	—	—
PVP–PdCl <sub>2</sub>	NaOAc (0.01)	25.2	92.5 (290)	76.3	18.5	3.7
PVP–PdCl <sub>2</sub>	NaOAc (0.02)	42.5	90.4 (240)	75.7	21.7	0.2
PVP–PdCl <sub>2</sub>	NaOAc (1.0)	80.2	100 (140)	97.8	2.0	0
PVP–PdCl <sub>2</sub> –FeCl <sub>3</sub>	NaOAc (0.02)	11.2	82.8 (430)	69.8	24.3	1.6
PVP–PdCl <sub>2</sub> –Co(OAc) <sub>2</sub>	NaOAc (0.02)	30.5	99.2 (350)	88.0	11.3	0
PVP–PdCl <sub>2</sub> –NiCl <sub>2</sub>	NaOAc (0.02)	nil	nil (60)	—	—	—
PVP–PdCl <sub>2</sub> –RhCl <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> (0.01)	6.6	88.5 (500)	27.4	70.2	2.2
PVP–RuCl <sub>3</sub>	NaOAc (0.01)	nil	—	—	—	—
PVP–PdCl <sub>2</sub> –RuCl <sub>3</sub>	—	1.6	5.5 (137)	10.2	89.8	0
PVP–PdCl <sub>2</sub> –RuCl <sub>3</sub>	NaOAc (0.01)	7.7	98.6 (520)	5.5	94.1	0.3
PVP–PdCl <sub>2</sub> –RuCl <sub>3</sub>	NaOAc (0.02)	10.1	98.0 (480)	36.6	62.8	0
PVP–PdCl <sub>2</sub> –RuCl <sub>3</sub>	NaOAc (1.0)	131.5	100 (100)	95.1	4.4	0
PVP–PdCl <sub>2</sub> –2RuCl <sub>3</sub>	NaOAc (0.01)	7.1	97.4 (560)	4.7	94.9	0
PVP–PdCl <sub>2</sub> –4RuCl <sub>3</sub>	NaOAc (0.01)	1.7	37.9 (450)	5.0	85.7	7.9
PVP–PdCl <sub>2</sub> –0.5RuCl <sub>3</sub>	NaOAc (0.01)	6.9	96.9 (630)	33.1	66.4	0.1
PVP–PdCl <sub>2</sub> –0.25RuCl <sub>3</sub>	NaOAc (0.01)	5.3	68.7 (520)	19.9	78.5	1.5

<sup>a</sup> 0.1 MPa, 65 °C, methanol (20 ml), catalyst (4 × 10<sup>-6</sup> mol Pd), substrate (4 mmol). <sup>b</sup> The value in parentheses is the mole ratio of a base to the substrate. <sup>c</sup> Calculated from the amount of dihydrogen uptake. <sup>d</sup> Conversion based on HPLC analysis at the time indicated in parentheses (min). CNB = *p*-chloronitrobenzene. <sup>e</sup> AN = aniline, CAN = *p*-chloroaniline, NB = nitrobenzene.

inhibit the oxidative addition of the C–Cl bond to the active palladium centres. A small amount of base is essential both for the hydrodechlorination and the reduction of the nitro group of *p*-chloronitrobenzene by using the polymer-anchored Pd or Pd–Ru catalysts. The role of the base may be related to its intervention in the catalytic cycles in some way.

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### Footnote

† To a mixture of 2 ml of 5 mol dm<sup>-3</sup> HCl and 0.056 g (0.31 mmol) of PdCl<sub>2</sub>, 150 ml of absolute methanol and 0.724 g of PVP was added. After stirring at room temp. for 48 h, a red-brown solution was obtained (the catalyst PVP–PdCl<sub>2</sub>, 2 × 10<sup>-3</sup> mmol Pd ml<sup>-1</sup>, N/Pd = 20). To the monometallic catalyst, a second transition metal compound (*e.g.*

FeCl<sub>3</sub>·6H<sub>2</sub>O, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, RuCl<sub>3</sub>·3H<sub>2</sub>O or RhCl<sub>3</sub>·3H<sub>2</sub>O) was added, then stirred at room temp. for 24 h, to yield the polymer-anchored bimetallic catalyst (PVP–PdCl<sub>2</sub>–*m*MX, 2 × 10<sup>-3</sup> mmol Pd ml<sup>-1</sup>, N/Pd = 20, M/Pd = *m*).

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