

# Effect of rare earths on the hydrogenation properties of *p*-chloronitrobenzene over polymer-anchored platinum catalysts

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## Abstract

The effect of rare earths ( $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{La}^{3+}$ ), base (inorganic or organic base) and substrate concentration on the hydrogenation properties of *p*-chloronitrobenzene (*p*-CNB) over poly-vinylpyrrolidone-anchored platinum (PVP–Pt) has been studied in ethanol at 303 K and normal pressure. The addition of rare earths except  $\text{Nd}^{3+}$  and  $\text{La}^{3+}$  to catalytic system improves the selectivity of *p*-chloroaniline (*p*-CAN) but has lower activity when PVP–Pt alone is used. The hydrogenation rate of *p*-CNB and selectivity of *p*-CNB to *p*-CAN increase significantly for PVP–RE–Pt and PVP–Pt catalysts in the presence of NaOH. PVP–Sm–Pt catalyst exhibits the highest selectivity (95.8%) of *p*-CAN when the molar ratio of NaOH to substrate is 0.12. In the same reaction condition, PVP–Ce–Pt\* catalyst using PVP (90,000) of large molecular weight as support exhibits the highest activity ( $60.5 \text{ mol H}_2 \text{ mol Pt}^{-1} \text{ min}^{-1}$ ) and selectivity of *p*-CAN (98.2%).

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## 1. Introduction

Aromatic haloamines are important intermediates in the chemistry of dyes, drugs, herbicides and pesticides. The traditional synthesis routes are usually harmful for the environment. It seems to be a best choice by selective hydrogenation of aromatic halonitro compounds to the corresponding haloamine; however, the process is difficult because of extensive dehalogenation [1]. Dehalogenation has been seen to occur with palladium [1–3], platinum [1–3], rhodium [4], nickel [5] and copper chromite [6] catalysts. Among these, platinum shows better selectivity of haloaniline and fast rate of reduction of the nitro group. To improve selectivity, the catalyst prepara-

tions are modified (alloying [7] and metal/support interaction [8], etc.) or specific additives (promoters or inhibitors) [9–11] are used in the reaction system.

Catalytic hydrogenation reactions are influenced by many factors, which include the presence of catalytic activators or poisons, the temperature, pressure, solvent agitation and other conditions specific to the particular process. One of the more important considerations is the catalyst support. Water-soluble polymer supports have received much attention in the recent years [12–15], they are often used as support for nano-size ultrafine particles. The polymers work not only as stabilizers of ultrafine particles but also as the materials functionalizing ultrafine particles. Their special features result in cooperative and multi-step catalysts in reaction [16].

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Lanthanides (rare earths) have been investigated and utilized in many fields [17]. The first report on the promotion effect of lanthanides appeared in the study of supported catalysts for synthesis gas conversion [18]. For adsorption characteristics, lanthanides and transition metals show higher efficiency when they are used together than when used separately; however, the promotion effect of lanthanides has been observed only in a heterogeneous system, and the promotion effect in a homogeneous system has seldom been successfully reported. In our experiment, we find that lanthanides also decrease catalytic activity for the hydrogenation of *p*-chloronitrobenzene (*p*-CNB), but they show high selectivity of *p*-chloroaniline (*p*-CAN).

## 2. Experimental

Poly-vinylpyrrolidone-anchored platinum (PVP–Pt) catalysts are prepared by alcoholic reduction in the presence of PVP, of average molecular weight 30,000 or 90,000, purchased from BASF. A mixture of  $8.7 \times 10^{-5}$  mol hexachloroplatinic acid, 30 ml ethanol and 0.222 g PVP ( $1.00 \times 10^{-2}$  mol as monomeric unit) is refluxed in a 50 ml flask for 3 h under air. The black catalyst is abbreviated as PVP–Pt (or PVP–Pt\*).

PVP–rare earth–Pt catalysts are prepared as follows: A mixture of 0.222 g of PVP, 20 ml ethanol and  $5.2 \times 10^{-6}$  mol rare earth nitrate is refluxed for 1 h, and then  $8.7 \times 10^{-5}$  mol hexachloroplatinic acid and 7 ml of ethanol are added to it. The mixture is also refluxed for 2 h under air. The orange catalyst is abbreviated as PVP–RE–Pt (or PVP–RE–Pt\*).

Hydrogenation of *p*-CNB is carried out at 303 K and atmospheric pressure. A mixture of 2.0 ml PVP-anchored platinum catalyst ( $5.8 \times 10^{-6}$  mol Pt),

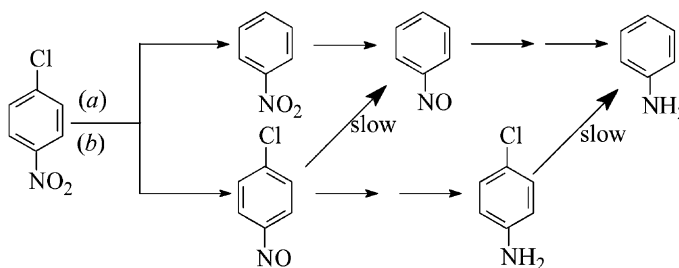
and 8 ml ethanol solution containing NaOH are placed in a 3-necked flask closed with a silicon rubber cap and connected to a hydrogen gas burette. The mixture is treated under hydrogen at 303 K for 30 min before 10 ml ethanol solution of *p*-CNB ( $4 \times 10^{-3}$  mol substrate) is injected into the reactor. The hydrogen consumption is monitored with a graduated gas burette. Chemical analysis of the products is performed by gas chromatography Perkin-XL equipped with a FID detector and SE-30 capillary column. Reactants and products are identified by comparison with authentic samples. Biphenyl is used as internal standard.

## 3. Results and discussion

### 3.1. Effect of base concentration and different base

Hydrogenation of *p*-CNB is a tedious process as shown in Scheme 1 [13], and it often yields many by-products at the same time. It is well known that alkali in large quantities promotes dehalogenation; critical amounts of special inorganic [19] or organic [20] bases can greatly increase the selectivity of platinum catalyst. Base modifies the catalytic activity, probably they can enhance the solubility of hydrogen in ethanol. In our experiment, we also obtain similar results that are listed in Tables 1 and 2.

From Table 1, it is found that the hydrogenation of *p*-CNB can also be catalyzed by PVP–Pt under normal pressure of hydrogen at 303 K without the addition of NaOH, but both catalytic activity and selectivity increase remarkably in the presence of NaOH. Only 25 min is required to complete the reaction in the presence of  $4.8 \times 10^{-4}$  mol NaOH, whereas without NaOH only 94.1% of the conversion takes place in



Scheme 1.

Table 1  
Effect of NaOH concentration on the hydrogenation of *p*-CNB over PVP–Pt catalyst<sup>a</sup>

NaOH <sup>b</sup>	TOF <sup>c</sup>	Conversion (%) (reaction time, min)	Selectivity (%) <sup>d</sup>	
			AN	CAN
–	21.6	94.1 (100)	7.8	78.5
0.01	19.6	100 (110)	8.0	91.2
0.02	23.9	100 (90)	5.9	92.5
0.05	60.1	100 (35)	3.6	91.1
0.12	83.9	100 (25)	8.4	89.2
0.31	84.9	100 (25)	8.5	89.9
0.63	23.2	100 (85)	6.8	81.7

<sup>a</sup> Reaction condition:  $5.8 \times 10^{-6}$  mol Pt;  $4 \times 10^{-3}$  mol *p*-CNB; reaction temperature, 303.3 K; *P*, 0.1 MPa.

<sup>b</sup> The molar ratio of NaOH to substrate.

<sup>c</sup> The average reaction rate, mol H<sub>2</sub> mol Pt<sup>-1</sup> min<sup>-1</sup>, calculated from the amount of H<sub>2</sub> uptake.

<sup>d</sup> Some products with high boiling point could not be determined by GC analysis; AN: aniline.

100 min, and the selectivity of *p*-CAN is improved from 78.5 to 91.1%. Increasing the amount of NaOH up to 0.05–0.31 mol%, the catalytic activity is kept constant, and the selectivity declines appreciably. From Table 2, we can see that using other inorganic bases, such as KOH, K<sub>2</sub>CO<sub>3</sub> and NaOAc, also gives good catalytic activity but has no effect on the selectivity of *p*-CAN except when KOH is used. Using *n*-Bu<sub>3</sub>N and Et<sub>2</sub>NH organic base also give similar results, the catalytic activity and selectivity of *p*-CAN increased markedly. The catalytic activity decreases slightly in the presence of NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, but the selectivity of *p*-CAN reaches 96.5%. The reason is

Table 2  
Effect of various bases on the hydrogenation of *p*-CNB over PVP–Pt catalyst<sup>a</sup>

Base <sup>b</sup>	TOF	Conversion (%) (reaction time, min)	Selectivity (%)	
			AN	CAN
–	21.6	94.1 (100)	7.8	78.5
NaOH	83.9	100 (25)	8.4	89.2
KOH	85.1	100 (25)	3.0	89.9
K <sub>2</sub> CO <sub>3</sub>	35.6	100 (60)	5.8	79.6
NaOAc	36.5	100 (60)	8.4	78.1
<i>n</i> -Bu <sub>3</sub> N	36.4	100 (60)	7.1	92.4
Et <sub>2</sub> NH	39.9	100 (45)	7.6	88.4
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	16.6	96.6 (120)	–	96.5

<sup>a</sup> Reaction conditions are similar to Table 1.

<sup>b</sup> The molar ratio of base to substrate is 0.12.

Table 3  
Effect of substrate concentration on the hydrogenation of *p*-CNB over PVP–Pt catalyst<sup>a</sup>

Substrate ( $\times 10^{-3}$ mol)	TOF	Conversion (%) (reaction time, min)	Selectivity (%)	
			AN	CAN
4.0	60.5	100 (35)	8.4	89.2
3.2	72.1	100 (23)	6.7	88.0
2.0	73.3	100 (14)	15.9	80.4
0.7	61.1	100 (6)	33.1	64.9

<sup>a</sup> Reaction conditions are similar to Table 1; the molar ratio of NaOH to substrate is 0.12.

that the amino group in NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> has strong coordination with Pt, which decreases the active sites of the catalyst, and hydrogenolysis of the C–Cl bond is inhibited. The role of the base may be related to its intervention in the catalytic cycle in some way.

In our experiment, we also find that the selectivity of *p*-CAN increases with the increase in the concentration of the substrate. The results are listed in Table 3. High concentration of the substrate probably prevents the products from contacting with the active sites, which partly inhibits hydrogenolysis of the C–Cl bond [21].

### 3.2. Effect of rare earth ions

The results of the hydrogenation of *p*-CNB catalyzed by PVP–RE–Pt are summarized in Table 4. From Table 4, we can see that the hydrogenation rate of *p*-CNB decreases, obviously with the introduction of rare earth ions, but the addition of Sm<sup>3+</sup>, Pr<sup>3+</sup> and Ce<sup>3+</sup> shows positive effect on the selectivity of *p*-CNB to *p*-CAN. In the presence of NaOH, catalytic activities and selectivities increase significantly. PVP–Sm–Pt catalyst exhibits the best selectivity of *p*-CAN (96.8%).

Different cross-linking of PVP has a different character. Table 5 lists the results on the hydrogenation of *p*-CNB over PVP–RE–Pt\* catalysts (the average molecular weight of PVP is 90,000). From Table 5, we can see that the effect of rare earths except Nd<sup>3+</sup> and La<sup>3+</sup> on the catalytic activity and selectivity is not obvious without the addition of NaOH. In the presence of NaOH, catalytic activity is also improved but the selectivity of *p*-CNB to *p*-CAN varies desultorily. PVP–Ce–Pt\* catalyst exhibits the best selectivity of *p*-CAN (98.2%). On Comparing Table 4 with Table 5,

Table 4  
Results of the hydrogenation of *p*-CNB over PVP–RE–Pt catalysts<sup>a</sup>

Catalyst	Base <sup>b</sup>	TOF	Conversion (%) (reaction time, min)	Selectivity (%)	
				AN	CAN
PVP–Pt	–	21.6	94.1 (100)	7.8	78.5
PVP–Pt	NaOH	83.9	100 (25)	8.4	89.2
PVP–Sm–Pt	–	2.6	90.7 (760)	7.8	91.2
PVP–Sm–Pt	NaOH	42.1	100 (50)	2.4	96.8
PVP–Nd–Pt	–	2.5	90.1 (775)	7.6	75.6
PVP–Nd–Pt	NaOH	24.5	100 (85)	–	90.8
PVP–Pr–Pt	–	1.8	53.2 (600)	4.0	85.5
PVP–Pr–Pt	NaOH	18.6	94.4 (110)	–	92.1
PVP–Ce–Pt	–	2.7	91 (760)	7.2	82.9
PVP–Ce–Pt	NaOH	30.1	100 (70)	–	92.2
PVP–La–Pt	–	1.8	63 (725)	5.0	72.3
PVP–La–Pt	NaOH	4.5	100 (450)	5.9	77.4

<sup>a</sup> Reaction conditions are similar to Table 1.

<sup>b</sup> The molar ratio of NaOH to substrate is 0.12.

we can conclude that support takes on an important role for this reaction. Teranishi et al. [15] pointed out that weak coordination between PVP and Nd<sup>3+</sup> is a reason for low activity. Low cross-linking of PVP has a weak coordinative ability to rare earth ions especially for Nd<sup>3+</sup> and La<sup>3+</sup>. Rare earth ions also influence the coordination between PVP and Pt. In the experiment, we find that some platinum black forms for low cross-linking of PVP-supported platinum catalyst, and the phenomena is always accompanied with

low activity. In high cross-linking of PVP catalytic system, these phenomena are not observed.

The effect of Ce<sup>3+</sup> on the hydrogenation of *p*-CNB over PVP–Pt\* catalyst is also investigated. Fig. 1 demonstrates the effect on catalytic activity and selectivity with the addition of Ce<sup>3+</sup>. From Fig. 1, it is found that catalytic activity is inhibited remarkably when a small amount of Ce<sup>3+</sup> is added in PVP–Pt\* catalyst, and selectivity is also low in the presence of NaOH. It is interesting that catalytic activity and

Table 5  
Results of the hydrogenation of *p*-CNB over PVP–RE–Pt\* catalysts<sup>a</sup>

Catalyst	Base <sup>b</sup>	TOF	Conversion (%) (reaction time, min)	Selectivity (%)	
				AN	CAN
PVP–Pt*	–	21.8	100 (100)	7.7	81.8
PVP–Pt*	NaOH	77.3	100 (27)	10.3	88.6
PVP–Sm–Pt*	–	16.9	100 (130)	7.0	81.2
PVP–Sm–Pt*	NaOH	53.1	100 (40)	9.0	84.5
PVP–Nd–Pt*	–	2.9	100 (730)	7.8	79.6
PVP–Nd–Pt*	NaOH	35.5	100 (60)	4.7	90.1
PVP–Pr–Pt*	–	12.6	100 (150)	5.4	85.7
PVP–Pr–Pt*	NaOH	52.6	100 (40)	6.2	91.7
PVP–Ce–Pt*	–	15.9	100 (140)	6.0	80.0
PVP–Ce–Pt*	NaOH	60.5	100 (35)	–	98.2
PVP–La–Pt*	–	3.4	100 (630)	2.8	79.9
PVP–La–Pt*	NaOH	30.3	100 (70)	6.2	90.6

<sup>a</sup> Reaction conditions are similar to Table 1. Average molecular weight of PVP is 90,000.

<sup>b</sup> The molar ratio of NaOH to substrate is 0.12.

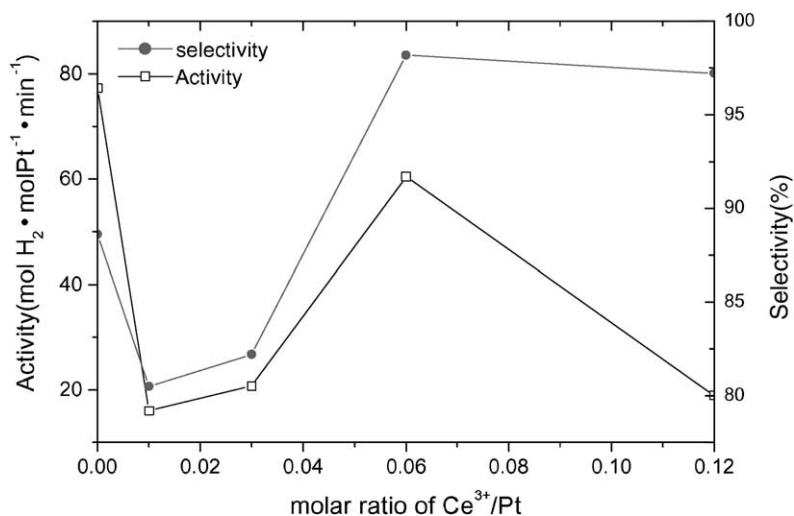


Fig. 1. The effect of molar ratio of Ce<sup>3+</sup>/Pt on the hydrogenation of *p*-CNB to *p*-CAN catalyzed by PVP–Ce–Pt\*.

selectivity to *p*-CAN increase monotonously with increasing molar ratio of Ce<sup>3+</sup>/Pt from 0.01 to 0.06. The average rate of the hydrogenation of *p*-CNB increases from 16.0 to 60.5 mol H<sub>2</sub> mol Pt<sup>-1</sup> min<sup>-1</sup>, and the selectivity to *p*-CAN also increases from 80.5 to 98.2%. However, the catalytic activity decreases sharply again and selectivity also decreases slightly when the molar ratio of Ce<sup>3+</sup>/Pt is higher than 0.06. We suspect that the effect of rare earth ions is related to the interaction of ions with support, reaction substrate, product or metallic catalyst. Further investigations are being done now.

#### 4. Conclusions

The addition of Sm<sup>3+</sup>, Ce<sup>3+</sup> and Pr<sup>3+</sup> to catalytic system improves the selectivity of *p*-CAN but have lower catalytic activity when PVP–Pt is used alone. In the presence of NaOH, the hydrogenation rate of *p*-CNB and selectivity of *p*-CNB to *p*-CAN increases significantly for PVP–RE–Pt and PVP–Pt catalysts. PVP–Sm–Pt catalyst exhibits the highest selectivity (95.8%) of *p*-CAN when the molar ratio of NaOH to substrate is 0.12. In the presence of other inorganic/organic base, such as KOH, *n*-Bu<sub>3</sub>N and Et<sub>2</sub>NH, the catalytic activity and selectivity of *p*-CAN also increase markedly for PVP–Pt catalyst. High cross-linking PVP has strong coordina-

tive ability with rare earth and Pt, which probably increases the catalytic activity. PVP–Ce–Pt\* using PVP (90,000) as support exhibits the best activity (60.5 mol H<sub>2</sub> mol Pt<sup>-1</sup> min<sup>-1</sup>) and selectivity of *p*-CAN (98.2%) in the presence of 4.8 × 10<sup>-4</sup> mol NaOH. The amount of Ce<sup>3+</sup> in PVP–Ce–Pt\* catalyst influences markedly the catalytic properties. Catalytic activity and selectivity of *p*-CAN are highest when the molar ratio of Ce<sup>3+</sup>/Pt is 0.06.

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