

# Layered material $\gamma$ -ZrP supported platinum catalyst for liquid-phase reaction: a highly active and selective catalyst for hydrogenation of the nitro group in *para*-chloronitrobenzene

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Received (in Cambridge, UK) 2nd January 2008, Accepted 28th January 2008

First published as an Advance Article on the web 20th February 2008

DOI: 10.1039/b719831k

**Chemoselective hydrogenation of *para*-chloronitrobenzene without any dechlorination over Pt/ $\gamma$ -ZrP catalyst proceeds effectively, which provides a clean and convenient approach to produce useful *para*-chloroaniline with excellent activity and selectivity.**

Chloroanilines (CANs) are an important class of industrial intermediates for the synthesis of organic fine chemicals, such as dyes, drugs, herbicides and pesticides. At present these widely applied CANs are mainly produced through selective hydrogenation of the corresponding chloronitrobenzenes (CNBs). For this type of hydrogenation reaction, various precious catalysts (Pt, Pd, Ru, Rh) and Raney-nickel catalyst have been well-studied.<sup>1–10</sup> However, it has been found that the hydrogenation process is accompanied by hydrogenolysis of the carbon–halogen bond over most of catalysts, and that hydrogen chloride produced from this process is corrosive to the reactor. Therefore, many efforts have been made to overcome this problem over the past decades, including introducing special additives (promoters and inhibitors),<sup>1,11</sup> modifying the active metal with a second metal component,<sup>2,4</sup> and tuning the particle sizes of the catalysts.<sup>1,12</sup> However, none of these methods have been completely satisfactory, and it still remains a big challenge to develop eco-friendly heterogeneous catalysts that would ensure the selective hydrogenation of the nitro group in chloronitrobenzenes without hydrogenolysis of the carbon–halogen bond. It is also extremely interesting to researchers to pursue this kind of catalysts for industrial application.

Catalytic hydrogenation reactions are influenced by many factors with one of the more important considerations being the catalyst support. Very recent exploratory work on Ru-based<sup>9</sup> and Pt-based<sup>10</sup> catalysts prepared using SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively, as supports exhibit excellent selectivity for the CNB hydrogenation to CAN. Layered materials, such as zirconium phosphates, are of considerable interest because of their practical applications mainly in the areas of ion-exchange, intercalation, catalysis and sorption. However, only a few excellent applications as catalysts or catalyst precursors

have emerged by far.<sup>13–15</sup> We have recently shown a novel Ag/ $\gamma$ -Zr(PO<sub>4</sub>)(NH<sub>4</sub>HPO<sub>4</sub>) (hereafter  $\gamma$ -ZrP) catalyst, prepared by an ion-exchange method, exhibiting prominent catalytic performance for the allylic oxidation of cycloolefins to enols.<sup>16</sup> In this paper, we present a new strategy for the design of high-performance Pt-based catalyst utilizing  $\gamma$ -ZrP as the support. Over this catalyst, we attempted the synthesis of CAN from CNB. It is known that a high selectivity for CAN is difficult to maintain once the substrate has been exhausted completely over most metal-supported catalysts. What interests us is that, Pt nanoparticles on  $\gamma$ -ZrP exhibits excellent catalytic activity and stability for the selective hydrogenation of the nitro groups in CNB without any dechlorination at complete conversion.

The Pt/ $\gamma$ -ZrP catalyst was prepared by capture of the synthesized PVP-protected Pt nanoparticles on the support  $\gamma$ -ZrP. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was reduced in a mixed solvent (ethanol, isopropanol and distilled water) in the presence of poly(vinylpyrrolidone) to give a dark brown sol, then  $\gamma$ -ZrP was mixed with the colloidal solution and continually stirred for 24 h at room temperature. The  $\gamma$ -ZrP supported platinum was filtered off and washed with distilled water for several times. The catalyst was dried under vacuum at 80 °C (platinum content: 1.1%). The Pt 4f peaks in the XPS spectra is shown in Fig. 1. The binding energies of Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> levels in the Pt/ $\gamma$ -ZrP catalyst were 70.49 and 73.79 eV, which are lower than that of PVP-protected Pt nanoparticles (70.99, 74.34 eV) by 0.5 and 0.45 eV, respectively, suggesting that the electron transfer occurred from the support to the Pt particles, so that Pt was electron-enriched. Transmission electron microscopy (TEM) images evidenced that the Pt nanoparticles have an average size of 3 nm and are highly dispersed on the  $\gamma$ -ZrP

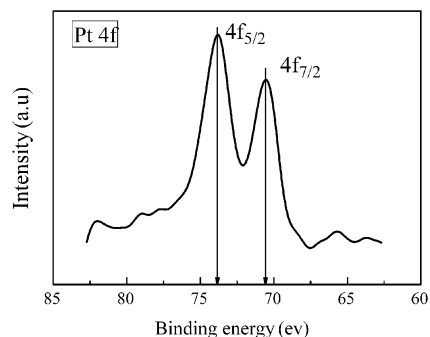
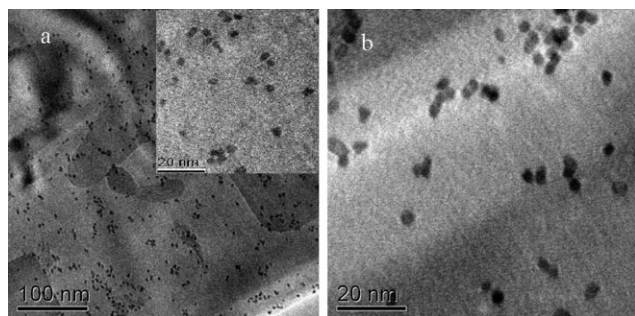


Fig. 1 XPS spectra of Pt in Pt/ $\gamma$ -ZrP catalyst.

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**Fig. 2** TEM images of (a) fresh Pt/γ-ZrP catalyst and (b) recovered Pt/γ-ZrP catalyst after the fourth reaction cycle.

support (Fig. 2(a)). The homogeneous dispersion of Pt nanoparticles is attributed to a relatively strong metal–support interaction between the metal nanoparticles and surface groups of the support. Recovered catalyst after the fourth reaction cycle was also observed by TEM (Fig. 2(b)). X-Ray diffraction (XRD) revealed that diffraction signal of Pt nanoparticles in the Pt/γ-ZrP catalyst was not detected because of the low metal content and small particle size.

The results of selective hydrogenation of *para*-chloronitrobenzenes are shown in Table 1. The reproducibility of the results was good as manifested by the error analysis, where the error bars represented the standard deviations (SD,  $n = 3$ ). The data showed that the conversion of *p*-CNB reached 100% within 28 min when the hydrogen pressure was increased from 2 to 4 MPa, and that the hydrogen pressure had no notable effect on CAN selectivity (entries 1–3). In addition, the hydrodechlorination of CAN was avoidable over the Pt/γ-ZrP catalyst when using a suitable amount of catalyst (entries 4–9). When more than 5 mg of catalyst was used to catalyze the selective hydrogenation of *p*-CNB catalytic dehalogenation occurred during the reaction (entries 1 and 10), while when the amount of catalyst was decreased from 5 to 2 mg, dechlorination product was not detected in the reaction mixture. A possible reason for the absence of dechlorination product is that decreasing the amount of catalyst can prevent

the product *p*-CAN from contacting with active sites so inhibiting hydrogenolysis of the C–Cl bond.<sup>12</sup> Special attention was paid to distinguish the by-products of the hydrogenation reaction with GC-MS, with *para*-chloronitrosobenzene and dichloroazoxybenzene detected as the main by-products in the reaction of *p*-CNB. These two kinds of by-products as intermediates, can be further hydrogenated to the desired product *p*-CAN, which is supported by the increase in the selectivity of the desired *p*-CAN with the extension of reaction time (entries 4–7). The *p*-CAN selectivity could reach 100% at 30 °C because no dehalogenation reaction occurred and the other by-products were further hydrogenated to the desired product *p*-CAN within 55 min (entry 12). At a higher than 30 °C temperature, the hydrogenation rate increased and dehalogenation reaction was also observed, moreover, the amount of dechlorination product increased when the reaction temperature was increased (entries 1 and 13), which indicates that the hydrogenolysis rate of the C–Cl bond increases with increasing reaction temperature. Pure γ-ZrP was also tested, showing that hydrogenation reaction did not occur (entry 11), which clearly proves that platinum particles are the active component in the *p*-CNB hydrogenation reaction. Based on the above experimental results, the undesired hydrodechlorination reaction usually observed over most other metal catalysts<sup>1–8</sup> can be successfully avoided over the Pt/γ-ZrP catalyst.

The Pt/γ-ZrP catalyst is reusable (Table 2). The catalytic activities were slightly decreased with the increasing of cycle times. The decrease of catalytic activity might be caused by aggregation or leaching of Pt particles, the former should be the main reason in this case, because it was confirmed by induced coupled plasma techniques (ICP) that the Pt content of recycled catalyst was the same as that of the fresh samples and no Pt was detected in the filtrate. For product *p*-CAN selectivity, we can draw a conclusion that 100% *p*-CAN selectivity could be obtained over recovered catalysts by prolonging the reaction time, which was supported by the following facts: (1) no hydrodechlorination products were observed over recovered catalyst (Table 2, entries 3 and 4);

**Table 1** Catalytic properties for the selective hydrogenation of *p*-CNB over Pt/γ-ZrP catalyst<sup>a</sup>

Entry	Catalyst amount/mg	$t$ /min	$P$ /MPa	Conv. <sup>b</sup> (%)	Product selectivity <sup>c</sup> (%)		
					Dechlor.	CAN	Others <sup>d</sup>
1	10	28	2	100	0.50	99.3	0.20
2	10	28	3	100	0.30	99.5	0.20
3	10	28	4	100	0.13	99.7	0.17
4	2	60	2	74.4	0	90.0	10.0
5	2	210	2	100	0	94.0	6.0
6	2	240	2	100	0	95.9	4.1
7	2	275	2	100	0	100	0
8	5	60	2	100	0	96.6	3.4
9	5	80	2	100	0	100	0
10	7	60	2	100	0.31	99.4	0.29
11 <sup>e</sup>	10	60	2	0	0	0	0
12 <sup>f</sup>	10	55	2	100	0	100	0
13 <sup>g</sup>	10	20	2	100	1.3	98.7	0

<sup>a</sup> Reaction conditions: 3 mmol substrate in 8 ml methanol, 40 °C. The reaction system was stirred with a magnetic stirrer. <sup>b</sup> The reproducibility of the conversion results is within the range of  $\pm(0.1\text{--}1.2)\%$ . <sup>c</sup> The reproducibility of the product selectivity results is within the range of  $\pm(0.07\text{--}2.1)\%$ . <sup>d</sup> Products were identified with authentic samples, and GC-MS coupling, other products are *para*-chloronitrosobenzene and dichloroazoxybenzene as intermediates. <sup>e</sup> Reaction was performed over γ-ZrP. <sup>f</sup> Reaction temperature: 30 °C. <sup>g</sup> Reaction temperature: 50 °C.

**Table 2** Reusability of Pt/ $\gamma$ -ZrP catalyst for the selective hydrogenation of *p*-CNB<sup>a</sup>

Cycle	Conv. <sup>c</sup> (%)	Product selectivity <sup>d</sup> (%)		
		Dechlor.	CAN	Others <sup>b</sup>
1	99.9	1.0	97.2	1.9
2	97.3	0.03	92.4	7.5
3	95.8	0	91.1	8.9
4	92.9	0	90.3	9.7

<sup>a</sup> Reaction conditions: 3 mmol substrate in 8 ml methanol, 10 mg Pt/ $\gamma$ -ZrP, 2 MPa H<sub>2</sub>, 40 °C, 20 min. <sup>b</sup> See footnote *d* in Table 1. <sup>c</sup> The reproducibility of the conversion results is within the range of  $\pm(0.1\text{--}2.8)\%$ . <sup>d</sup> The reproducibility of the product selectivity results is within the range of  $\pm(0.05\text{--}2.0)\%$

(2) other by-products, *para*-chloronitrosobenzene and dichloro-azoxybenzene as intermediates, could be further hydrogenated to the desired product *p*-CAN with the extension of reaction time, which was supported by the results of Table 1 (entries 4–7). A possible reason for 100% *p*-CAN selectivity over recovered catalyst could be the aggregation of the Pt particles. TEM measurements (Fig. 2) showed that the size of Pt particles of 7 nm in the recovered Pt/ $\gamma$ -ZrP sample was significantly larger than that in the fresh (unreacted) sample (3 nm), which suggested the highest selectivity in *p*-CAN (100%) was achieved on larger Pt particles, this conclusion was in agreement with the result reported in previous literature.<sup>12</sup> In conclusion, we believe it would be possible to achieve a 100% CAN selectivity at complete CNB conversion by optimizing the size of Pt particles with  $\gamma$ -ZrP as support.

Coq *et al.* studied the effect of supports on the selective hydrogenation of *para*-chloronitrobenzene over Pt-supported catalysts, among different supported platinum catalysts, a selectivity of 99.3% for *p*-CAN was obtained at 99.7% conversion of *p*-CNB when platinum was supported on titania and reduced at high temperature, this unique behaviour is due to a strong metal–support interaction (SMSI) state for platinum. However, the dehalogenation reaction was unavoidable over the Pt/TiO<sub>2</sub> and better selectivity of CAN was not maintained by longer reaction time.<sup>1</sup> Over Pt/ $\gamma$ -ZrP catalyst, dechlorination product was avoidable, even when the reaction time was extended over 5 h after *p*-CNB was exhausted, and we conclude that the suppression of *p*-CAN hydrodechlorination is responsible for high selectivity for *p*-CAN. For the mechanism in the hydrodehalogenation reaction of aromatic halides, most researchers agreed that is caused by electrophilic attack of cleaved hydrogen on the absorbed aromatic halides.<sup>17</sup> According to this mechanism, we believe that the protection of CAN against dechlorination over Pt/ $\gamma$ -ZrP catalyst can be explained in terms of: (1) the amino group of produced CAN molecules as an electron-donating substitution

in the aromatic ring would favor the hydrogenolysis of the carbon–halogen bond in aromatic haloamines, but acid–base interaction between the OH groups of  $\gamma$ -ZrP and NH<sub>2</sub> groups of produced CAN molecules decreases the electron-donating ability of NH<sub>2</sub> groups, so the hydrodechlorination of CAN is suppressed. (2) A strong metal–support interaction (SMSI) between the  $\gamma$ -ZrP support and the Pt particles weakens the extent of electron feedback from the Pt atom to the aromatic ring in CAN, which would further suppress the hydrodechlorination of CAN. It is well known that adsorption of substrate molecules to the surface of the catalyst is the main factor determining catalytic activity.<sup>18</sup> Based on the XPS data, Pt is electron-enriched while the nitro group of CNB is a strong electron-withdrawing group. As a result, the electropositive nitrogen atom of the nitro group is absorbed on the surface of electron-enriched Pt atom, therefore, the N=O bond of CNB, which is activated by electronic interaction between the nitrogen atom of the nitro group and Pt atoms, becomes more susceptible to hydrogen attack, thereby promoting the hydrogenation of CNB. From Table 1 (entry 7), we can observe that the conversion and the selectivity can reach 100% even when the turnover number is >26 000. To the best of our knowledge, this excellent catalytic performance for the hydrogenation of *p*-CNB over Pt-based catalysts has rarely been reported up to now.

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