

## 凹凸棒土负载铂催化剂上对氯硝基苯的高活性高选择性液相加氢反应

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**摘要:** 分别采用乙醇-异丙醇、H<sub>2</sub> 和 NaBH<sub>4</sub> 还原方法制备了凹凸棒土负载铂催化剂(分别标记为 Pt/PAL(I)、Pt/PAL(II)和 Pt/PAL(III)), 其在对氯硝基苯(*p*-CNB)的催化选择加氢反应中表现出不同的催化性能. 在 Pt/PAL(II)催化剂上, 对氯苯胺(*p*-CAN)的选择性达到了 100%, 并且在 *p*-CNB 完全转化的情况下, 脱氯反应得到了完全的抑制. 在 Pt/PAL(I)和 Pt/PAL(III)催化剂上, 尽管脱氯反应没有得到完全的抑制, 但也分别得到 99.7%和 99.9%的 *p*-CAN 选择性. Pt/PAL(I)催化剂表现出最高的催化活性, 转化频率(TOF)值高达 27010 h<sup>-1</sup>. Pt/PAL(II)和 Pt/PAL(III)催化剂表现出稍微低的催化活性, TOF 值分别为 17193 和 24871 h<sup>-1</sup>. 利用透射电镜(TEM)、X 射线衍射(XRD)和傅里叶变换红外光谱(FTIR)对催化剂样品进行了表征, 结果表明优异的催化性能主要归因于铂粒子尺寸和凹凸棒土载体的影响.

**关键词:** 铂催化剂; 对氯硝基苯; 选择加氢; 脱氯; 凹凸棒土

**中图分类号:** O643

## Palygorskite Supported Platinum Catalysts with High Activity and Selectivity for the Liquid-Phase Hydrogenation of *para*-Chloronitrobenzene

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**Abstract:** The palygorskite supported platinum catalysts, Pt/PAL(I), Pt/PAL(II), and Pt/PAL(III) were prepared by different reduction methods (ethanol-isopropanol, H<sub>2</sub>, and NaBH<sub>4</sub>), and exhibited different catalytic properties for the hydrogenation of *para*-chloronitrobenzene (*p*-CNB). Over the Pt/PAL(II) catalyst the selectivity of *para*-chloroaniline (*p*-CAN) reached 100% and the hydrodechlorination reaction was fully suppressed during the complete conversion of *p*-CNB. Superior selectivities of 99.7% and 99.9% for *p*-CAN were also obtained over Pt/PAL(I) and Pt/PAL(III) catalysts, respectively, although the dehalogenation reaction was not completely avoided. Pt/PAL(I) was the most active catalyst with a turnover frequency (TOF) of up to 27010 h<sup>-1</sup>. Pt/PAL(II) and Pt/PAL(III) catalysts showed slightly lower activity with a TOF of 17193 and 24871 h<sup>-1</sup>, respectively. These excellent catalytic properties are attributed to the effects of Pt particle size and the palygorskite support, which was confirmed by transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns of the catalysts as well as Fourier transform infrared (FTIR) spectra of the palygorskite.

**Key Words:** Platinum catalyst; *para*-Chloronitrobenzene; Selective hydrogenation; Dechlorination; Palygorskite

Received: February 23, 2009; Revised: May 18, 2009; Published on Web: June 17, 2009.

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Chloroanilines (CANs) are an important class of industrial intermediates for the synthesis of organic fine chemicals, such as dyes, drugs, herbicides, and pesticides. These widely applied CANs are currently produced through the reduction of the corresponding chloronitrobenzenes (CNBs), either with a metal-acid reduction system or with selective hydrogenation over various metal catalysts. The latter route is now preferred because it offers several advantages, including low cost operation, easy product separation, and less pollutant generated. For this type of hydrogenation reaction, catalysts based on noble metals and Raney nickel catalyst have been well-studied in both industrial production and academic research<sup>[1-7]</sup>. However, it has been found that the hydrogenation process is accompanied by hydrogenolysis of the carbon—halogen bond, which significantly limits the selectivity to CANs and leads to a lot of waste. Furthermore, hydrogen chloride produced from hydrogenolysis of the carbon—halogen is also corrosive to the reactor. Therefore, many efforts have been made to overcome this problem over the past decades, including introducing special additives<sup>[8-11]</sup>, modifying the active metal with a second metal component<sup>[12,13]</sup>, tuning the particle sizes of the catalysts<sup>[11,13]</sup> and choosing suitable supports such as SnO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub><sup>[14,15]</sup>. These works pave the way for subsequent investigations on further improving the selectivity to CANs in the catalytic hydrogenation of CNBs. However, dehalogenation of CANs can not be completely inhibited over most of metal catalysts reported previously, it still remains a big challenge to develop eco-friendly heterogeneous catalysts that would ensure the selective hydrogenation of the nitro in CNBs without hydrogenolysis of the carbon—halogen.

One of the natural materials available that could be used for scientific research particularly in heterogeneous catalysis is the clay mineral. Some important properties, such as ion exchange ability, large specific surface area, considerable porosity, and thermal stability, have made them promising as catalysts or catalyst supports. Palygorskite as a natural clay mineral is widely used in different industrial fields, but it has been rarely applied in the preparation of metal catalysts<sup>[16-18]</sup>. In this paper, we report the excellent catalytic properties of palygorskite supported platinum catalysts prepared by different reduction methods. Over these catalysts, we attempted the synthesis of *para*-chloroaniline (*p*-CAN) from *para*-chloronitrobenzene (*p*-CNB). It is known that a high selectivity for *p*-CAN is difficult to maintain once the substrate has been exhausted completely over most metal-supported catalysts. What interests us is that, hydrodechlorination of *p*-CAN was fully suppressed at complete conversion by controlling the size of Pt particles on palygorskite support. The effects of the size of Pt particles and palygorskite support on the catalytic properties were also clarified.

## 1 Experimental

### 1.1 Materials and preparation of catalysts

All chemicals used in the experiments were purchased in analytical purity and used without any purification. The sample of

palygorskite (PAL) was received from Kai-Xi Co. (Gansu, China). Chemical composition (*w*, mass fraction) of the palygorskite clay was as follows: SiO<sub>2</sub> (53.34%), Al<sub>2</sub>O<sub>3</sub> (18.02%), Fe<sub>2</sub>O<sub>3</sub> (9.00%), MgO (8.13%), CaO (4.68%), Na<sub>2</sub>O (1.27%), K<sub>2</sub>O (3.83%), TiO<sub>2</sub> (0.74%), P<sub>2</sub>O<sub>5</sub> (0.28%), and SO<sub>3</sub> (0.34%). The BET surface area  $S_{\text{BET}}$  of original palygorskite was 104 m<sup>2</sup>·g<sup>-1</sup>. For palygorskite clay, acid treatment is the usual method employed for eliminating mineral impurities and increasing its surface area. Acid-activation palygorskite was performed as follows: 5.0 g of palygorskite was immersed in 80 mL of 5% (*w*) H<sub>2</sub>SO<sub>4</sub> solution at 70 °C under stirring for 4 h, and then washed with distilled water for many times until pH value of 6.0 was achieved. The resulting sample was dried under vacuum at 65 °C to constant weight and stored in the desiccator. The BET surface area of acid treated palygorskite was 198 m<sup>2</sup>·g<sup>-1</sup>.

Acid treated palygorskite supported platinum catalysts were prepared by different reduction methods. Acid treated palygorskite (0.5 g) was suspended in 10 mL aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.0398 g) containing poly(vinyl pyrrolidone) (0.0857 g) and was stirred for 4 h, the samples impregnated were reduced by a mixed solvent of ethanol-isopropanol (110 °C, 5 h), H<sub>2</sub> (300 °C, 4 h), and NaBH<sub>4</sub> (room temperature, 3 h), respectively. After filtration, the solids were washed thoroughly with deionized water and dried at 333 K under reduced pressure. The catalysts are assigned as Pt/PAL(I), Pt/PAL(II), and Pt/PAL(III) (corresponding platinum mass fraction: 2.6%, 2.9%, and 2.4%).

### 1.2 Characterization of catalysts

Chemical composition of palygorskite in mass percentage of oxides was determined by the Panalytical Company with a Magix PW 2403 XRF Spectrometer. Fourier transform infrared spectra of absorbed *n*-butylamine were recorded using a Bruker IFS66V/S spectrometer. BET surface areas were obtained by physisorption of nitrogen at 77 K using a Micromeritics ASAP2010 instrument. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2400 diffractometer equipped with a Cu K<sub>α</sub> X-ray source operating at 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG ESCA-LAB 210 instrument. The transmission electron microscopy (TEM) images of catalysts were obtained using the JEOL JEM-2010 electron microscope. The Pt content was determined by a Varian Vista MPX inductively coupled plasmamass spectrometer (ICP-MS).

### 1.3 Catalytic test

Hydrogenation of CNB was performed with magnetic stirring in a stainless autoclave. Typically, the autoclave was charged with 5 mg Pt/PAL catalyst, 3 mmol *p*-CNB, and 8 mL methanol. Air in the system was removed by sweeping the system three times with hydrogen before it was pressurized to the desired H<sub>2</sub> pressure and placed in an oil bath maintained at the reaction temperature. The hydrogenation products were analyzed by GC-112A gas chromatography with a flame ionization detector (FID) and SE-54 capillary column.

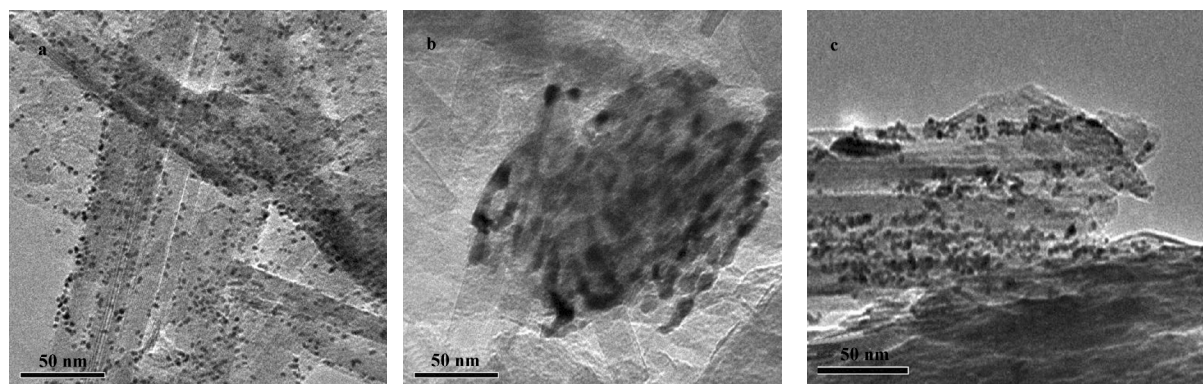


Fig.1 TEM images of (a) Pt/PAL(I), (b) Pt/PAL(II), and (c) Pt/PAL(III) catalysts

## 2 Results and discussion

In order to get detailed information about the shapes, mean size, and size distribution of metallic dispersions, Pt/PAL(I), Pt/PAL(II), and Pt/PAL(III) catalysts were examined with TEM (Fig.1). The TEM micrographs of catalysts clearly indicated that the particles were in nanometer range. The average size of Pt particles of 12.0 nm in the Pt/PAL(II) catalyst was significantly larger, which is probably due to agglomeration or sintering of partial Pt particles. The Pt particles in the Pt/PAL(I) and Pt/PAL(III) catalysts had an average size of 2.5 and 6.2 nm, respectively, which were smaller than that in the Pt/PAL(II) catalyst and homogeneously dispersed on the support.

Fig.2 shows the XRD patterns of palygorskite and supported platinum catalysts prepared by different reduction methods. The peak at  $2\theta=8.4^\circ$  had an interlayer distance ( $d$ ) of 1.04 nm and was attributed to the basal space of the palygorskite framework. The peaks at  $2\theta=20.8^\circ$ ,  $26.6^\circ$ ,  $50.1^\circ$  represented the Si-O-Si crystalline layers. The peak at  $2\theta=34.9^\circ$  was attributed to the impurities. The more intense characteristic diffraction peaks of Pt appeared at  $40^\circ$  and  $46^\circ$  in the Pt/PAL(II) catalyst, which corresponded to the (111) and (200) crystal faces. However, only one smaller and broad peak at around  $2\theta=46^\circ$  was obtained for Pt/PAL(I) and Pt/PAL(III) catalysts. According to the polycrystalline XRD theory, the weaker the diffraction peak, the smaller the dimension of Pt particles. That is to say, The XRD analysis showed that the mean size of Pt particles in the Pt/PAL(II) catalyst was significantly

larger than that in the Pt/PAL(I) and Pt/PAL(III) catalysts, which was in accordance with the TEM images.

To gain insight into the chemical states of the Pt species, the as-prepared catalysts were also characterized by XPS. The binding energies of Pt  $4f_{7/2}$  in the Pt/PAL(I), Pt/PAL(II), and Pt/PAL(III) catalysts were 70.63, 70.75, and 70.91 eV, respectively, which were very close to that of bulk Pt metal (70.9 eV)<sup>[15]</sup>. This revealed that platinum was in the form of  $Pt^0$  metal in the catalysts prepared by different reduction methods.

In order to tailor a material for a given catalytic application, it is essential to establish whether the active sites are basic or acidic. The adsorption of *n*-butylamine is widely used as a molecular probe in the characterization of acid character of solid surface. Fig.3 shows the FTIR patterns of palygorskite support absorbed with *n*-butylamine. The Lewis and Brønsted acid sites were situated at 1653 and 1468  $cm^{-1}$ , respectively.

The results of selective hydrogenation of *p*-CNB over Pt/PAL catalysts reduced by different methods are shown in Table 1. Special attention was paid to distinguish the products of the hydrogenation reaction with gas chromatography-mass spectrometry (GC-MS), *para*-chloronitrosobenzene, dichloroazoxybenzene, and dichloroazobenzenes were detected as the main intermediates in the reaction of *p*-CNB. These three kinds of 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 over Pt/PAL(I) catalyst with the extension of reaction time

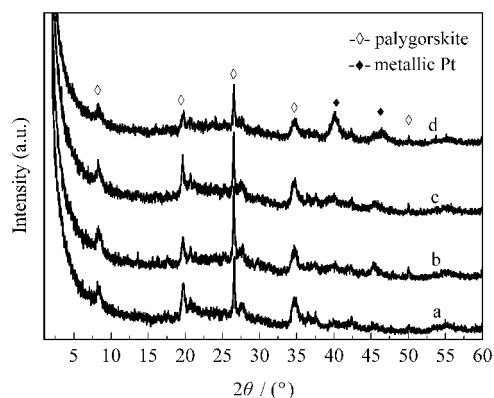


Fig.2 XRD patterns of palygorskite and Pt/PAL catalysts  
(a) palygorskite, (b) Pt/PAL(III), (c) Pt/PAL(I), (d) Pt/PAL(II)

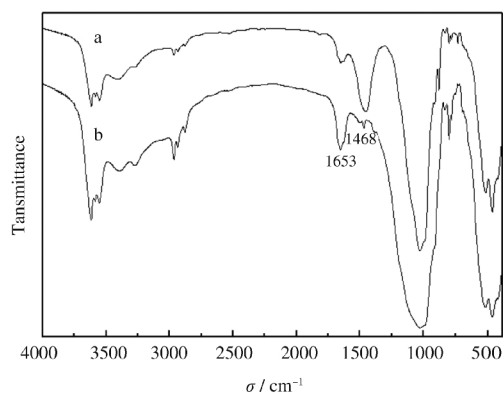


Fig.3 FTIR spectra of (a) original palygorskite and (b) acid treated palygorskite

**Table 1** Catalytic properties for the selective hydrogenation of *p*-CNB over Pt/PAL catalysts reduced by different methods<sup>a</sup>

Entry	Catalyst	<i>t</i> /min	Conversion (%)	Product selectivity(%)		
				dechlorination	<i>p</i> -CAN	others <sup>b</sup>
1	Pt/PAL(I)	5	79.5	0.08	93.6	6.32
2		10	99.9	0.16	96.9	2.94
3		18	100	0.15	99.6	0.25
4		30	100	0.13	99.7	0.17
5	Pt/PAL(II)	10	71.9	0.00	95.9	4.10
6		60	100	0.00	100	0.00
7		360	100	0.00	100	0.00
8 <sup>c</sup>		30	60.0	0.00	93.2	6.80
9	Pt/PAL(III)	10	85.0	0.12	94.2	5.68
10		162	100	0.05	99.9	0.05
11 <sup>d</sup>	Pt/PAL(II)	164	100	0.00	100	0.00
12 <sup>e</sup>		35	100	0.00	100	0.00
13 <sup>f</sup>		40	100	0.06	99.9	0.04
14 <sup>g</sup>		30	100	0.13	99.8	0.07
15	PAL	60	0.0	0.00	0.0	0.00

<sup>a</sup>reaction conditions: 5 mg catalyst, 3 mmol substrate in 8 mL methanol, 40 °C, 2 MPa H<sub>2</sub>; <sup>b</sup>Products were identified with authentic samples, and GC-MS coupling.

Other products are *para*-chloronitrosobenzene, dichloroazoxybenzene, and dichloroazobenzenes as intermediates; <sup>c</sup>atmospheric pressure and room temperature conditions; <sup>d</sup>hydrogen pressure: 1 MPa; <sup>e</sup>hydrogen pressure: 3 MPa; <sup>f</sup>reaction temperature: 80 °C; <sup>g</sup>reaction temperature: 100 °C

(Table 1, entries 1–4).

Platinum catalysts reduced by different reductants exhibited different catalytic properties for the hydrogenation of *p*-CNB. For the catalytic activity of the examined catalysts, the Pt/PAL (I) was the most active catalyst and the conversion of *p*-CNB reached almost 100% within 10 min when TOF was 27010 h<sup>-1</sup>. The Pt/PAL(III) catalyst showed better catalytic activity than the Pt/PAL(II) catalyst with the corresponding TOF of 24871 and 17193 h<sup>-1</sup>, the conversion of *p*-CNB at reaction time of 10 min was 85.0% and 71.9%, respectively. Under atmospheric pressure and room temperature conditions, the conversion of *p*-CNB was 60.0% and the selectivity reached 93.2% at reaction time of 30 min over Pt/PAL(II) catalyst. Over the Pt/PAL(II) catalyst, the selectivity of *p*-CAN could reach 100% at the complete conversion of *p*-CNB, most importantly, hydrodechlorination of the product *p*-CAN was completely suppressed even when the reaction time was extended over 5 h after *p*-CNB was exhausted. The superior selectivities of 99.7% and 99.9% *p*-CAN were also obtained over Pt/PAL(I) and Pt/PAL(III) catalysts, respectively, although dehalogenation reaction was not completely avoided. TEM images showed that the size of Pt particles of 12.0 nm in the Pt/PAL(II) catalyst was significantly larger than those in the Pt/PAL(I) (2.5 nm) and Pt/PAL(III) catalysts (6.2 nm), which suggested that hydrogenolysis of C—Cl bond was completely suppressed on larger Pt particles, this conclusion was in agreement with the result reported in previous literature<sup>[13]</sup>. So we believe that it would be possible to achieve the highest selectivity at complete CNB conversion by optimizing the size of Pt particles with palygorskite as support.

In addition, the effects of hydrogen pressure and temperature on the selective hydrogenation of *p*-CNB over Pt/PAL(II) catalyst were also tested (Table 1, entries 11–14). No loss of catalytic selectivity was observed when the H<sub>2</sub> pressure was increased from 1 to 3 MPa at 40 °C (entries 11, 6, 12). Hydrodechlorination of the product *p*-CAN occurred when reaction temperature was increased to 80 °C, moreover, the amount of dechlorination product increased when reaction temperature was further increased (entries 13, 14), which indicates that hydrogenolysis rate of C—Cl bond increases with increasing reaction temperature. Pure palygorskite was also tested, showing that hydrogenation reaction did not occur (entry 15), which clearly proves that platinum particles are the active component in the *p*-CNB hydrogenation reaction. In conclusion, the undesired hydrodechlorination reaction usually observed over most of other metal catalysts<sup>[1–7]</sup> can be successfully avoided over the Pt/PAL(II) catalyst.

The results of reusability of Pt/PAL catalysts are listed in Table 2. Among the three kinds of catalysts, the Pt/PAL(I) catalyst showed the best reusability, after being reused three times, the recovered catalyst maintained its catalytic activity. The Pt/PAL(III) catalyst exhibited a much better reusability than the Pt/PAL(II) catalyst, the catalytic activity of these two catalysts declined rapidly after the second cycle. Product *p*-CAN selectivities over Pt/PAL catalysts reduced by different methods were slightly decreased with the increasing of cycle times.

Coq *et al.*<sup>[1]</sup> studied the effect of supports on the selective hydrogenation of *p*-chloronitrobenzene over Pt-supported catalysts, among different supported platinum catalyst, 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 behavior is due to a strong metal/support interaction (SMSI) state for platinum. But 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/PAL(II) catalyst, dechlorination product was avoidable. Over Pt/PAL(I) and Pt/PAL(III) catalysts, although dehalogenation reac-

**Table 2** Reusability of Pt/PAL catalysts reduced by different methods for the selective hydrogenation of *p*-CNB<sup>a</sup>

Catalyst	Cycle	Conversion(%)	Product selectivity(%)		
			dechlorination	<i>p</i> -CAN	others <sup>b</sup>
Pt/PAL(I)	1	99.9	0.16	96.9	2.94
	2	90.2	0.12	95.2	4.68
	3	85.1	0.10	94.6	5.30
	4	83.7	0.06	93.8	6.14
Pt/PAL(II)	1	71.9	0.00	95.9	4.10
	2	61.8	0.00	93.8	6.20
	3	42.4	0.00	92.0	8.00
	4	36.4	0.00	90.0	10.00
Pt/PAL(III)	1	85.3	0.12	94.2	5.68
	2	76.8	0.10	92.8	7.10
	3	61.5	0.07	91.4	8.53
	4	56.2	0.04	90.1	9.86

<sup>a</sup>reaction conditions: 5 mg catalyst, 3 mmol substrate in 8 mL methanol, 40 °C, 2 MPa H<sub>2</sub>, 10 min; <sup>b</sup>the same as the footnote b in Table 1

tion was not avoided, dechlorination product was not increased even when the reaction time was extended over 5 h after *p*-CNB was exhausted (not shown in Table 1), which indicates that palygorskite also plays an important role in suppressing hydrodechlorination of the product *p*-CAN.

For the mechanism in the hydrodehalogenation reaction of aromatic halides, most researchers agreed that there was an electrophilic attack of cleaved hydrogen on the absorbed aromatic halides<sup>[19-21]</sup>. According to this mechanism, we think that the protection of CAN against dechlorination over Pt/PAL catalysts can be explained as follows: the amino group of the 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 acid sites of palygorskite and NH<sub>2</sub> groups of produced CAN molecules decreases electron-donating ability of NH<sub>2</sub> groups, so the hydrodechlorination of CAN is suppressed. In addition, from the point of view of catalytic activity, the Pt particles and the role of palygorskite are responsible for high activity of Pt/PAL(I) catalyst. It is well known that adsorption of substrate molecules to the surface of the catalyst is the main factor determining catalytic activity<sup>[22]</sup>. The Lewis acid sites of palygorskite are coordinated to the electronegative oxygen atom of the nitro group, therefore, the N=O bond of CNB, which is activated by electron interaction between oxygen atom of the nitro group and Lewis acid sites, becomes more susceptible to hydrogen attack, thereby promoting the hydrogenation of CNB. 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.

### 3 Conclusions

Palygorskite supported platinum catalysts prepared by different reduction methods exhibited excellent catalytic performance for the hydrogenation of *p*-CNB. The size of Pt particles and palygorskite support played an important role in catalytic properties. The results presented here highlight the great potential of palygorskite supported platinum catalysts in the selective hydrogenation of *p*-CNB on a large scale.

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