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# Selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over BNsupported Pt catalysts at room temperature



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Keywords: Boron nitride Pt/BN Selective hydrogenation Cinnamaldehyde Cinnamyl alcohol	BN-supported Pt catalysts were prepared by an impregnation method using $Pt(NH_3)_4(NO_3)_2$ as metal precursors and tested in the liquid-phase selective hydrogenation of cinnamaldehyde. It was found that the Pt/BN catalyst exhibited a high performance for the selective C=O hydrogenation at room temperature. A selectivity of over 85% towards cinnamyl alcohol at a cinnamaldehyde conversion of over 95% could be obtained. The effects of supports and Pt particle sizes were explored by N <sub>2</sub> physisorption, XRD, TEM, HRTEM, HAADF-STEM, TPD, H <sub>2</sub> - TPR, XPS, CO-DRIFTS, etc. The influences of solvents and operation conditions were investigated, and a sim- plified kinetics test was also carried out. The comparison of different supports suggested that BN with an inert surface and few acid-base sites possibly favors a simple adsorption mode of cinnamaldehyde dependent only on the supported Pt particles, resulting in a high selectivity to cinnamyl alcohol. While the abundant acid-base surface sites on the Pt/Al <sub>2</sub> O <sub>3</sub> or Pt/SiO <sub>2</sub> , possibly associated with the multiple adsorption modes of cinna- maldehyde, had an adverse effect on the selective C=O hydrogenation. The investigation of Pt size effect showed that large Pt particles with few low coordinated Pt sites displayed a higher selectivity to cinnamyl alcohol than small Pt particles with more low coordinated Pt sites on the Pt/BN catalysts. It was also revealed that water is a suitable solvent, and the presence of water in a mixture solvent is crucial for achieving a high

activity of the Pt/BN in cinnamaldehyde hydrogenation.

## 1. Introduction

Selective hydrogenation of cinnamaldehyde (CAL), a typical  $\alpha$ , $\beta$ unsaturated aldehyde, is of great scientific importance and also of industrial interest. CAL can be partially hydrogenated to hydrocinnamaldehyde (HCAL) or cinnamyl alcohol (COL), or fully hydrogenated to 3-phenylpropanol (PPL). Generally, the hydrogenation of the C=O carbonyl group to produce the unsaturated alcohol COL with a high selectivity is highly demanding, since the hydrogenation of the C=C double bond to form the saturated aldehyde HCAL is thermodynamically more favorable. Therefore, extensive efforts have been made in the past few decades to develop efficient catalyst systems and investigate the selective hydrogenation mechanism [1–4].

Platinum has been the most frequently used as an active metal for the selective hydrogenation of carbonyl groups. It is generally observed that the selectivity towards unsaturated alcohols highly depends on the morphology, size and electronic structure of Pt particles. Experimental [5–11] and theoretical [12–14] investigations suggest that large Pt

particles, more Pt(111) facets and/or fewer low coordinated Pt sites, help yielding unsaturated alcohols due to the favorable adsorption mode of the reactants, which may also be related to the surface reaction barrier and product desorption. The steric effect of adsorbed species on the metal surfaces of the catalysts, e.g., long-chain amines adsorbed on Pt-Co nanocrystals [15] or thiolates deposited on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts [16], has been demonstrated to influence the orientation of the adsorbed reactants as well, thus improving the selectivity of the C=O hydrogenation. On the other hand, for supported Pt catalysts, the supports also play an important role. It has been shown that the supports can affect the hydrogenation activities and selectivities by promoting the chemisorption and activation of carbonyl groups or adjusting the geometric and electronic properties of Pt [17-25]. Moreover, solvent effects, such as solvent polarity, hydrogen solubility as well as interactions between the catalyst and the solvent, have also been found to be significant factors in the liquid phase hydrogenation of CAL [22,26-28]. Up to now, although much progress in CAL hydrogenation has been made, the selective hydrogenation mechanism is still

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not entirely clear due to the complexity of catalysts and reaction systems, and the catalyst with a high activity and high COL selectivity at ambient conditions is still quite challenging.

Hexagonal boron nitride (h-BN) has large thermal conductivity, superior temperature stability, excellent acid-base resistance and specific coordinatively unsaturated edge sites, which can be used as catalyst supports [29–32] or a catalyst [33] in various catalytic reactions. Previous reports showed that a Pt catalyst supported on h-BN gave near 100% selectivity of the C=C hydrogenation in the temperature range of 30–100 °C for a vapor phase hydrogenation of crotonaldehyde [34], and the addition of Sn [35] or Fe [36] could enhance the selectivity of the C=O hydrogenation. In this work, the liquid phase selective hydrogenation of CAL over Pt/BN catalysts was explored, where the Pt/BN exhibited a high performance for the selective C=O hydrogenation to COL at room temperature. The effects of supports and Pt particle sizes were examined by N<sub>2</sub> physisorption, XRD, TEM, HRTEM, HAADF-STEM, NH<sub>3</sub>-TPD, CO<sub>2</sub>-TPD, H<sub>2</sub>-TPR, XPS, CO-DRIFTS, etc. The influences of solvents and operation conditions were also investigated.

#### 2. Experimental section

# 2.1. Catalyst preparation

The Pt/BN catalysts with a targeted Pt loading of 1.0 wt.% were prepared by impregnating h-BN (~25 m<sup>2</sup>/g, Aladdin, Shanghai) with aqueous Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Sino-Platinum, Kunming) solution. The impregnation mixture was dried by rotary evaporator at 50 °C for 2 h after stirring well, and further dried in an oven at 110 °C overnight. The dried sample, denoted as Pt/BN-Dry110, was reduced at 200, 300 and 400 °C for 1 h in a flow of hydrogen, and the obtained catalyst was denoted as Pt/BN-R200, Pt/BN-R300 and Pt/BN-R400, respectively. For comparison, the Pt catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and graphite were prepared by the same procedure as Pt/BN-R300. An extra Pt/BN catalyst, denoted as Pt-Cl/BN-R300, was also prepared by the same procedure as Pt/BN-R300 except that H<sub>2</sub>PtCl<sub>6</sub> was used as metal precursors.

## 2.2. Characterization

Nitrogen adsorption-desorption isotherms were recorded at 77 K on a Micromeritics ASAP 2020 instrument. Before the measurements, the samples were degassed at 250 °C for 6 h. The specific surface area was calculated by multipoint BET model, and the pore volume was obtained based on the adsorption at  $P/P_0 \approx 1$ .

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Rint D/MAX-2500/PC diffractometer using Cu K $\alpha$  radiation operated at 40 kV and 40 mA.

Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were taken on an FEI Tecnai G2F30 or G220 microscope using different modes. The specimen was prepared by ultrasonically dispersing the sample powder in ethanol, and drops of the suspension were deposited on a carbon-coated copper grid and dried in air.

X-ray photoelectron spectroscopy (XPS) data were collected by a Thermo Fisher Escalab 250Xi equipped with an Al K $\alpha$  monochromatic X-ray source (1486.6 eV) under ultrahigh vacuum condition (< 10<sup>-7</sup> Pa). The adventitious carbon 1 s peak was calibrated at 284.8 eV to compensate for any charging effects.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) or carbon dioxide (CO<sub>2</sub>-TPD), and temperature-programmed reduction (TPR) experiments were carried out on a Micromeritics Auto Chem 2920 instrument equipped with a thermal conductive detector (TCD). For NH<sub>3</sub>-TPD, 100 mg of the catalyst was initially heated in an 80 ml/ min of N<sub>2</sub> to 300 °C at a rate of 10 °C/min and held at this temperature for 0.5 h. After cooling to 100 °C under the N<sub>2</sub> flow, a 5% NH<sub>3</sub>/N<sub>2</sub> in a loop of 1 ml was periodically introduced until saturated adsorption. Then the sample was purged with N<sub>2</sub> for 0.5 h to remove the weakly adsorbed NH<sub>3</sub>. Finally, the sample was heated in N<sub>2</sub> from 100 to 700 °C at a rate of 10 °C/min. For CO<sub>2</sub>-TPD, a 40 ml/min of 5% CO<sub>2</sub>/He was introduced for 1 h to achieve the adsorption equilibrium at 50 °C, and 50–800 °C was used as the desorption temperature range. For TPR, the samples without pre-reduction were tested under a 5% H<sub>2</sub>/Ar atmosphere in a temperature range of 0–800 °C, and the interference of water and other products derived from the reduction or decomposition process on the TCD signal of H<sub>2</sub> consumption was eliminated by an isopropanol-liquid nitrogen trap. Another set of TPR experiments in a temperature range of -50–800 °C was also carried out using the prereduced and re-oxidized samples. Before TPR, the dried samples were pre-reduced at 300 °C for 1 h in a flow of hydrogen and then re-oxidized at 300 °C for 2 h in a flow of dry air.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data of CO adsorbed on Pt/BN catalysts were collected on a Nicolet 6700 spectrometer equipped with a diffuse reflectance accessory and a MCT/A detector. A high-temperature cell connected to a gas flow control and vacuum system was used for the in-situ reduction of catalysts and CO adsorption. The sample in the cell was reduced according to preparation conditions, purged with He for 0.5 h, and then cooled to 25 °C. After vacuum degassing for 0.5 h, the background spectrum was recorded. Subsequently, CO was introduced and the pressure was gradually increased from 0.25 to 50 mbar, and then the physically adsorbed CO was evacuated by again vacuum degassing. The CO adsorption spectra under different CO pressures and vacuum were collected using 16 scans referenced to the background spectrum.

# 2.3. Catalytic test

The liquid phase selective hydrogenation of CAL was carried out in a 50 ml autoclave equipped with a magnetic stirrer. The mass transfer limitation was eliminated when an agitation speed of 1732 rpm was used. In a typical reaction, 5.0 mmol of CAL, 16.0 ml of isopropanol, 4.0 ml of water, 0.2 ml of n-tetradecane and 100 mg of Pt catalysts were charged into the reactor, which was flushed with N2 for 6 times and further pressurized with H<sub>2</sub> to the desired pressure. Then the reaction temperature was raised to the desired value and agitation was started. After different reaction periods, the products were analyzed by an Agilent 7890B gas chromatograph equipped with a flame ionizing detector (FID) and a HP Innowax capillary column. The conversion of CAL and the selectivity of products were calculated on the basis of the mass balance of carbon using n-tetradecane as an internal standard. In the experiments on solvent effect, a total amount of the solvent added was kept at 20 ml. In some kinetics measurements, a constant H<sub>2</sub> pressure was kept. All the experiments were conducted in triplicate for reproducibility of the data and the results were within an error of  $\pm$  5%.

#### 3. Results and discussion

# 3.1. CAL hydrogenation over the Pt/BN and the effect of supports

Table 1 compares the catalytic performance of the Pt catalysts supported on BN and other three common supports,  $Al_2O_3$ ,  $SiO_2$  and graphite. A CAL conversion of 95.8% with the COL selectivity of 85.2% was achieved over the Pt/BN at room temperature. For CAL hydrogenation, the BN supported Pt exhibited an unexpected high activity and high selectivity of C=O hydrogenation, which was far better than Pt/Al\_2O\_3, Pt/SiO\_2 and Pt/G, as shown in Table 1. The Pt/Al\_2O\_3 displayed a higher HCAL selectivity (49.8%) and a lower COL selectivity (34.1%), and the same order could be observed on the Pt/SiO\_2, indicating that the C=C hydrogenation is preferential on both of the catalysts. Similar to the Pt/BN, the Pt/G also exhibited a considerable COL selectivity, but its activity was too low. The BN alone had little activity for CAL hydrogenation.

In order to elucidate the great difference in the catalytic

#### Table 1

Catalytic performance of the Pt catalysts over different supports for cinnamaldehyde hydrogenation.

Catalyst	CAL Conversion (%)	Selectivity (%)			Carbon Balance (%)
		COL	HCAL	PPL	
BN	0.8	11.6	6.1	15.9	33.6
Pt/BN	95.8	85.2	5.1	9.7	100.0
Pt/Al <sub>2</sub> O <sub>3</sub>	79.2	34.1	49.8	16.6	100.5
Pt/SiO <sub>2</sub>	63.1	27.4	51.1	24.8	103.3
Pt/G	7.2	80.7	7.9	11.6	100.2

Reaction condition: CAL, 5.0 mmol; isopropanol, 16 ml; H<sub>2</sub>O, 4.0 ml; n-tetradecane, 0.2 ml; catalyst loading, 100 mg; agitation speed, 1732 rpm; temperature, 25 °C; initial H<sub>2</sub> pressure, 4.0 MPa; reaction period, 2.0 h. The BN support and all of the Pt-based catalysts using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as metal precursors were reduced at 300 °C for 1 h in a flow of hydrogen before catalytic tests. G denotes the graphite support. CAL, COL, HCAL and PPL stands for cinnamaldehyde, cinnamyl alcohol, hydrocinnamaldehyde and phenylpropanol, respectively.

performance of the Pt-based catalysts over different supports, the physicochemical properties of the four catalysts were characterized by means of various technologies and summarized in Table 2.

 $\rm N_2$  physisorption measurements showed that loading Pt had not significantly changed the geometric characteristics of the supports, as the specific surface areas and pore volumes of the four catalysts and the corresponding supports were almost the same. Atomic absorption spectrometry tests showed that the actual Pt content, for all of the four catalysts, was slightly lower than the targeted Pt loading of 1.0 wt.%, which was in a range of 0.83-0.95 wt.%.

The XRD patterns of the Pt catalysts over different supports are depicted in Fig. 1. For the Pt/BN, a series of peaks at 26.8, 41.7, 43.9, 50.3, 55.2 and 76.1° corresponding to the (002), (100), (101), (102), (004) and (110) diffractions of hexagonal boron nitride could be observed. In addition to the diffractions derived from the support BN, three peaks at 39.8, 46.3 and 67.5° appeared, which could be indexed to the (111), (200) and (220) diffractions of face-centered cubic Pt metal, suggesting a reduction of Pt species. The similar diffractions of metallic Pt could also be observed on the other three catalysts. Using Debye-Scherrer formula, the crystallite sizes of X-ray detectable metallic Pt on different catalysts were estimated and listed in Table 2. The Pt crystallite sizes on Pt/BN (13.6 nm) and Pt/G (25.3 nm) were larger than those on Pt/Al<sub>2</sub>O<sub>3</sub> (4.6 nm) and Pt/SiO<sub>2</sub> (6.9 nm), which was possibly responsible for the higher selectivity of C=O hydrogenation on Pt/BN and Pt/G (both higher than 80%). This seems in accordance with the previous reports on Pt size effect in CAL hydrogenation [5,7,9]. The selectivity for the C=O bond hydrogenation increased with increasing crystallite size due to repulsive interactions between the phenyl ring and the large metal crystallites, which resulted in tilted adsorption of CAL, hindering the C=C bond to approach the metal surface and favoring the approaching of the C=O bond. This repulsive effect was



Fig. 1. XRD patterns of the Pt catalysts over different supports. All of the catalysts were prepared using  $Pt(NH_3)_4(NO_3)_2$  as metal precursors and were reduced at 300 °C for 1 h in a flow of hydrogen before tests. G denotes the graphite support.

absent with smaller metal crystallites, so the C=O and the C=C bonds could approach the metal surface. On the other hand, large Pt particles generally have a high fraction of (111) planes and a low fraction of low-coordinated Pt sites. Theoretical calculations [12] have demonstrated that CAL prefers the adsorption via the C=O bond on Pt(111), via both the C=O and C=C bonds on Pt(100), and via the C=C bond or both the C=O and C=C bonds on the low-coordinated Pt sites. These different adsorption modes cause different product distributions, therefore large Pt particles with a high fraction of (111) planes displayed a higher COL selectivity. Obviously, the too large Pt size on Pt/G due to a weak dispersive ability of the graphite support with a low surface area reduced the number of Pt active sites, causing the low activity of Pt/G despite its high COL selectivity.

Fig. 2 shows the TEM images of the Pt catalysts over different supports. The corresponding size statistics of Pt particles is given in Fig. S1, and the average particle sizes are listed in Table 2. It could be found that, for Pt/BN, the Pt particle size (4.4 nm) from the TEM statistics was

Table 2							
Physicochemical	properties	of	the Pt	catalysts	over	different s	upports.

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Catalyst <sup>a</sup>	BET surface area <sup>b</sup> (m <sup>2</sup> /g)	Pore volume <sup>b</sup> (cm <sup>3</sup> /g)	Pt content <sup>c</sup> (wt.%)	Pt crystallite size <sup>d</sup> (nm)	Pt particle size <sup>e</sup> (nm)	NH <sub>3</sub> -TPD (μmol/g)	CO <sub>2</sub> -TPD (µmol/g)
Pt/BN	24.3 (25.8)	0.137 (0.135)	0.87	13.6	4.4 (4.0)	35	45
Pt/Al <sub>2</sub> O <sub>3</sub>	138 (140)	0.663 (0.632)	0.95	4.6	7.6	614	355
Pt/SiO <sub>2</sub>	357 (365)	1.345 (1.158)	0.83	6.9	7.3	427	206
Pt/G	4.6 (4.2)	0.024 (0.019)	0.85	25.3	73	5	9

<sup>a</sup> All of the Pt-based catalysts were prepared using  $Pt(NH_3)_4(NO_3)_2$  as metal precursors with a targeted Pt loading of 1.0 wt.% and were reduced at 300 °C for 1 h in a flow of hydrogen before tests. G denotes the graphite support.

<sup>b</sup> Calculated by N<sub>2</sub> adsorption-desorption. The BET surface area and pore volume of the corresponding supports are given in parentheses.

<sup>c</sup> Measured by atomic absorption spectrometry.

<sup>d</sup> Estimated by XRD.

<sup>e</sup> From TEM statistics (see Fig. S1). The datum in parentheses is derived from the statistics of HAADF-STEM images (see Fig. 5b).



Fig. 2. TEM images of the Pt catalysts over different supports. (a, b) Pt/BN. (c, d) Pt/Al<sub>2</sub>O<sub>3</sub>. (e, f) Pt/SiO<sub>2</sub>. (g, h) Pt/G. All of the catalysts were prepared using Pt  $(NH_3)_4(NO_3)_2$  as metal precursors and were reduced at 300 °C for 1 h in a flow of hydrogen before tests. G denotes the graphite support.



**Fig. 3.** H<sub>2</sub>-TPR profiles of the Pt catalysts over different supports. Before tests, the dried samples were purged at 110 °C for 1 h in a flow of helium or prereduced at 300 °C for 1 h in a flow of hydrogen and then re-oxidized at 300 °C for 2 h in a flow of dry air. G denotes the graphite support.

lower than the crystallite size from the XRD measurements. The possible reason is that lots of Pt particles smaller than 3 nm were present on the Pt/BN (see Fig. S1), which were beyond the XRD detection limit. These small Pt particles, mainly located on the coordinatively unsaturated edge sites of BN, were counted in the TEM statistics and in turn they pulled down the numerical average value of Pt particle size in the TEM statistics. It should be noted that more than 20 TEM images of the Pt/BN were taken at random to ensure the representativeness of size statistics, and the HAADF-STEM statistics (Fig. 5b) also confirmed this average Pt particle size of about 4 nm on the Pt/BN. In fact, the Pt/BN with a higher COL selectivity had a lower average Pt size in contrast to the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, thus this difference in COL selectivity on the Pt-based catalysts over different supports cannot be explained solely by the size effect of Pt, which requires further investigations.

Fig. 3 shows the H<sub>2</sub>-TPR profiles of the Pt catalysts without prereduction and the pre-reduced and re-oxidized ones over different supports. For the Pt/BN without pre-reduction, two H<sub>2</sub> consumption peaks at 128 and 162 °C, and a shoulder at 200 °C could be observed, indicating a triple-stage reduction process. The reduction process of the dried Pt/BN catalyst was monitored simultaneously by an on-line MS to analyze the reductive products (see Fig. S2). After the Pt/BN was prereduced and re-oxidized, the TPR profile showed that the H<sub>2</sub> consumption amount significantly decreased, and the decreased amount was much more than the difference in theoretical hydrogen consumption between the reduction of  $Pt(NH_3)_4(NO_3)_2$  and Pt oxide. Obviously, the pre-reduced Pt supported on BN could not be completely re-oxidized, which is related to the low bonding strength between Pt and BN, as previous report [29] suggested. For the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, the pre-reduced and re-oxidized samples displayed relatively large H2 consumption amount, indicating a more complete re-oxidation and thus a higher bonding strength between Pt and supports. Moreover, the Pt/ Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, either dried samples or pre-reduced and re-oxidized ones, displayed higher temperatures of H<sub>2</sub> consumption peaks compared with the corresponding Pt/BN, whereas the Pt/G showed the lowest one. According to the temperatures of H<sub>2</sub> consumption peaks, it



**Fig. 4.**  $NH_3$  (a) and  $CO_2$  (b) TPD profiles of the Pt catalysts over different supports. All of the catalysts were prepared using  $Pt(NH_3)_4(NO_3)_2$  as metal precursors and were reduced at 300 °C for 1 h in a flow of hydrogen before tests. G denotes the graphite support.

could be found that the relative reducibility of the Pt species followed the order of Pt/G > Pt/BN > Pt/SiO<sub>2</sub> > Pt/Al<sub>2</sub>O<sub>3</sub>, implying a reverse order of the interaction strength between the supports and the Pt species to a large extent. It is reasonable that the Pt/BN and Pt/G exhibited weak support-metal interactions because both BN and graphite have inert surfaces, while Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with a large surface area have rich surface defects and hydroxyl groups, so relatively strong support-metal interactions existed on the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>. Maybe the different support-metal interactions also affected the COL selectivity on the Pt catalysts. However, for the non-reducible supports used here, the support-metal interaction is limited, acid-base property is a more critical factor related to catalysis. Therefore, NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD were performed to examine the acidity and basicity of the four Pt catalysts.

As shown in Fig. 4, only a small amount of NH<sub>3</sub> and CO<sub>2</sub> desorption could be observed on the Pt catalysts supported on the inert BN and graphite, while the large amount of NH<sub>3</sub> and CO<sub>2</sub> were desorbed at different temperatures on the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, indicating that the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub> had abundant acidic and basic surface sites with different strength. The densities of acidic and basic sites on different catalysts were also listed in Table 2. In combination with the results of CAL hydrogenation, it seems that the abundant acidic and basic sites on the Pt/Al<sub>2</sub>O<sub>3</sub> or Pt/SiO<sub>2</sub> had an adverse effect on the COL selectivity, whereas the Pt/BN or Pt/G with few acid-base sites exhibited a high COL selectivity. This is possibly related to the adsorption and activation of CAL on different catalysts. A reasonable speculation is that the support with abundant surface groups could provide extra adsorption sites other than that related to Pt, which made the adsorption more complicated, causing diverse adsorption modes of CAL on the Pt/Al<sub>2</sub>O<sub>3</sub> or Pt/SiO<sub>2</sub>. So either the C=C or the C=O, or both were activated at



**Fig. 5.** Typical HAADF-STEM images of different Pt/BN catalysts and the corresponding Pt particle size statistics. (a) Pt/BN-R200. (b) Pt/BN-R300. (c) Pt/BN-R400. (d) Pt-Cl/BN-R300. The insert HRTEM image in (b) shows the clear lattice fringes attributed to the Pt (111) and h-BN (002). The frequency of count × size<sup>2</sup> represents the contribution of the Pt particles with different sizes to the total Pt surface area. Pt/BN-R200, -R300 and -R400 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 200, 300 and 400 °C, respectively. Pt-Cl/BN-R300 reduced at 300 °C.

different adsorption sites, and the C=C hydrogenation was relatively preferential due to a favorable thermodynamics. For the Pt/BN or Pt/G, the adsorption of CAL depended only on Pt, since there was almost no effect of the supports. As a result, a high COL selectivity was achieved on the Pt/BN or Pt/G when the property of Pt particles was suitable for C=O adsorption and activation. CAL-TPD experiments (see Fig. S3) confirmed the effect of different supports on CAL adsorption.

A previous report [34] showed that a Pt/BN catalyst gave near 100% selectivity of the C=C hydrogenation in a vapor phase crotonaldehyde hydrogenation, which is obviously different from the above selectivity result of CAL hydrogenation. This is most likely due to the structure characteristics different from CAL that crotonaldehyde has no phenyl ring. So there is no repulsive interaction between crotonaldehyde and Pt surface, causing that the C=C bond in crotonaldehyde is easy to approach the Pt surface and then be hydrogenated. While the repulsive effect of the phenyl ring in CAL hindered the C=C bond to approach the Pt surface, favoring a high selectivity of unsaturated alcohols. Moreover, different reaction modes and different catalyst preparation procedures might contribute to the discrepancy of selectivity for crotonaldehyde and CAL hydrogenation.

Considering the weak support-metal interaction and few acid-base sites, the Pt/BN is especially suitable for the study on the size effect of the Pt particles in CAL hydrogenation. Thus in the next section, a series of Pt/BN catalysts were prepared and investigated with focus on the size effect of Pt.

#### 3.2. Effect of Pt particle sizes

Fig. 5 shows the HAADF-STEM images of different Pt/BN catalysts and the corresponding Pt particle size statistics. By means of varying the reduction temperatures, three Pt/BN catalysts with different Pt sizes were successfully prepared, as shown in Fig. 5a–c. It could be found that higher reduction temperatures resulted in larger Pt particles. The average Pt size of Pt/BN-R200, -R300 and -R400 was  $3.2 \pm 0.2$ ,  $4.0 \pm 0.2$  and  $4.6 \pm 0.3$  nm, respectively. The CAL hydrogenation tests (Fig. 6) gave the COL selectivity of 81.7, 85.2 and 86.3% over Pt/ BN-R200, -R300 and -R400, indicating large Pt particles do favor unsaturated alcohols, which is in line with the previous literature [5,7,9]. Note, the Pt/BN catalysts in this work had a broad size distribution, and 58.7, 41.1 and 36.9% of Pt particles were smaller than 3 nm over Pt/ BN-R200, -R300 and -R400. According to the previous report [5], metal particles smaller than 3 nm should lead to a lower COL selectivity.



**Fig. 6.** Catalytic performance of different Pt/BN catalysts for CAL hydrogenation. Reaction condition: CAL, 5.0 mmol; isopropanol, 16 ml; H<sub>2</sub>O, 4.0 ml; ntetradecane, 0.2 ml; catalyst loading, 100 mg; agitation speed, 1732 rpm; temperature, 25 °C; initial H<sub>2</sub> pressure, 4.0 MPa; reaction period, 2.0 h. Pt/BN-R200, -R300 and -R400 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 200, 300 and 400 °C, respectively. Pt-Cl/BN-R300 stands for the catalyst using H<sub>2</sub>PtCl<sub>6</sub> as precursors and reduced at 300 °C. CAL, COL, HCAL and PPL stands for cinnamaldehyde, cinnamyl alcohol, hydrocinnamaldehyde and phenylpropanol, respectively.

Another literature [37] also suggested that the COL selectivity is independent of the Pt size in a range of 1.5-2.5 nm. This seems to contradict our results that the Pt/BN catalysts showed a high COL selectivity (> 80%), although lots of small Pt particles existed. However, taking into account the contribution of the Pt particles with different sizes to the total Pt surface area, only 12.4, 8.7 and 4.3% of the total Pt surface area was derived from the Pt particles smaller than 3 nm over Pt/BN-R200, -R300 and -R400. Therefore, the effect of these small particles on CAL hydrogenation is not as great as it seems by counting statistics.

By comparing the CAL conversions between the Pt/BN-R200 (83%) and Pt/BN-R300 (95.8%), it could be found that the Pt/BN-R200 with smaller Pt particles displayed a lower activity for CAL hydrogenation, which is possibly due to an incomplete reduction of Pt. The TPR profile of the dried Pt/BN (Fig. 3) showed that a tailing peak of H<sub>2</sub> consumption extended to about 250 °C, which is higher than the reduction temperature of 200 °C used for the Pt/BN-R200 preparation. The presence of non-reductive Pt might decrease the number of effectively exposed metallic Pt active sites on the Pt/BN-R200, and thus resulting in a lower activity. This incomplete reduction of Pt on the Pt/BN-R200 was also corroborated by XPS analysis.

Fig. 7 shows the N1 s, B1 s and Pt4f XPS spectra of different Pt/BN catalysts. The binding energies (B.E.) and ascriptions of different species and the Pt/B ratios on different Pt catalysts are summarized in Table 3. For all of the samples, two main B.E. peaks at about 190.5 and 398.1 eV could be attributed to the B1 s and N1 s of the support BN. For the dried sample Pt/BN-Dry110, two well separated spin-orbit components at 73.7 and 76.9 eV were corresponded to the Pt4f<sub>7/2</sub> and Pt4f<sub>5/2</sub> of the Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> precursors. The additional N1 s B.E. peaks at 400.8 and 406.6 eV could be observed, which were derived from the NH<sub>3</sub> and NO<sub>3</sub><sup>-</sup> of the Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> precursors. After a reduction at 200 °C, most of Pt were reduced to metallic state evidenced by a  $Pt4f_{7/2}$ B.E. of 71.1 eV, and a few of it gave a Pt4f<sub>7/2</sub> B.E. of 72.5 eV corresponding to Pt<sup>2+</sup>, indicating an incomplete reduction of Pt. The B.E. peak of NH<sub>3</sub> completely disappeared, and the peak of NO<sub>3</sub><sup>-</sup> attenuated significantly and moved to a lower B.E., corresponding to NO<sub>2</sub><sup>-</sup>. When the reduction temperature was increased, all of Pt were reduced to metallic state, and all of N from the precursors were removed, as shown on the Pt/BN-R300 and Pt/BN-R400. The Pt/B atomic ratio can reflect the dispersion of Pt, and a larger Pt/B ratio represents a higher dispersion of Pt, i.e., smaller Pt particles. The Pt/B ratios on different Pt catalysts shown in Table 3 are consistent with the Pt particle size statistics in Fig. 5.

Fig. 8 shows the DRIFTS spectra for CO adsorption on different Pt/ BN catalysts and the corresponding fitting curves of linear CO chemisorption. With the increasing CO pressure, linearly adsorbed and bridge-adsorbed CO on metallic Pt surface, and gaseous CO could be observed in the frequency range of 2000-2100, 1800-1900 and 2100–2200 cm<sup>-1</sup>, respectively. After a high-vacuum treatment, CO chemisorption spectra were obtained. The linearly adsorbed CO frequency on the Pt/BN-R200, -R300 and -R400 was 2052, 2063 and  $2072 \text{ cm}^{-1}$ , respectively, which indicates the extent of the electron back-donation from Pt particles to the CO molecule. It seems that the increasing size of Pt particles resulted in the decreasing electron backdonation, as evidenced by the blue shift of CO frequency. The linearly adsorbed CO curves were also fitted and separated into three peaks: CO adsorption on the Pt(111) facet, on the Pt(100) facet and at low coordinated Pt sites, such as steps, edges, corners and defect sites [11]. Consistent with the common understanding, the smallest Pt particles on the Pt/BN-R200 had the fewest Pt(111) components and the most low coordinated Pt sites, while the largest Pt particles on the Pt/BN-R400 had the most Pt(111) components and the fewest low coordinated Pt sites. These different structural features caused the difference in COL selectivity of the Pt/BN catalysts.

Maybe the Pt<sup>2+</sup> on the Pt/BN-R200 affected the COL selectivity in CAL hydrogenation, causing that the above conclusion on Pt size effect



Fig. 7. N1 s, B1 s and Pt4f XPS spectra of different Pt/BN catalysts. Pt/BN-Dry110, -R200, -R300 and -R400 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and dried at 110 °C or reduced at 200, 300 and 400 °C, respectively. Pt-Cl/BN-R300 stands for the catalyst using H<sub>2</sub>PtCl<sub>6</sub> as precursors and reduced at 300 °C.

Table 3					
XPS binding energies,	ascriptions	and Pt/B	ratios of	different Pr	catalysts

Sample	Binding Energy / eV		Near-surface atomic ratio Pt/B ( $\times 10^{-3}$ )	
	Pt4f7/2	B1 s	N1 s	
Pt/BN-Dry110	73.67, [Pt(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	190.56, BN	398.17, BN (94.3%) 400.77, -NH <sub>3</sub> (3.2%) 406.63, NO <sub>3</sub> <sup>-</sup> (2.5%)	5.90
Pt/BN-R200	71.12, Pt° (79%) 72.50, Pt <sup>2+</sup> (21%)	190.52, BN	398.14, BN 405.89, NO <sub>2</sub> <sup>-</sup> (trace)	1.02
Pt/BN-R300	71.19, Pt°	190.45, BN	398.05, BN	0.97
Pt/BN-R400	71.24, Pt°	190.50, BN	398.10, BN	0.79
Pt-Cl/BN-R300	71.21, Pt°	190.46, BN	398.07, BN	1.17

Pt/BN-Dry110, -R200, -R300 and -R400 stands for the catalyst using  $Pt(NH_3)_4(NO_3)_2$  as precursors and dried at 110 °C or reduced at 200, 300 and 400 °C, respectively. Pt-Cl/BN-R300 stands for the catalyst using  $H_2PtCl_6$  as precursors and reduced at 300 °C.

are questionable. In order to completely eliminate the influence of  $Pt^{2+}$ , a fully reduced catalyst Pt-Cl/BN-R300 with the smallest Pt particles was prepared using H<sub>2</sub>PtCl<sub>6</sub> as metal precursors. The average Pt size on the Pt-Cl/BN-R300 was 2.3  $\pm$  0.1 nm (Fig. 5d). XPS showed that all of Pt on the Pt-Cl/BN-R300 were reduced to metallic state. As expected, the Pt-Cl/BN-R300 with the smallest Pt particles exhibited the lowest COL selectivity of 65.2% at a CAL conversion of 97.6%, which well supported the size effect of Pt on COL selectivity.

#### 3.3. Effect of solvents

As shown in Table 4, four polar solvents were used to explore the solvent effect on CAL hydrogenation over the Pt/BN catalyst. It was found that the solvent polarity had a considerable impact on the activity and selectivity. The lowest CAL conversion (2.5%) and the lowest COL selectivity (40.7%) were obtained in the aprotic dioxane with the weakest polarity, while the CAL conversion was increased to over 10%, and the COL selectivity was about 80% in the protic isopropanol or ethanol with stronger polarity. When water with the strongest polarity was used as a solvent in CAL hydrogenation, both CAL conversion and COL selectivity were more than 80%. And the CAL conversion could be further increased by using a mixture solvent of isopropanol and water, which is possibly due to a higher solubility of hydrogen. It seems that the polar C=O is more easily activated and converted than nonpolar C=C in the protic solvent with stronger polarity. Therefore the presence of water is crucial for achieving a high activity of the Pt/BN in

CAL hydrogenation.

The strong bases (e.g., NaOH, KOH) in reaction media were found to enhance both catalyst activity and selectivity to COL by suppressing side reactions or promoting the adsorption and activation of carbonyl group in several reports [1,21,22,38]. However, adding strong bases had no effect on the catalytic performance of the Pt/BN catalysts in a mixture solvent of isopropanol and water. Moreover, no acetals or other by-products could be observed over the Pt/BN catalysts in almost all the tests. The Pt/BN with few acidic and basic sites inhibited the occurrence of possible side reactions.

# 3.4. Effect of operation conditions and a simplified kinetics test

Fig. 9 shows the CAL conversion and COL selectivity over the Pt/BN as a function of reaction time,  $H_2$  pressure, reaction temperature and catalyst reuse times. It could be found that in a reaction period of 2 h, the CAL conversion gradually increased to over 95% with the prolongation of reaction time, while the COL selectivity remained almost constant at about 85%, suggesting that the COL selectivity was independent of the CAL conversion. An increasing PPL selectivity, indicating that the PPL was mainly derived from the further hydrogenation of the HCAL. The effect of  $H_2$  pressure on CAL conversion was also greater than that on COL selectivity slightly decreased with an increasing  $H_2$  pressure. In general, the hydrogenation rates usually



Fig. 8. DRIFTS spectra for CO adsorption on different Pt/BN catalysts and the corresponding fitting curves of linear CO chemisorption. Pt/BN-R200, -R300 and -R400 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 200, 300 and 400 °C, respectively.

#### Table 4

Effect of solvents on cinnamaldehyde hydrogenation over the Pt/BN-R300 catalyst.

Solvent	Dielectric	Conversion of CAL (%)	Select	tivity (%)	Carbon	
	constant		COL	HCAL	PPL	(%)
Dioxane Isopropanol Ethanol Water 50 v.% Isopropanol / Water 80 v.% Isopropanol / Water	2.25 18.3 25.7 80.1 43.7 24.4	2.5 11.6 12.3 85.1 93.7 95.8	40.7 79.0 85.7 83.2 83.6 85.2	20.3 9.9 7.7 6.7 4.5 5.1	30.6 8.6 7.1 9.2 11.7 9.7	91.6 97.5 100.5 99.1 99.8 100.0

Reaction condition: CAL, 5.0 mmol; solvent, 20 ml; n-tetradecane, 0.2 ml; catalyst loading, 100 mg; agitation speed, 1732 rpm; temperature, 25 °C; initial H<sub>2</sub> pressure, 4.0 MPa; reaction period, 2.0 h. The Pt/BN-R300 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 300 °C. CAL, COL, HCAL and PPL stands for cinnamaldehyde, cinnamyl alcohol, hydrocinnamaldehyde and phenylpropanol, respectively.

increase with increasing temperatures. However, an activity maximum was observed at 40–50 °C in the present system. The higher temperature led to the decrease in CAL conversion, possibly due to the partial deactivation of the catalyst caused by some side reactions, which were more likely to occur at high temperatures. When the Pt/BN catalyst was reused for three times under the selected conditions, the CAL conversion and COL selectivity did not decrease, but increased a little, showing that the Pt/BN catalyst is quite stable in CAL hydrogenation.

Fig. 10 shows the kinetics test result of CAL hydrogenation over the Pt/BN catalyst under a constant  $H_2$  pressure of 4.0 MPa. In a temperature range of 15–45 °C, linear plots of  $ln(C_0/C)$  versus reaction time

could been obtained, indicating that the reaction under the constant  $\rm H_2$  pressure follows pseudo first order kinetics for CAL. The corresponding Arrhenius plots were given in Fig. 10b, and the apparent activation energy of CAL hydrogenation over the Pt/BN catalyst was estimated to be 35.0  $\pm$  5.0 KJ/mol. The reaction order with respect to catalyst amount was also examined by varying the catalyst loading from 25 to 100 mg. The initial reaction rate versus catalyst amount displayed good linearity, showing a first order kinetics with respect to catalyst amount. However, the plot of initial reaction rate versus catalyst amount did not pass through the origin, which was possibly caused by catalyst poisoning.

## 4. Conclusions

BN-supported Pt catalysts were prepared by an impregnation method using  $Pt(NH_3)_4(NO_3)_2$  as metal precursors and tested in the liquid-phase selective hydrogenation of CAL. It was found that the Pt/ BN catalyst exhibited a high performance for the selective C=O hydrogenation at room temperature. The comparison of different supports suggested that BN with an inert surface and few acid-base sites possibly favors a simple adsorption mode of CAL dependent only on the supported Pt particles, resulting in a high selectivity to COL. The investigation of Pt size effect showed that large Pt particles with few low coordinated Pt sites displayed a higher selectivity to COL than small Pt particles with more low coordinated Pt sites on the Pt/BN catalysts. It was also revealed that water is a suitable solvent, and the presence of water in a mixture solvent is crucial for achieving a high activity of the Pt/BN in CAL hydrogenation.

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Fig. 9. Effect of reaction conditions on cinnamaldehyde hydrogenation over the Pt/BN-R300 catalyst. (a) Reaction time. (b) Initial  $H_2$ pressure. (c) Temperature. (d) Reuse times. Typical reaction condition: CAL, 5.0 mmol; isopropanol, 16 ml; H<sub>2</sub>O, 4.0 ml; n-tetradecane, 0.2 ml; catalyst loading, 100 mg; agitation speed, 1732 rpm; temperature, 25 °C; initial  $H_2$ pressure, 4.0 MPa; reaction period, 2.0 h. The Pt/BN-R300 stands for the catalyst using Pt (NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 300 °C. CAL, COL, HCAL and PPL stands for cinnamaldehyde, cinnamyl alcohol, hydrocinnamaldehyde and phenylpropanol, respectively.

**Fig. 10.** Kinetic test of cinnamaldehyde hydrogenation over the Pt/BN-R300 catalyst. (a)  $Ln(C_0/C)$  vs. reaction time under different temperatures with a catalyst dosage of 100 mg. (b) Arrhenius plot. (c)  $Ln(C_0/C)$  vs. reaction time under different catalyst loadings at 25 °C. (d) Initial reaction rate vs. catalyst loading at 25 °C. Reaction condition: CAL, 5.0 mmol; isopropanol, 16 ml; H<sub>2</sub>O, 4.0 ml; n-tetradecane, 0.2 ml; agitation speed, 1732 rpm; constant H<sub>2</sub> pressure, 4.0 MPa. The Pt/BN-R300 stands for the catalyst using Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> as precursors and reduced at 300 °C.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

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